# Silicon Carbide Thin Films for MEMS Nanoreactors for *in-situ* Transmission Electron Microscopy

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Bruno Morana

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# Silicon Carbide Thin Films for MEMS Nanoreactors for *in-situ* Transmission Electron Microscopy

## PROEFSCHRIFT

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# CHAPTER 1

# **Background and Motivation**

## 1.1 Introduction

Due to their scientific and industrial relevance interactions between solid nanostructured materials and gasses is today a subject of extensive studies in science and industry. These interactions play a fundamental role in the emerging research areas of nanoscience and nanotechnology. Many important fields are predicted to benefit from developments in these areas. Heterogeneous catalysis, for example, can be considered as the one currently taking the greatest advantage. The use of nanostructure-based catalysis (nanocatalysis) is in fact allowing important improvements in the production of essential chemical products. Moreover, it is enabling new developments, such as the controlled synthesis of nanomaterials, the realization of efficient fuel cells, advanced gas sensing and filtering, effective pollution reduction, and hydrogen storage. The understanding of gas-solid interaction phenomena like adsorption/desorption, oxidation/reduction, and surface/bulk atomic reorganization is crucial in the development and synthesis of specific or dedicated nanocatalysts. These phenomena are characterized by dynamic events taking place at the nanoscale. An essential condition for their study is therefore the availability of characterization tools which allow to reproduce these events while enabling their direct observation with atomic resolution.

In this chapter, the importance of nanocatalysis will be explained together with a brief review of the available characterization approaches based

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on the use of transmission electron microscopes (TEMs). Advantages and limitations of these approaches are discussed. Finally the most promising among them, the nanoreactor, is presented. This tool is a miniaturized reaction chamber enabling the *in-situ* study of nanostructured materials in the presence of gasses at high pressures and at elevated temperatures. To improve the functionality and the versatility of the nanoreactor, the development of new construction materials and of microfabrication techniques is then introduced as the main focus of this thesis.

## 1.2 Catalysis

Catalytic reactions are at the base of the production of more than 85% of the synthetic materials and chemicals essential to humans. Products like fuels, lubricants, fertilizers, medicines, paints, plastics, rubbers and thousands of other materials and value-added chemicals are produced by means of catalysts [1]. A catalyst is a substance that increases the rate of a chemical reaction without being consumed by it (see Fig. 1.1). Catalysts act by lowering the activation energy necessary to reach a given transition state of the reactants thus enabling an efficient (sustainable and cost-effective) conversion of big amounts of raw materials into fine chemicals, value-added chemicals, synthetic materials, and so on. Besides for production purpose, catalysts are also widely employed for the cleaning of poisonous and polluting gasses, like those generated by engines in the transport sector, or the flue gasses produced by power plants, or even the fumes generated by charcoal broilers of restaurants [1]. Depending on the phase (solid, liquid or gas) of the catalyst and that of the reactants, catalytic reactions can be roughly classified as homogeneous or heterogeneous. In homogeneous catalysis both the catalyst and the reactants have the same phase, that is liquid or gas. On the contrary, in heterogeneous catalysis the reactants and the catalyst have different phases, usually with the catalyst in a solid phase and the reactants in gaseous or liquid phase. Both homogeneous and heterogeneous catalysis reactions have advantages and disadvantages. The first offers better catalytic activity and better selectivity than the latter. On the other hand, heterogeneous catalysis offers better recoverability of the catalysts and allows for more stability in the reactions compared to homogeneous catalysis. Activity, selectivity, recoverability and stability are all crucial properties for a catalyst. Despite the high activity and selectivity offered by homogeneous catalysis would allow very efficient catalytic processes, nowadays approximately 80% of all catalysis processes are heterogeneous. This is due to the difficulty in the recovery and handling of the catalyst in homogeneous

catalysis. Most of homogeneous catalysts are expensive transition metal complexes dissolved in a liquid. For this kind of catalysts, when possible, very expensive recovery techniques are required in order to avoid contamination of the products, and pollution of the environment.



Figure 1.1: (a) Catalysis action in a chemical reaction. The catalyzed reaction requires a lower activation energy compared to the uncatalyzed one. There is no difference in the energy release by the reaction in the catalyzed and uncatalyzed case. (b) Diagram showing a general catalytic cycle. In the cycle the catalyst is not consumed and can be reused. Adapted from [2,3], respectively.

## 1.3 Nanocatalysis

The need of efficient and environmental friendly processes, together with the necessity to reduce or contain depletion of raw materials, is strongly

pushing towards the development of catalysis processes that combine the advantages of both homogeneous and heterogeneous approaches. These processes are often referred to as green catalysis. The idea actually dates back to the seventies, when the catalysis scientific community started pioneering work following two different schools of thought, one proposing the molecular and the other the solid state approach as a solution. Despite some interesting results were obtained using both approaches, a common and effective solution to the problem was not found. It was only in the nineties that the concrete possibility of bridging homogeneous and heterogeneous catalysis was offered by the specific developments taking place in nanoscience and nanotechnology. In particular, the use of nanoparticles (NPs) as catalysts and/or as support structure for catalysts, revealed as the key for the solution to the problem. NPs exhibit unique catalytic properties as a result of their reduced size. These properties were unintentionally exploited in some important processes already at the beginning of the 20th century, or maybe even earlier. An example is the production of ammonia by the Haber-Bosch process which was exploiting the catalytic properties of iron-based nanocatalysts. The first reported application of NPs as catalyst dates back to 1941 with the ground-breaking work of Rampino and Nord [4]. Then, as extensively described in [5], between the seventies and the end of the eighties some pioneering work showing the possibility of using NPs as catalysts was performed. Finally, the nineties saw a proliferation of extended studies on the catalytic activity of NPs [5–7]. Since then research on NPs-based catalysts continued with increasing intensity and with exciting results until the first years of the twenty-first century, when it finally experienced an explosive growth.

Nanocatalysis is today still a subject of extensive study in both the academic and industrial research environment. In addition, it is already at the base of many modern industrial catalytic processes falling in the field of green catalysis. Catalysts based on nanostructured materials are today referred to as nanocatalysts. As suggested in [6], nanocatalysis can be defined as the use of nanoscale materials in catalysis, often with effective catalytic properties, that is, efficient catalytic activities as well as ease of catalysts separation, recovery and reuse. In order to better understand why nanocatalysts are very advantageous it is important to realize that catalytic reactions take place directly at the surface of a catalyst. Catalytic NPs typically have a size in the range 1-10 nm [5]. The extremely high surface-to-volume ratio of NPs allows to drastically reduce the total required mass of catalytic material, thus reducing the costs. Moreover, the reduced size causes the NPs morphology and electronic structure to strongly differ from those of the corresponding bulk material. If properly exploited these differences

can be source of great advantages. For example, specific features, such as edges, steps, corners, terraces and defects, are present at the surface of NPs as a consequence of the increased faceting [5, 7, 8]. These features can be chemically extremely active, thus enhancing or promoting unique catalytic properties such as activity and selectivity. Some of the structural parameters of NPS affecting the catalytic properties are shown in Fig. 1.2. The type, properties, and amount of surface features strongly depend on the size and shape of the NPs. Consequently, many materials show unprecedented catalytic activity when their size is reduced to the nanoscale. For example, gold, usually not active as bulk material, shows catalytic activity already at room temperature when NPs smaller than 5 nm are employed. Similarly, cobalt oxide becomes active at room temperatures while high temperatures are needed to achieve catalytic activity when its bulk form is employed. Therefore, many noble metals can be replaced by less costly ones (e.g. Fe, Al, Ni) and by metal oxides (e.g. MnO, CuO). In addition, carbon based nanostructures such as nanotubes and nanowires, can also be employed as catalyst.



Figure 1.2: Illustration of some of the structural parameters that affect the catalytic properties of NPs. From [8].

Nanocatalysts are today widely employed in the field of heterogeneous catalysis as they generally allow for improved efficiency and selectivity. Catalytic NPs for heterogeneous catalysis include materials such as metals, sulphides, oxides, and other compounds. For their use the NPs are usually dispersed on specifically designed highly porous support materials to achieve what is referred to as supported catalysts. The support allows for the thermochemical stabilization of the NPs and the maximization of their exposed surface area. Typical support materials are binary oxides, transition aluminas, zeolites, carbons in various forms [9]. Their size is usually in the ranges from tens to hundreds of nanometers. The support material often plays an important role in the catalytic action of the NPs (see Fig. 1.2). Therefore, it might be more correct to associate the term nanocatalyst to the system NPs-support material. To ease their handling, nanocatalysts are arranged in larger millimeter-size structures with different shapes such as pellets, spheres, granules, rings, cylinders etc. (Figs. 1.3 and 1.4). Finally, catalyst NPs can be also advantageously employed for homogeneous catalysis. For example, nanocatalysts consisting of transition metal nonsupported NPs finely dispersed in organic or aqueous solutions (colloids) offer improved recovery and reuse possibilities.



Figure 1.3: Picture and schematic showing the size of the typical pellet-type nanocatalyst supports. Adapted from [10].



Figure 1.4: TEM images showing Pt nanoparticles dispersed on (a) porous silica and (b) on a carbon nanotube. Adapted from [11] and [12], respectively.

In general, we could say that in nanocatalysis the catalyst is a recoverable solid with enhanced catalytic properties that can be effectively immersed in the reactants. Therefore, nanocatalysis allows bridging the world of homogeneous and heterogeneous catalysis by effectively combining the advantages of both approaches. This is extremely advantageous as allows to achieve cost-effective, more efficient, more sustainable (eco-friendly) catalysis processes for standard products (fuels, fertilizers plastic, pharmaceutical etc.) (Fig. 1.5). Moreover, nanocatalysis can also be employed to make important applications, like fuel-cells, feasible and to realize innovative concepts in the field of the green-energy as the achievement of hydrogen storage, gas filtering, production of bio-fuels, etc. Finally, nanocatalysis can be also advantageously used for the growth of novel nanostructured materials that can themselves work as catalyst or as support material for catalysts, or that can be employed in other cutting-edge applications.



Figure 1.5: Illustration of some of the beneficial impact of nanocatalysis. Adapted from [13].

## 1.4 *Operando* characterization of nanocatalysts in TEM

Nanocatalysts are already employed to improve important heterogeneous catalysis reactions, such as those involved in the chemical processes for the refining of crude oil and those taking place in automotive catalytic converters. However, the optimal exploitation of nanocatalysts and the widening of their application range are currently restrained by the poor understanding of their behavior in relation to their physical-chemical properties. This is in fact the key knowledge that would allow to synthesize dedicated nanocatalysts, each with high activity, high selectivity, high efficiency, good recoverability and long lifetime. Nevertheless, studying the relation between behavior and physical-chemical properties of nanocatalysts is not an easy task. The reason is that catalytic reactions are regulated by very complex dynamic phenomena taking place at atomic level at the nanocatalyst surface. The characterization of these phenomena requires very powerful instrumentation. A technique allowing the real-time observation with atomic scale resolution and the accurate chemical characterization of the nanocatalysts during their operation is required.

Transmission electron microscopes (TEMs) are currently the instruments of choice for the study of nanocatalysts. TEMs are the only instruments enabling direct observation of nanometric samples with atomic resolution. In addition, chemical characterization of the samples by means of spectroscopy analysis techniques (i.e.  $EDX^1$  and  $EELS^2$ ), can be directly implemented during TEM imaging. Furthermore, nanomaterials are particularly well suited to be observed in TEMs as their size is small enough to allow the required transparency. TEMs are also preferred above characterization instruments using X-rays, which, despite their very powerful chemical mapping and spectroscopy capabilities, are not suited for obtaining atomic level information of the samples.

As stated above, in order to fully understand the behavior of nanocatalysts, it is necessary to be able to observe and analyze them during their operation and therefore under the real environmental conditions, typical of a given reaction. The real-time study of chemical reactions under real operating conditions is nowadays referred as operando characterization. Commercial catalytic reactions usually take place at high temperature and high pressures, typically in the range of 300-600 °C and 0.1-10 GPa (1-100 bar), respectively. In some cases even higher values are employed, that is up to 1100 °C and 30 GPa. However, these environmental conditions are quite extreme and very far from the normal operating conditions of a TEM. As will be explained more in detail in section 3.2.1.3 in a TEM samples are imaged and characterized by using electrons as a probe. A schematic of TEM is shown in Fig. 1.6. The electrons are generated by an electron source (electron gun) which needs to operate in ultra-high vacuum ( $< 10^{-6}$ Pa ;  $10^{-8}$  mbar). The interaction between any type of gas and the gun would in fact cause its degradation and require its replacement. This must

<sup>&</sup>lt;sup>1</sup>Energy-Dispersive X-ray Spectroscopy

<sup>&</sup>lt;sup>2</sup>Electron Energy Loss Spectroscopy

be avoided as this procedure is very expensive and time consuming. Once generated the electrons are accelerated towards the sample. The interaction between the electrons and the sample allows to obtain information on its atomic structure and composition (see section 3.2.1.3). The electrons travel for a certain distance in what is referred to as the TEM column (see section 3.2.1.3). To achieve images with high spatial resolution and high accuracy in the analysis, it is imperative that the electrons do not interact with anything else than the sample. Therefore, to avoid electron-gas scattering also the TEM column needs to be kept to pressures below  $10^{-5}$  Pa ( $10^{-6}$  mbar). Finally, TEM characterizations are very sensitive to any dynamic mechanical deformation of the microscope parts. Therefore, in order to prevent thermally-induced mechanical deformations, TEMs needs also to be kept at a very stable temperature, typically close to 20 °C.



Figure 1.6: Schematic illustrations of a TEM working principle and its main parts. From [14].

The normal operating conditions of a TEM are therefore in strong contrast with those required for the *operando* study of nanocatalysts. The temperature problem can be effectively addressed by using specifically designed TEM sample holders, either integrating miniaturized heating elements such as resistive wires, or capable of accommodating microfabricated devices with heating features [15–19]. These allow heating up the specimen to very high temperatures, directly inside the TEM. The heat effect on the performance of the TEM is minimized as this is localized at the specimen area. In this respect microfabricated devices offer the best performances. Following the same philosophy, gasses can be also confined in the surroundings of the

specimen area, so not to affect the operating conditions of the electron-gun and to minimize their impact on the performance of the TEM. However, creating an atmosphere of a certain composition and pressure localized at the specimen is not simple, especially when very high pressures are involved. Finding a systematic and effective technological solution to pursue this idea has kept scientist busy for a long time. The idea of confining the gasses around the specimen was implemented already in 1942 by Ruska [20], one of the original inventors of the TEM [21]. The purpose was to prevent the drying of hydrated samples inside the high vacuum of the microscope. Since then many efforts have been made to image samples in TEM in their natural environment, that is gas, liquid or both. This technique is today referred to as environmental transmission electron microscopy (ETEM). Technologies for gas ETEM have greatly improved and today are successfully employed to perform in-situ studies of nanostructured materials in the presence of gasses and at elevated temperatures. As defined by Pereira in [22] the technique of *in-situ* TEM refers to a broad class of experiments whereby the dynamic response of a material to an externally applied stimulus is observed as it happens inside the microscope. This technique is opposed to conventional ex-situ TEM where samples are characterized before and after an event with the consequent loss of the information on dynamic phenomena. Operando TEM characterization of heterogeneous nanocatalysis reactions can be considered as a particular case of *in-situ* gas ETEM where the temperature (by external stimuli) and pressure (by environment) are the same as those of the real process. In the following section the most advanced technologies currently available to perform *in-situ* gas ETEM are briefly introduced and their suitability to the operando characterization of nanocatalysts discussed.

#### 1.5 ETEM state of the art

In-situ gas ETEM can be achieved by following two different approaches sharing the general idea of confining the gasses in the surroundings of the specimen. In the first approach the gasses are confined in the pole piece section of the TEM by means of a differential pumping system. The second approach makes use of a small windowed environmental cell (E-cell) built around the specimen at the tip of the TEM holder to confines the gasses.

#### 1.5.1 Differentially pumped E-chamber

The differential pumping approach was first proposed in 1942 by Ruska [20]. The idea was to introduce gasses directly into the pole piece section

of the TEM, that is where the specimen is located, and to pump them out immediately at the exit of this section by means of additional pumps. With this approach an environmental chamber (E-chamber) is defined inside the TEM. Modern E-chambers are based on the differential pumping scheme outlined in 1972 by Swann and Tighe [23] employing diffusion limiting apertures and a turbo-molecular pump (TMP) to confine the gasses. In the nineties this scheme was extensively developed by E.D. Boyes & P.L. Gai who in 1997 created a two-level differentially pumped TEM allowing a spatial resolution of 0.23 nm at 30 Pa of N<sub>2</sub> [24]. A schematic drawing of this system is shown in Fig. 1.7. Here the gas E-chamber corresponds to the volume comprised between the upper and lower objective lenses. As for conventional TEMs the specimen to be studied is placed in the middle of this space by means of a TEM holder (see Chapter 3). Gas lines directly connected to the E-chamber allow the fast introduction and evacuation of the gasses. As previously explained, the propagation of gasses to the rest of the column has to be avoided to prevent the damaging of the electron-gun and preserve the high spatial resolutions of the TEM. Two pairs of small circular apertures fitted at the upper and lower objective lenses are employed to limit the gas flowing out of the E-chamber and at the same time to allow the passage of the electrons. A TMP is connected to the space between each pair of apertures allowing the fast evacuation of the gasses flowing out of the E-chamber. This pumping scheme is replicated above and below the first one, to evacuate the gas leaking from the first apertures pair. More details on the origin, evolution, and performance of differentially pumped TEMs can be found in [15, 17, 25].

The differentially pumped E-chamber approach is advantageous as it allows safe operation of the TEM in presence of gases. Moreover, this approach allows the use of standard TEM holders or of holders integrating heating elements which in general are relatively inexpensive and readily available. Also, samples can be prepared and loaded in a standard way. However, differentially pumped TEMs are costly systems. The integration of a two-level differential pumping scheme and of the gas in-out system represents a deep modification of a standard TEM. This translates into elevated costs for the system itself and for the required maintenance and repairs. Furthermore, the addition of the differential pumping system comes at the expense of the already little space available in the column of the microscope making the integration of elements necessary for implementing spectroscopy features more complex and therefore more costly.

The main drawback of the differential pumping approach is the maximum pressure that can be set in the E-chamber. In Fig. 1.7 an indication of the vacuum levels achieved in the various sections of the column of a dif-

ferentially pumped TEM is given. In order to keep the vacuum at a suitable level in the rest of the microscope, the maximum operating pressure in the E-chamber is limited to pressures between 10 to 50 kPa. However, when spatial resolutions below 0.2 nm need to be achieved the pressure has to be kept to values lower than about 3 kPa. It is important to notice that such spatial resolution is necessary when studying nanocatalysts as most of the transition metals of interest have lattice spacing below this value. The reason why the pressure limits the resolution is that the electrons have to cross the gas for a path length roughly equal to the thickness of the E-chamber. This is referred to as the pole-piece gap and has a typical value of comprised between 5 and 10 mm. This value is already very low, but not low enough to prevent loss of resolution due to the scattering of electrons with the gas atoms at elevated pressures. At a fixed gas path length the number of gas atoms, and the consequent scattering events, increases with the pressure. For example the mean free paths of an electron accelerated toward a specimens with an energy of 200 keV are about 4.1 mm and 41 mm in an  $O_2$ atmosphere of 10 kPa and 1 kPa, respectively. Considering a pole-piece gap of 5.4 mm, these mean free paths correspond to a probability of an electron being scattered at least once of about 73% and 12%, respectively [26, 27].



Figure 1.7: Schematic (not to scale) of key elements of the differentially pumped TEM design developed by the Boyes & Gai in the 1990s. The pressure levels in the various section of the TEM column are shown. Adapted from [28].

Currently differentially pumped TEM with excellent performances is commercialized by FEI Company (Titan ETEM G2 shown in Fig. 1.8. This TEM uses a 300 keV electron-gun and an advanced differential pumping scheme. This system as well as its predecessors (TECNAI F20), for example, allowed to perform several *in-situ* gas ETEM experiments involving nanoparticles [29]. A study investigating the maximum achievable resolution in gas environment demonstrated a spatial resolution of 0.12 nm at 2 kPa of N<sub>2</sub> [29]. Despite this performance, remarkable high spatial resolutions at pressure above 2 kPa have not been demonstrated. This pressure is far below the one required for the *operando* characterization of nanocatalysts. For this reason an alternative approach is required. In the next section the use of the E-cell approach is discussed as a possible alternative.



Figure 1.8: Differentially pumped TEM Titan ETEM G2, including a sketch of the vacuum system highlighting the pressure-limiting apertures at the pumping stages. From [29].

#### 1.5.2 Windowed E-cell ETEM

In the windowed environmental cell (E-cell) approach specimens are enclosed in a very small chamber that can be mounted in the tip of the TEM holder and directly inserted into the microscope as schematically shown in Fig. 1.9. Windowed E-cells are made to prevent fluids from leaking into the high vacuum of the TEM, while allowing the observation of the specimens. This is achieved by means of so-called electron transparent windows, consisting of a layer thin enough to allows the passage of electrons and yet strong enough to withstand the pressure difference once inside the TEM.

The idea of building a small sealed cell around the specimen dates back to 1935 when Marton built a windowed E-cell to observe biologic hydrated specimens in their natural atmosphere [30]. Later, scientists attempted to apply this technology also to the study of solid samples in the presence of gasses. However, by using the first versions of the windowed E-cell it was not possible to achieve the required atomic resolution. This was due to the limited transparency of the E-cells, i.e. the windows were too thick [15,17,31]. To overcome this problem, ultra-high voltage (1 MV) microscopes were developed to increase the penetration of the electrons through the windows and improve the quality of the images. Some encouraging results were obtained [15, 31], but the high cost and safety issues severely limited the use of ultra-high voltage TEMs. This together with the developments in differentially pumped TEMs caused the windowed E-cells to be employed for long time only for imaging biological hydrated samples, which require less resolution. The use of windowed E-cell was not reconsidered until the aforementioned drawbacks of differentially-pumped TEMs became clear. In 2006 Ciorgio et al., reported a windowed E-cell allowing atomic resolved images of  $TiO_2$ -supported Au nanoparticles at 0.4 kPa of  $H_2$  and at 350 °C using a conventional TEM operated at 300 kV [32]. Also, this E-cell was demonstrated to withstand a pressure difference of at least 20 kPa outside the TEM. The E-cell was achieved by superimposing two circular perforated copper plates covered with a 10 nm thin amorphous carbon layer working as window. The spacing between the top and bottom plates was set to 1 mm, by means of spacers to accommodate a resistive wire working as heater. The leak-tight sealing of the E-cell was achieved by pressing the plates against O-rings. The E-cell was mounted in the tip of a specifically designed TEM holder provided with electrical contacts and inlet/outlet gas apertures. These were respectively connected to electrical wiring and pipes running through the holder to allow the external control of the E-cell. Two year after this important achievement, Creemer et al. [33] reported a fully integrated windowed E-cell which allowed a resolution of 0.18 nm while observing ZnO supported Cu nanoparticles at 120 kPa of  ${
m H}_2$  and at a temperature of 500 °C. For this experiment a TEM operated at 300 kV and a custom designed TEM holder were employed. This impressive result represented a milestone in the operando ETEM as it was the first time that TEM atomic resolved images were acquired at such high pressure combined with high temperature [34, 35]. The key behind the results of Creemer is the realization of an ultra-thin (4-40 µm) windowed E-cell [33, 36]. This drastically reduces the amount of gas the electrons have to cross, so even at elevated pressures the resolution is not degraded. The realization of such an E-cell was achieved by means of microfabrication techniques typically



Figure 1.9: Schematic drawing of the E-cell approach. The gasses are confined inside the E-cell and the high vacuum of the microscope is not affected. Adapted from [17].

employed in the fabrication of micro electro mechanical systems (MEMS), thus it was named MEMS nanoreactor. In addition, the device directly integrated electron transparent windows and a microheater. This integration enabled local heating to relatively high temperatures with very low thermal drift. It also avoided many assembly steps which, for such small structures, are very delicate and time-consuming. A detailed description of the MEMS nanoreactor and the dedicated holder is reported in Chapter 2.

Creemer's results clearly show the enormous advantage in terms of maximum pressure of the windowed E-cell above the differentially pumped approach. In addition, the reduced volume is beneficial as it allows for faster change and/or evacuation of gasses, faster thermal response, and more accurate mass spectrometry/gas analysis. Finally, another important advantage is that the windowed E-cell does not require modifications of the TEM microscope but only the use of a dedicated TEM holder which is relatively low cost and easy to build compared to a differential pumping scheme. Therefore, this approach is also economically attractive and allows great flexibility in the choice of the microscope.

The aforementioned benefits have encouraged more researchers to use this technique. Some works confirm the possibility of achieving atomic resolution at high pressures [37, 38] often coupled to high temperatures [27, 39, 40]. Also, they report interesting developments for the assembly, realization and operation of the E-cell [38, 39, 41]. Besides the interesting scientific results and technical developments contained in these publications, all the proposed E-cell solutions are based on the approach of Giorgio et al.,

where the E-cell is assembled at the tip of the TEM holder. Although this approach allows the direct placing of the specimens inside the E-cell, the reported E-cells have the drawback of a difficult and tedious assembly, which is often coupled with alignment problems especially when small volumes needs to be achieved and when heating elements need to be integrated. This makes their use very difficult, and sometimes impossible, thus preventing the achievement of good and reproducible results. In addition reliability is also a problem, as the rupture of non-properly designed plates and windows would cause serious damage to the TEM microscope. Cleanliness is also an issue e.g. hydrocarbon contamination. MEMS fabricated nanoreactors are instead advantageous in this aspect. First they do not require assembly at the tip of the holder then the microfabrication approach has advantages from the reliability and performance point of view (both temperature and pressure and cleanliness). The capabilities of the MEMS nanoreactor have been demonstrated, quite recently with a more advanced type (see Chapter 2), reporting the first operando characterization of nanocatalyst particles a TEM [42], thus further highlighting the huge potential of this approach.

#### **1.6** Motivation e and thesis outline

The MEMS nanoreactor in combination with a multifunctional holder provides the best solution so far for *operando* ETEM for studying interactions between gas and solid nanostructured materials in a TEM. However, several challenges are still open in the fabrication, the operation and use of this device. In this thesis we will focus on the development of alternative materials and modified fabrication techniques with the aim of improving the MEMS nanoreactor performance and thus expanding its possibilities.

In Chapter 2, the instrumentation for operating the nanoreactor will be illustrated. Then the requirements for the main elements of the MEMS nanoreactor will be discussed. The design of the MEMS nanoreactor will be described, showing three different nanoreactor configurations. Finally, the motivation behind the introduction of SiC as alternative material for the nanoreactor, as well as the need of a more robust fabrication process, will be addressed. The equipment and techniques employed for the fabrication and characterization of the proposed alternative materials will be described in Chapter 3. The use of SiC in different forms for the three main parts of the nanoreactor, the window, the channels and the heater, is extensively reported in Chapters 4, 5 and 6, respectively. Finally, a fully SiC MEMS nanoreactor is fabricated and the results presented in Chapter 7. Main conclusions and suggestions for future work are given in Chapter 8.

# CHAPTER 2

## The MEMS Nanoreactor

## 2.1 Introduction

As discussed in the previous chapter, the MEMS nanoreactor, is a promising approach for the *operando* characterization of solid nanocatalysts and more in general for conducting *in-situ* studies of interactions between gasses and solid nanostructured materials at elevated temperature and/or pressure in TEMs. The advantages and key performances of the MEMS nanoreactor directly derive from the fabrication technology employed for its realization. MEMS technology, based on silicon integrated circuit manufacturing, allows the integration of the required functional elements with the necessary performances and in a reproducible way. This enables the realization of a real miniaturized reaction chamber (or chemical reactor) suitable for performing experiments in a reliable and repeatable way.

A schematic drawing illustrating the concept of the MEMS nanoreactor and its main elements is shown in Fig. 2.1. The MEMS nanoreactor basically consists of a microchannel integrating a microheater and a set of electron transparent windows in its central section. The central section of the microchannel is the reaction chamber of the nanoreactor. Here the microheater brings the specimens to the required temperature while the electron transparent windows enable their observation. The central section of the microchannel is realized by superimposing two large and thin suspended membranes. The microheater is integrated in the center of one of the two membranes. This design enables for a fast thermal response, accurate tem-

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Figure 2.1: Schematic drawing illustrating the operating principle of the MEMS nanoreactor ant its main elements.

perature control low power consumption (section 2.3.2), which translates in high accuracy in the experiments and reduced image drift, respectively. In addition, the membrane design makes possible the integration of the electron transparent windows in the form of very thin freestanding membranes on both top and bottom sides of the microchannel. In this respect MEMS technology is essential for creating aligned electron transparent windows of reduced size. Due to the small channel thickness the factor limiting the resolution is in first place the thickness of the windows (section 2.4.3). The thinner the windows the higher the transparency. Achieving windows with a reduced width is also extremely important to allow their reliable operation at elevated pressures (section 2.3.1).

The two remaining microchannel sections, at the sides of the central one, bring the gases in and out of the reaction chamber. Also, they allow the loading of the specimens. To achieve this, inlet and outlet apertures are integrated at the outermost sides of the microchannel. Electric wiring running out from the reaction chamber and ending in contact pads located outside of the microchannel area, are provided to control the microheater. A custom made loading tool is employed for bringing the specimens inside the nanoreactor prior to the experiments. Finally, the nanoreactor is designed to fit at the tip of a custom made TEM holder provided with gas lines and electrical contacts. These are interfaced to gas supply and temperature control systems, which are needed to set the desired pressure and temperature in the reaction chamber of the nanoreactor. In the following sections a description of the instrumentation necessary for the operation of the nanoreactor in a TEM (i.e. holder, gas system, electronics, loading tool) is first reported. Then we present a detailed description of the three main elements of the nanoreactor (i.e. windows, microchannel and microheater) together with their function and requirements. Finally, we describe the three generations of MEMS nanoreactors recently developed and discuss their advantages and disadvantage.

#### 2.2 Nanoreactor instrumentation and tools

To operate the nanoreactor specific instrumentation and tools are required. These are: the TEM holder, the gas system, the temperature control system, and the loading tool. In the following subsections a short description and explanation of their functions is provided.

#### 2.2.1 TEM holder

The positioning of specimens inside a TEM is normally achieved using a holder. This consists of a cylindrical metal rod of variable section embedding a slot in its tip, which is designed for the housing of specimen supporting-structures. Once inserted in the TEM, the holder places the specimen directly under the electron beam. A motorized clamping system allows the movement of the holder in the three spatial directions for the fine focusing and exploration of the specimen. TEM microscopes are equipped with load-lock system to consent the insertion of the holder. This integrates a series of O-rings preventing air to leak into the column of the microscope during and after the insertion of the holder. With the same aim an O-ring is directly mounted also on the TEM holder.

A custom made holder suitable for MEMS nanoreactors is shown in Fig. 2.2. The holder is specifically designed to allow the precise and leak-tight housing of the nanoreactor in its tip and to enable its control from outside the TEM. The holder is provided with two gas tubes running through it and ending by one side into two gas connectors. At the opposite site the gas tubes end into two apertures located at the bottom of the housing-slot and designed to face the inlet and outlet of the nanoreactor. The dimensions of the gas tubes are such that their conductance is much larger compared to that of the microchannel of the nanoreactor. A pressure at the inlet of the nanoreactor can thus be set by pressurizing the corresponding gas line. The leak-tight connection between the inlet and outlet apertures of the holder and those of the nanoreactor is ensured by means of O-rings. A metal lid is employed to press the nanoreactor against them. A hole is present in the lid to let the TEM electron beam pass through the reaction chamber of the nanoreactor and through its electron transparent windows. For the same reason, a hole is present at the bottom of the housing-slot. In order to

control the microheater integrated in the nanoreactor the holder is provided with 4 spring loaded needles located at one edge of the housing-slot. These are designed to press on the contact-pads of the microheater. The needles are connected to wires running through the holder and ending in a connector. The wiring system is sealed in such a way that no air can leak into the microscope through the holder. The section of the holder integrating the housing-slot is made of phosphor bronze. This material has a very low  $(18 \times 10^{-6} \text{ K}^{-1})$  linear thermal expansion coefficient, which helps to minimize any movement resulting from thermally induced deformations as those resulting from the operation of the microheater. Moreover, all the materials employed in the construction of the holder as well as the procedures followed for its assembly are designed to be compatible with the high vacuum of the TEM. This is required to prevent that the holder acts as a source of contaminants (e.g. hydrocarbons) which would have a destructive effect on the experiments. For more details on the TEM holder of the MEMS nanoreactor please refer to [36].



Figure 2.2: (a) Picture of a TEM holder for MEMS nanoreactors. (b) Picture of the tip of the holder with the nanoreactor inserted and connected by the four contact needles. (c) Schematic cross-section of the tip of the holder showing the tubes, the electrical contacts and the positioning of the nanoreactor. Adapted from [36].

#### 2.2.2 Gas system

A dedicated gas system is employed to control the atmosphere inside the microchannel of the nanoreactor. By controlling the pressure at its inlet and outlet apertures a static or dynamic regime of gasses can be achieved. In flow-mode a gas or a mixture of gasses with a given pressure is applied at the inlet while the outlet is evacuated. This results into a gas flow and into a non constant pressure profile along the microchannel. Alternatively, in plug-mode the pressure in the reaction chamber can be set to a given value by maintaining both inlet and outlet at the same pressure. The gas system consists of a system of valves and pipes allowing the connection of the gas bottles containing process gasses (e.g. CO2, O2, He, N2, H2 etc.) and of one or more turbo molecular pumps (TMPs) to the TEM holder. The gas system also includes a mass spectrometer for the analyzing the by-products of the chemical reactions taking place in the nanoreactor. An example of this system is shown in Fig. 2.3. The coupling of vibration from the gas system to the TEM holder and therefore to nanoreactor needs to be as small as possible. Vibrations would in fact prevent the acquisition of atomic-resolved images. For this reason the tubes connecting the gas-system to the TEM holder are chosen to be very thin and flexible, usually PEEKsil<sup>®</sup> tubes are employed. In some cases a dumping stage can also be employed to decouple the vibrations. As for those of the holder the dimensions of these tubes are chosen such that their conductivity is much larger than that of the microchannel of the nanoreactor. In this way the pressure dropping across the gas tubes is negligible compared to that dropping across the microchannel. Advanced gas systems can be computer controlled and optimized to minimize dead gas volumes and to allow a fast switching between the process gasses during experiments. Finally, to avoid any contamination (e.g. those from hydrocarbons), procedures and parts that are typical for ultra-high vacuum instrumentation are employed for the realization of the gas system.

#### 2.2.3 Temperature control system

The temperature in the reaction chamber of the nanoreactor can be set to a value higher than room temperature by regulating a current flow into the resistive microheater. This task is performed by means of a temperature control system consisting of an electronic box and PC. The electronic box, shown in Fig. 2.4, integrates a custom made electronic circuit and a digital data acquisition card (NI-DAQ). The box is connected via USB to the PC and via a shielded four-wire cable to the TEM holder. The data acquisition card is controlled by a LabView custom made script running on the PC. The electric resistance of the microheater is temperature dependent. This property is employed to set and monitor the temperature of the reaction chamber. A four wire/contact configuration is employed to control the microheater. The electronic circuit implements a proportional-integral closed-loop capable of flowing into the microheater the current needed to



Figure 2.3: Picture showing a gas system built aside of a Philips CM 300 TEM. The location in the TEM column of the load-lock and the holder are also indicated.

heat up and maintain it to the required temperature. The data acquisition card integrates digital-to-analog (D/A) and analog-to-digital (A/D) converters. These allow to generate the set point for the analog closed loop system and to acquire several electrical variables from the circuit and from the the microheater. Among these there is the current flowing in the microheater and the voltage drop across its sensing terminals. These are displayed in the graphic interface of the LabView script together with the calculated dissipated power and the temperature. These are also stored in a log-file together with other useful data. The readout of these values is performed in time intervals of 0.5 seconds. The closed-loop is instead much faster and allows to reach the required temperature in a few milliseconds. The conversion of the temperature into resistance, necessary to create the set-point, is performed by means of a second order equation expressing the relation between these two variables (Chapter 6). In a similar way the resistance measured at the sensing terminals of the microheater is translated into temperature and displayed by the LabView script. The coefficients of the equation are typically obtained by calibrating the microheater up to 200 °C. For higher accuracy the calibration can be extended to higher temperatures as discussed in Chapter 6. The electronic circuit can provides a max current of 20 mA with a max voltage drop of 6.5 V across the power terminals of the microheater thus delivering a maximum power of 130 mW.



Figure 2.4: (a)Electronic box for the control of the microheater. (b) Screenshot of the graphic interface of the LabView interface.

#### 2.2.4 Loading procedures and tools

The loading of samples in the nanoreactor can be a difficult task. A specific methods and tools have been developed to solve this problem. The loading of the specimens in the reaction chamber of the nanoreactor is achieved by means of a liquid suspension or a liquid solution. For example, nanoparticles or nanostructured materials can be dispersed into a liquid that can be flown into the microchannel of the nanoreactor to reach the reaction chamber. When the liquid evaporates the nanostructured specimens remains into the microchannel. To achieve a fast evaporation at room temperature ethanol is typically employed as suspension liquid. However, also water can be employed. A salt precursor of the material that needs to be studied can be dissolved in water and nanoparticles or nanostructures are formed upon the exposure to low or moderately low temperatures which at the same time causes the evaporation of the water. In both cases the nanostructured materials that will lie on the windows can then be studied in the TEM. The liquid employed needs to be of very high purity to avoid the contamination of the nanoreactor or of the specimens itself. To flow the liquid suspension or the liquid solution into the microchannel a custom made loading-tool is employed (Fig. 2.5). This consists of a metal block integrating a housingslot for the nanoreactor provided with holes in correspondence of the inlet and outlet apertures. This slot is similar to the one present at the tip of the TEM holder. Also, in a similar way O-rings are employed to achieve a leak-tight system and a lid is employed to press the nanoreactor against them. A reservoir containing the liquid is connected to one of the holes of the metal holder. Usually a barrel of a syringe of 10 ml is employed for this. A leak-tight connection between the barrel and the inlet of the metal block is ensured by means of a fluidic connector. At this point, a small amount of liquid can automatically flow by capillarity, filling the microchannel of the nanoreactor. If more liquid needs to be flown, vacuum can be created at the outlet of the metal holder by suction. This is typically achieved using a syringe with a rubber plunger seal connected to the outlet of the loading-tool by means of a fluidic pipe and adapters. To achieve the correct loading, the concentration, as well as the amount of liquid flown, needs to be tuned taking into account also the size and characteristics of the dispersed nanostructured material or those of the dissolved salt.



Figure 2.5: (a) Picture showing the loading tool.(b)Housing-slot for the nanoreactor. (c) Metal piece pressing the nanoreactor against the O-rings.

## 2.3 Nanoreactor components and requirements

The three main elements of the nanoreactor are the electron transparent windows, the microchannel and the microheater. They need to be integrated in the same fabrication process and thus compatibility among the specific fabrication steps need to be insured. Moreover, specific requirements for each of the element need to be satisfied to allow the correct operation of
the nanoreactor. In the following subsections the functions of each of these three elements, together with their implications on the design and on the properties of the materials selected, are presented.

### 2.3.1 Electron transparent windows

Electron transparent windows are an essential element of the nanoreactor as they enable the observation of the specimens in the reaction chamber during operation while preventing the leak of gasses inside the TEM column. In the last decade TEM microscopy has greatly benefited from the use of electron transparent windows made by silicon-based microfabrication (or MEMS) technology. Examples of applications of microfabricated electron transparent window are schematically depicted in Fig. 2.6. These structures are normally achieved as a free-standing thin film integrated on a supporting silicon frame (see Fig. 2.6 (a)) [43–49]. Typically, they function as support for the preparation and the imaging of samples as an alternative to the classical copper mesh coated with holey carbon or polymer films. More importantly, in the field of *in-situ* TEM, electron transparent windows allow important improvements and open new possibilities. (see Fig. 2.6 (b)) [18, 19, 36, 50]. (Fig. 2.6) [15, 41, 51–56].

To effectively perform their task, the electron transparent windows of the nanoreactor have to satisfy a number of requirements: (i) electron transparency, (ii) resistance to heat, (iii) mechanical strength, (iv) electron-beam resistance, (v) chemical resistance, (vi) wettability, and (vii) electrical conductivity. The constraints placed by these requirements on the choice of the material and on the design of the window are explained below.

Electron transparency: TEM image acquisition and material characterizations techniques (e.g. HRTEM STEM, EDX, EELS etc.) are based on the interaction between the TEM electron beam and the sample under study. Therefore, any additional material/object interposed/interposing between the electron beam and the sample acts as disturbance. The scattering of the electron beam with the windows causes loss in the spatial resolution of TEM images. The scattering scales with the material density, the atomic number, and thickness [16, 58]. Therefore, to minimize this effect the material the windows are made of should have low atomic number (Z) and low density ( $\rho$ ). At the same the thickness of the windows should be the lowest possible (typical thicknesses are below 50 nm). In addition, the material of the windows should be amorphous to provide a featureless background to the image. Low roughness is a desirable property to get images with a better contrast and is needed when studies on self-assembled monolayers



Figure 2.6: Examples of applications of microfabricated electron transparent windows in transmission electron microscopy (TEM): (a) as a support for small samples; (b) in a microhotplate as sample support during *in-situ* heating experiments; (c) in a liquid cell to image hydrated specimens. Adapted from [57].

are performed. For similar reasons windows should be flat. Generally flat freestanding membranes that do not buckle even at elevated temperatures are achieved by using materials with slightly tensile intrinsic stress. Finally another factor that needs to be considered is the when choosing the window material is the influence that this has when material analysis techniques are employed. The chemical elements composing the windows can interfere with or mask the signals coming from the samples. Therefore, the elemental composition of the windows should also be compatible with that of the sample under study.

<u>Resistance to heat</u>: electron transparent windows have to be able to withstand the high temperatures at which the nanoreactor operates. Therefore, high temperature resistant material such as those Si-based or ceramic are usually the best choice.

<u>Mechanical strength</u>: as for the case of E-cells the windows of the nanoreactor should possess high fracture strength to withstand the elevated pressure differences caused by the pressurization of the reaction chamber.

Mechanical strength is also desirable to ease: fabrication, handling and sample preparation. Very thin layers are necessary to obtain electron transparency. A recent study [59] performed on thin  $SiN_x$  membranes deposited by low pressure chemical vapor deposition (LPCVD) demonstrated that down to 15 nm these have a much higher fracture strength compared to thicker ones. However, below a certain thickness high defect density in the form of pinholes (discontinuous layer) may appear in layers. Defect density has to be minimized to ensure mechanical strength thus posing a lower limit to the thickness and therefore the transparency.

<u>Electron beam resistance</u>: depending on its energy and dose, the TEM electron beam can damage the window material [16,60]. Effects like radiolysis, knock-on damage, sputtering and heating can take place [16]. Also, the beam can promote chemical reactions between the gasses and the window material (e.g. oxidation) [61]. These effects could lead to the thinning of the layer and eventually the formation of holes into the window. This could cause the leakage of gasses from the nanoreactor into the TEM vacuum column [62]. Another problem could be the contamination of the sample under study as a result of a beam-induced exchange of atoms between the window and the sample. Therefore, the material and the thickness of the windows have to be chosen to allow elevated beam-resistance. The stronger the chemical bonds between the atoms composing the material and the thicker the material the better.

<u>Chemical inertness</u>: this property is useful to prevent the damage of the windows during either the preparation or the study of the samples. In these phases the windows can be exposed to harsh experimental conditions such as corrosive chemicals and corrosive gasses often in the presence of high temperatures. Moreover, chemical inertness prevents the interaction between the windows and the sample under study thus avoiding its contamination. Finally the use of a chemically inert material is advantageous and in some cases necessary for the fabrication of the windows itself.

Wettability: as explained in section 2.2.4 the samples are loaded into the nanoreactor in the form of liquid suspensions or solutions. Therefore, to allow the positioning of the samples right on top of the windows it is necessary that these last are made of a hydrophilic material.

Electrical conductivity: during imaging electron charging could cause blurry images, and unwanted random sample displacement or agglomeration [63]. To prevent these effects the ideal window material should be to some extent electrically conductive.

Materials typically employed for the fabrication of MEMS electron transparent windows are amorphous silicon (a-Si), silicon dioxide  $(SiO_2)$  [44], and amorphous silicon nitride [43–47]. In particular low stress, silicon-rich silicon nitride  $(SiN_x)$  is the most employed because it combines good electron transparency with mechanical robustness, chemical inertness, resistance to heat, smoothness, flatness, and ease of fabrication [58]. This is why until now  $SiN_x$  has been chosen as fabrication material for the windows of the nanoreactors. Usually thicknesses between 15 and 20 nm are employed to allow good transparency and mechanical strength.

### 2.3.2 Gas microchannel

The gas microchannel brings the gasses in and out the reaction chamber. Also it is employed to achieve the loading of the specimens to be studied by flowing liquid suspensions or solutions. Moreover, the central section of the microchannel forms the reaction chamber of the nanoreactor. To achieve the described functionalities the microchannel has to satisfy a number of requirements, that is: (i) electron transparency, (ii) mechanical robustness and stiffness, (iii) resistance to heat and chemical inertness, (iv) wettability, (v) optical transparency, (vi) electrical isolation, and (vii) reduced thermal mass and conductivity. The constraints placed by these requirements on the choice of the material and on the design of the microchannel are explained below.

Electron transparency: in a similar way as for the windows, the electron beam scatters with the gases contained into the channel causing loss in spatial resolution. The number of atoms the electron beam has to cross depends on the height of the channel and on the pressure of the gasses confined by it. Therefore, to minimize the scattering the gas microchannel should be as thin as possible. On the other hand a minimum thickness is necessary to allow the loading of the specimens. Microchannels with a height smaller than 1  $\mu$ m generally result difficult to load due to the reduced flow especially in the case of liquid suspensions.

<u>Mechanical robustness and stiffness</u>: the microchannel should be enough mechanically robust to prevent deformations and failures due to the elevated pressures (102-104 kPa) required by the experiments. Failures obviously need to be avoided as they would compromise the experiment and damage the TEM electron-gun. In addition, mechanical robustness is also desirable for ease of fabrication, handling, and preparation of the experiments (loading). On the other hand the deformation (bulging) of the microchannel causes an increase in the height of the channel leading to a change in the distance between the windows and consequently to focusing problems. Moreover, as explained above an increased height would cause a degradation of the spatial resolution of the TEM images. For these reasons a mechanically stiff channel is preferred. Therefore, materials with high elastic modulus and fracture strength need to be employed for the fabrication of the microchannel. This has to be combined with an adequate design allowing for the required mechanical stiffness.

<u>Resistance to heat and chemical inertness</u>: the same considerations as those made for the windows apply to the microchannel.

Wettability: to allow the loading of the samples into the reaction area of the nanoreactor it is necessary that the surface of the microchannel is hydrophilic. This property in fact enables flowing liquid suspensions or solutions into the microchannel. This can be achieved by fabricating the microchannel using a hydrophilic material. In alternative, coating the internal surface of the microchannel with a hydrophilic material is also an option.

Optical transparency: inspection by optical microscopy is a fast and inexpensive way to monitor and verify the loading of the specimens into the microchannel. For this reason optical transparency is a desirable property. Due to its suspended configuration the reaction chamber is already transparent by construction. A complete optically transparent microchannel is however preferred.

<u>Electrical isolation</u>: the microheater is integrated on the top or bottom membrane of the reaction chamber and embedded in thin electrically isolating layers. In case of an electrically conductive microchannel this design ensures the electrical isolation of the microchannel during steady current flows. However, during transients capacitive coupling might take place. Any flow of charge to the TEM microscope has to be avoided to prevent its malfunctioning. Therefore, the construction material of the microchannel should preferably be electrical isolating.

Reduced thermal mass and conductivity: the mass that the microheater has to heat up needs to be minimized to allow a fast thermal response (short settling time). At the same time, the power dissipated by the microheater to keep the reaction chamber at a certain temperature has to be as small as possible. These are the reasons why the central section of the microchannel is realized by superimposing two large and thin suspended membranes. This design allows creating a reaction chamber with a small mass thus enabling for a fast thermal response. In addition the thin membrane creates a low conductive thermal path between the microheater area and the rest of the microchannel thus enabling for low power consumption. Therefore, in order to minimize both the thermal mass and the conductivity the structural layer of the microchannel should be as thin as possible and the material employed has low thermal conductivity.

Today the vast majority of MEMS microchannels are made in polymers, typically PDMS in combination with a rigid substrate (glass, silicon or polymer). This success is due to features like optical transparency, biocompatibility, ease of fabrication, design flexibility and low cost [64-68]. However, polymers lack of well-defined surface chemistry, resistance to heat, chemical inertness, mcchanical robustness and contain hydrocarbons (which can cause contamination). Glass, which is widely employed for the fabrication of microchannels [64, 66, 69], would fulfill many of the requirements for the microchannel of the nanoreactor. However, the accuracy and the fine integration of functional and structural elements required by this application are very difficult if not impossible when using glass. Silicon micromachining techniques are instead extremely powerful and flexible in this respect [70]. In addition, these techniques allow the combination of a wide range of materials including Si-based materials and metals [64, 66, 70]. Examples of microchannels realized by using silicon micromachining can be found in [64, 65, 70–75].

Silicon micromachining is the technique of choice for fabricating the gas microchannel of the nanoreactor. As for the windows, LPCVD  $\operatorname{SiN}_x$  is the main material employed for the fabrication of the microchannel of current MEMS nanoreactors. LPCVD  $\operatorname{SiN}_x$ , thanks to its low intrinsic stress, its high elastic modulus and mechanical strength, is well suited for the fabrication of freestanding structures. Moreover, it possesses good chemical inertness and it is heat resistant. In addition, LPCVD  $\operatorname{SiN}_x$  has low thermal conductivity, is electrically isolating, and is hydrophilic.

### 2.3.3 Microheater

The function of the microheater is to heat up and keep to the desired temperature the central area of the reaction chamber. At the same time, the microheater is employed for sensing the temperature in the same area. The heating is achieved by exploiting the Joule effect, which is the generation of heat upon the passage of current into a material. The sensing instead is performed by exploiting the temperature-induced variation of the electrical resistance of the heating material. These functionalities place some requirements on the microheater: (i) fast thermal response, (ii) low power, (iii) uniform heat distribution, (iv) high temperature, (v) feasible sensing, and (vi) material compatibility. As previously mentioned, the microheater is directly integrated in one of the membranes that constitute the reaction chamber of the nanoreactor. Therefore, some of these requirements are strictly related to some of the microchannel requirements.

<u>Fast thermal response</u>: even though a sharp increase in temperature does not frequently occur in industrial chemical reactions, it is instead a convenient and interesting feature to study in depth the temperature behavior of the nanoparticles. A fast thermal response can be achieved by properly designing the central section of the microchannel such that this last has a small thermal mass (see section 2.3.2).

Low power: a microheater with low power consumption is required to minimize the drift in the TEM image, resulting from thermally-induced deformations of the nanoreactor-holder system. Low power dissipation can be achieved by properly designing the central section of the microchannel such that this last has a small thermal conductivity (see section 2.3.2).

<u>Uniform heat distribution</u>: form the experimental point of view it would be advantageous that all the windows of the nanoreactor are at the same temperature. For example this would allow observing phenomena in multiple samples during the same experimental session thus increasing the statistical value of the experiment. In reality the temperature sensed is an average of the microheater temperature. Therefore, the temperature at which a phenomenon takes place can be accurately determined only if the relationship between the average temperature and the temperature at the observation window is known. Consequently, a uniform temperature distribution in the windows area is very important to ease this task and obtain an accurate reading of the temperature. A uniform temperature distribution across the window area can be achieved by properly designing the dimensions and spacing and shape of the microheater wires.

<u>High temperature</u>: the microheater has to be able to reach elevated temperatures to reproduce the real conditions of the gas-solid interaction under investigation. It is therefore necessary that the material of the microheater is capable to with stand very high temperatures, also in the presence of reactive gasses. A protective layer as LPCVD  $SiN_x$  is typically employed to prevent the direct interaction between the heated microheater and the gasses.

<u>Feasible sensing</u>: the sensing of the temperature is normally achieved by reading the resistance of the microheater. This can be translated into a temperature once the resistance-temperature relation is known. Ideally this relation should be linear or at least monotonic to simplify the calibration procedures and ease the temperature reading.

Material compatibility: the materials employed for the fabrication of the microheater are typically metals. At the same time the nanoparticles under study are also metals. During spectroscopic analysis the signal originating from the microheater can be quite intense compared to that of the nanoparticles thus masking the features of interest.

Micromachined microheater for this application are typically made of Pt [18], Mo [76], and TiN [77]. These are realized by using the same technology employed for the fabrication of MEMS microhotplates for gas sensing.

## 2.4 MEMS nanoreactors: design and fabrication

The MEMS nanoreactor first introduced in 2008 has already been developed in three different configurations. The first two, the glued nanoreactor and the wafer bonded nanoreactor, use two separate dies that are then assembled by means of glue or thin film sealing technique. The third one, the surface micromachined nanoreactor, uses a single substrate for the realization of the complete device.

### 2.4.1 The glued nanoreactor

As shown in Fig. 2.7 the first version of the MEMS nanoreactor consists of two dies assembled together. Each die is obtained by using surface micromachining techniques carried out on (100) Si wafers. The bottom die has a size of  $10 \times 3.33$  mm and integrates in its center a SiN<sub>x</sub> square-shaped suspended membrane released by etching the Si substrate. The membrane has a size of  $1 \times 1$  mm and a thickness of  $1 \mu$ m. This element constitutes the bottom part of the suspended microchannel. A resistive Pt microheater having a double-wound coil shape is embedded on the  $SiN_x$  support membrane. This is arranged in an area of  $0.34 \times 0.34$  mm. The positioning and size of the microheater allows for thermal isolation and therefore for low power consumption and fast thermal response. The suspended  $SiN_x$  membrane also integrates 20 electron transparent windows made of LPCVD  $SiN_x$ . These are elliptically shaped with a size of 8  $\times$  22  $\mu$ m and are arranged between the windings of the microheater. The thickness of the windows is 10 nm. The top die has a size of  $8.5 \times 3.33$  mm and integrates a recession of 1  $\mu$ m in the construction layers which is necessary to form the microchannel. Also for this die the Si substrate is removed in the central part to achieve a suspended  $SiN_x$  membrane. As for the bottom die 20 electron transparent windows are here integrated. However, these are rotated of 90° to maximize the superimposition with the bottom windows. To fix the microchannel height in the membrane area and prevent its stiction to the bottom membrane an array of circular 1.2  $\mu$ m-high SiN<sub>x</sub> spacers is integrated on the top membrane. Finally two apertures are present in the bottom die. These are the inlet and outlet of the microchannel necessary to flow gasses in and out of it. They are obtained by substrate removal at the same time of the release of the  $SiN_x$  membrane.

For the assembly, the two dies are brought together and aligned by using



Figure 2.7: (a) 3D sketch of the glued version of the MEMS nanoreactor. (b) Schematic cross-section showing the fabrication layers. (c) Optical image of the nanoreactor. (d) Optical microscope images of the reaction chamber. (e) TEM image of two superimposed electron transparent windows. Adapted from [36].

a custom made holder and a manual contact aligner. A good alignment is very important as the superimposition of the electron transparent windows has to be achieved to ensure the transparency of the nanoreactor. The alignment is then fixed by using a drop of UV-curing epoxy adhesive. Finally, the complete assembly and the sealing are achieved by manually dispensing a stripe of a specifically selected epoxy-adhesive all around the sides of the two dies. Once the dies are assembled, the two suspended membranes face each other creating a suspended reaction chamber. In this design, the reaction chamber is located below the surface of the dies. This allows for the protection of this delicate part against possible damage during handling and loading procedures. The two-die fabrication approach is also advantageous as the fabrication steps needed to achieve each of the two separate dies are relatively simple and small in number.

As shown in Fig 2.8, using this MEMS nanoreactor a resolution of 0.18 nm has been demonstrated at 120 kPa and 500 °C [33].



Figure 2.8: A representative high resolution TEM image of Cu/ZnO catalyst during exposure to 1.2 bar hydrogen at 500 °C. The image displays lattice fringes of a Cu nanocrystal and of the ZnO support [33].

However, this nanoreactor design presents also a number of drawbacks in terms of performances and fabrication and reproducibility. From the point of view of performances the maximum pressure is limited by the membrane design. Under pressure the suspended membranes bulges deforming the reaction chamber. The bulging of each membrane has been calculated be between 17 and 21  $\mu$ m already at 100 kPa [36]. As explained in section 2.3.2 this can cause focusing issues. More importantly the bulging causes an increase in the number of atoms the electron beam has to cross and therefore

a decrease in the spatial resolution of the TEM images. As proposed in [36], we can calculate the atomic density  $N_C$  projected along the beam using the ideal gas law:

$$N_C = \int_{beampath} n_c q \mathrm{d}z = P \frac{q w_0}{kT} \tag{2.1}$$

where  $n_c$  is the molecular density in the channel, q is the number of atoms per gas molecule, k is the Boltzmann's constant, T is the absolute temperature, z is the coordinate along the beam direction, P is the pressure,  $w_0$  is the gas path length. This last corresponds to the actual channel height given by the sum of the nominal channel height plus the bulging distance of the membranes. Assuming for this calculation a bulging distance of 17  $\mu$ m we obtain a  $w_0$  of 35  $\mu$ m. For a diatomic gas at a P=100 kPa, and T=300K we obtain a projected density of about  $1.7 \times 10^3$  atoms/nm<sup>2</sup>. This can be compared with the density of scattering atoms contained in one SiN<sub>x</sub> electron transparent window, which as proposed in [36] is given by:

$$N_C = \int_{beam} n_w \mathrm{d}z = \frac{t_w \rho}{A_{av}} \tag{2.2}$$

where,  $n_w$  is the volumetric atomic density,  $t_w$  is the window thickness,  $\rho$  is the mass density, and  $A_{av}$  is the average atomic mass of the material. For SiN<sub>x</sub>,  $\rho \approx 3.00$  g/cm<sup>3</sup> [78], and  $A_{av} \approx 21 \times u$ , where u is the atomic mass unit  $(1.66 \times 10^{-27} \text{ Kg})$ . Using Eq. 2.2 we find that one SiN<sub>x</sub> window of 10 nm adds an extra amount of matter corresponding to  $0.86 \times 10^3$ atoms/nm<sup>2</sup> along the electron beam direction. Therefore, already at 100 kPa the contribution of the gas layer in terms of scattering atoms is comparable to that of two windows. This is still acceptable. However, supposing that the membranes would not burst, at higher pressures (e.g. 0.5 or 1 MPa) the higher number of gas atoms would cause an increase in the scattering degrading the resolution of the TEM images. Apart from the resolution, the membrane design also limits the maximum operating pressure of the nanoreactor. According to simulations the max pressure sustainable by the membrane is below 300 kPa. An additional a problem related to the membrane is its recessed position. The location about 0.5 mm below the top surface limits the magnification during inspection with optical microscopes thus making integrity and post-loading inspections difficult.

From the point of view of fabrication poor yield and production time are the main drawbacks. The windows of this nanoreactor are very fragile as a result of their asymmetric shape and their small thickness. This results in many leaky devices and thus in a poor yield. The glue-based assembly method results extremely time consuming and dominates the production time [79]. This is highly undesirable because the MEMS nanoreactor is meant to be a batch fabricated, disposable device. The reason behind this is that the alignment and sealing is done manually and separately for each reactor. Second, the reactors often suffer from contamination by hydrocarbons. Hydrocarbon molecules are released by the employed epoxy adhesive when it is not entirely cross-linked. These molecules are cracked when they come in contact with the electron beam of an electron microscope. As a consequence, a layer of carbon is deposited on the nanoreactor windows and on the nanostructured materials under investigation. This obscures the images and, more importantly, interferes with the chemical surface reactions under study. Finally, the inclusion of particles during the assembly causes increase in the conductance of the microchannel with a factor up to 100 above the designed value [79]. The variation of the conductance between different nanoreactors is not desirable for the repeatability of the experiments. To solve this issue a high level of cleanliness is required during assembly. However, for several reasons this cannot be easily achieved [79].

To solve some of the problems mentioned above, a novel method for the assembly and sealing of the nanoreactors was developed by Mele [79]. This is described in the following section.

### 2.4.2 The fusion bonded nanoreactor

The fusion bonded nanoreactor is also based on the assembly of two separate dies. The main features reported for the glued nanoreactor, such as the dimensions, the hermeticity in a high vacuum environment, and the maximum operating pressure of at least 100 kPa are preserved [79]. However, a new assembly-sealing method was specifically developed mainly to solve the problems related to assembly and sealing described in section 2.4.1. The method is based on the silicon fusion bonding technique and on the thin-film encapsulation of electrical feedthroughs. Wafer bonding and encapsulation are performed at wafer level making this approach significantly less time consuming than the original die by die assembly. Moreover, this method avoids the use of adhesives, thus preventing hydrocarbons contamination. In order to integrate the fusion bonding and encapsulation steps into the original fabrication process [79], the fabrication of the top and bottom dies was modified. The top and bottom dies contains exactly the same elements as those of the glued version. Also, the construction materials employed are the same. The main difference is that the elements are fabricated in a 3  $\mu$ m deep cavity created into the Si substrate (see Fig 2.9 (a)). Once all the fabrication steps needed to achieve the two dies are completed, the construction layers are removed from the top surface of the dies to uncover



Figure 2.9: Schematics and images of the fusion bonded version of the MEMS nanoreactor. (a) Schematic cross-section showing the fabrication layers. (b) SEM image of the sealing at of the electrical feedthroughs. (c) Infrared image of a two bonded wafers. (d) Image of the fusion-bonded nanoreactor after dicing. (d) Optical images of the reaction chamber. (e) TEM image of two superimposed electron transparent windows. Adapted from [79].

the bare silicon surface, so to achieve a clean bonding surface. In order to achieve an effective bonding and high yield, particular attention has been placed on the protection and treatment of the bonding surfaces. Once the bonding surfaces are ready, the two wafers containing the top and bottom dies are aligned and bonded together. Another difference is that the central membranes are released only after the assembly. A detailed description of the fabrication of the dies, preparation of the bonding surfaces, and of the bonding procedures can be found in [36]. Due to the presence of the electrical wires necessary for the control of the microheater a continuous bonding surface on the bottom die cannot be achieved. Therefore, an additional layer was needed to seal the side of the nanoreactor where the wires pass through. For this step, a layer of 4  $\mu$ m of PECVD TEOS is employed .

This layer and the bonded wafers are then covered with an additional 500 nm of LPCVD SiN<sub>x</sub> (see Fig 2.9 (b)). By using this last layer as a mask the membranes of the top and bottom die forming the reaction chamber of the nanoreactor are released by etching the silicon substrate. During this step also the inlet and outlet are formed. The individual nanoreactors are then obtained by dicing the bonded wafers. Finally, the inlet and outlet apertures and contact-pads are opened by dry etching the stacks of layers present in those regions. Other differences between the first and this second nanoreactor version are the nominal channel height which now is 2  $\mu$ m and the thickness of the windows which has been increased to 15 nm. The first difference is a result of the fabrication process; this has the beneficial effect of allowing easier loading. The second difference was introduced to obtain more robust windows with the aim of improving the production yield. Compared to the first version the second version provides an easier, faster and more reproducible assembly of the nanoreactors. However, yield problems still exits due to the complex fabrication steps involved for the realization of the dies on the wafers and to the bonding and sealing procedures. In particular the problems encountered were void formation and misalignment during the bonding. In addition, the problems related to the suspended membrane design remains. To solve these problems a completely new fabrication method was developed, resulting in a third version, described in the following section.

### 2.4.3 The surface micromachined nanoreactor

The third nanoreactor version is designed to solve the bulging and max pressure problems and at the same time to allow a more reliable batch production, by eliminating the assembly and sealing steps. The main idea is create a nanoreactor as a single die using surface micromachining techniques which are widely employed for the fabrication of microchannels [65, 70, 74, 75]. In general, surface micromachining offers several advantages compared to the other fabrication techniques for microchannels. It enables an excellent control of channel dimensions and shape. It leads to the fabrication of microchannels located at the surface of the substrate and separated from the external environment by only a thin membrane. This provides transparency, as well as a small working distance which is required for high-resolution analytical equipment such as optical microscopes. Finally, surface micromachining is compatible with conventional planar IC technology, simplifying the integration of sensors and actuators into the channel. These advantages are also beneficial for the nanoreactor.

The third nanoreactor design is shown in Fig 2.10 (a). It consists of a

 $SiN_x$  surface micromachined channel achieved by the etching of a sacrificial oxide layer (see Fig 2.10 (b)). The thickness of this layer roughly establishes the thickness of the channel. Nanoreactors with a very thin channel of approximately 1  $\mu$ m where designed as well as thicker channel of with 4.5  $\mu$ m. The microchannel is 5.4 mm long and 300  $\mu m$  wide. The ceiling of the microchannel is equipped with an array of pillars which anchor it to the floor also made of  $SiN_x$ . The anchoring prevents the bulging and increases the max operating pressure to 900 kPa. Moreover, it prevents stiction during the sacrificial etching. The microheater is embedded on the outer surface of the ceiling in the central section of the microchannel. Here a set of electron transparent windows is integrated. In a similar way a set of electron transparent windows is integrated also on the floor of the microchannel. These are positioned such that they result aligned to the top windows. In the central section the microchannel is embedded on a suspended support membrane made also of  $SiN_x$  and sacrificial oxide. As for the previous two versions of the nanoreactor this membrane is square-shaped with a side length of 1 mm. The release of the membrane is achieved by anisotropic wet etch of the Si substrate. During this step the inlet outlet apertures are also formed. The position and size of the inlet and outlet apertures is the same as for the two previous versions of the nanoreactor.



Figure 2.10: Schematics and images of the surface micromachined nanoreactor. (a) Schematic 3D. (b) Schematic cross-section showing the fabrication layers and topography. (c) Optical image of the nanoreactor. (d) Optical images of the reaction chamber. (e) TEM image of two superimposed electron transparent windows. Adapted from [80].

Besides the increased maximum operating pressure and the stable channel height, this design brings some additional advantages. The location of the microchannel at the surface allows for optical inspection at high magnification. This expedites the inspection procedures necessary during the device fabrication and the preparation of the experiments. The elimination of complicated assembly procedures drastically improves the yield, cleanliness, and reproducibility.

However, some drawbacks are also present. The microchannel, being at the surface and not buried as for the previous versions, is more vulnerable and can be easily damaged during the handling of the nanoreactor. The inlet and outlet apertures present a perforated membrane structure which can cause problems during the loading of the nanoparticles (they act as a filter that gets clogged). Also, due to the high topography resulting from the fabrication process, the loading of the samples on the windows is problematic. Finally, the sealing of the channel leads to high topography with subsequent problems during the fabrication (see Chapter 5).

### 2.4.4 Design and fabrication improvements

The previously developed MEMS nanoreactor configurations have validated the potential of this technology for the study of solid gas interactions in TEM. With each version improved performance, increased versatility and yield has been achieved. However, there are still some aspects that need to be addressed. The surface micromachined reactor maintains its designed channel height also under elevated pressures. Due to the reduced gas layer thickness, the contribution of the windows to the loss of spatial resolution in the TEM images becomes now dominant. This is shown in the graph of Fig 2.11 where the projected density of scattering atoms has been calculated using Eqs. 2.1 and 2.2. The contribution of the gas layer for the currently employed channels heights, i.e. 1  $\mu$ m and 5  $\mu$ m, is negligible compared to that of the windows up to a pressure of 1MPa (10 bar) and 0.1 MPa (1 bar), respectively. At the same time the maximum operating pressure of the nanoreactor is currently limited to pressure below 1 MPa. Therefore, to improve the nanoreactor performance in terms of resolution alternative materials and/or design modifications needs to be explored. To increase the resolution for pressures lower than 1 MPa (10 bar) it is interesting to investigate alternative materials for the windows (Chapter 4). To increase the maximum operative pressure above 1 MPa, modification on the channel design or material choice should be considered (Chapter 5). In a similar way it is interesting to explore alternative configurations or materials that could enhance the performance in terms of heating (Chapter 6).



Figure 2.11: Graph showing the atomic projected density of scattering atoms for two  $SiN_x$  windows of 15 nm and for the gas contained in microchannels of increasing thickness as a function of the gas pressure.

From the technological point of view a more robust and flexible process compared to the one used so far, is highly desirable. This would increase the yield, an essential aspect considering the disposable nature of the nanoreactors and the large volumes that might be required for the type of experiments mentioned in Chapter 1. Moreover, some topography issues or processing constraints should be addressed to improve performance and yield while lowering the overall manufacturing costs.

In this thesis, silicon carbide (SiC) will be investigated as alternative material to try to address the aforementioned points. In fact, SiC possess many intrinsic properties that fulfill several of the requirements outlined for the three main elements of the nanoreactor. Thin SiC layers, either amorphous or polycrystalline, will be employed as window, channel or heater material. In addition, we will show that the use of these layers can helps "relaxing" few steps which are critical for the nanoreactor fabrication, with beneficial effects to reproducibility and yield.

A modular approach has been followed, i.e. the materials currently employed for the fabrication of each of the individual elements of the nanoreactor will be replaced by specifically developed SiC layers fulfilling the requirements indicated in this chapter. In addition we will show that the three SiC elements are fully compatible, as proven by the realized SiC-based nanoreactor presented at the end of this thesis work (Chapter 7).

In the following chapter a brief introduction to the LPCVD system and

process employed in the deposition of the SiC layers is presented together with a description of the tools and techniques used for their characterization.

# CHAPTER 3

# Deposition of SiC Thin Films and Characterization Techniques

### 3.1 Deposition of SiC layers

The SiC layers to be considered as fabrication material for the alternative versions of the three main elements of the nanoreactor were deposited by LPCVD. A description of the system employed for the deposition is first described. The tree different SiC layer types, obtained as a function of the deposition parameters, are then introduced.

### 3.1.1 The LPVCD system

The system employed is a hot-wall commercial horizontal LPCVD reactor (Tempress Systems). A schematic illustration of the system is shown in Fig. 3.1. It consists of a cylindrical fused silica tube with a length and a diameter of 175 cm and 22 cm, respectively. For thermal isolation this is inserted into a cylindrical shaped furnace made of refractory stone. The tube is heated up by means of three resistive coils placed into contact with its central part. A Digital Temperature Controller (DTC) controls the temperature by regulating the current flowing through each of the heating coils. Three equidistantly spaced thermocouples are placed into contact with the tube to sense its temperature. The DTC reads the temperature of each of the thermocouples and compare it to that reported on a temperature cali-

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bration table. This contains the temperature values that the thermocouples need to read to obtain the desired temperature inside the tube. In addition, the temperature set point of each coil is such that a constant temperature is established in the central part of the tube. This enables for a uniform layer deposition across a number of wafers. A series of vacuum pumps connected at the backside of the tube by means of a pipe are employed to establish the desired pressure. The leak tight connection of the pipe is ensured by a sealing metal flange equipped with O-rings resistant to high temperatures ensures. These are also water-cooled to extend their life preventing its failure when long depositions are performed at very high temperatures. Thanks to this system temperatures up to about 860 °C can be reached. The wafers, sustained in a vertical position by a quartz boat, are loaded into the furnace by means of a silicon carbide cantilever paddle.



Figure 3.1: Schematic of the LPCVD system employed for the deposition of the SiC layers. The main elements of the system are shown.

The insertion of the paddle into the tube is performed at a slow constant speed by means of a motorized arm. Once the wafers are loaded, a circular metal plate mounted on the paddle press against an O-ring mounted on a metal flange allowing the sealing of the tube. Process and purging gasses are injected in the tube by apertures present in this flange. The purging gas employed for our system was ultra-pure nitrogen (N<sub>2</sub>) obtained from a liquid nitrogen source. During the deposition the gasses (section 3.1.2) flow from these apertures to the back of the tube. In their path they form intermediate species that react at the heated wafer surface to form the layer. The amount of gasses flowing into the tube is regulated by means of mass flow meters allowing flows from 0 to 500 standard cubic centimeters per minute (sccm). The desired pressure inside the tube is established by regulating the speed pump. The pressure is monitored by means of pressure gauge located at the front flange. The achievable pressure depends on the amount of gasses injected in the tubes and the capabilities of the pump. For our system the lowest achievable pressure was about 60 Pa (0.6 mbar). The mass flow meters and the speed of the pump are controlled with a feedback loop by a Digital Process Controller (DPC). This contains the instruction of the program of the specific deposition process together with its parameter. A complex system of valves inserted at the gas lines to ensure safe operation is also controlled by the DPC.

The low pressure, key for LPCVD processes, means high diffusivity of the gas species towards the surface of the wafer. This translates into reaction-limited depositions also at elevated temperatures. This enables to deposit layers with high uniformity, high quality, and high step coverage [81,82]. In addition, it allows batch processing a large number of wafers as these can be closely packed [81,82].

Despite the high diffusivity, the deposition can be however influenced by the total amount of gas injected in the reaction tube. The gas speed, in fact, depends on both the pressure and the amount of gas [81]. At a given pressure the higher the total amount of gasses the faster is the flow in the tube. Alternatively, given a certain amount of gasses, the higher the pressure the lower the speed of the gas species. Therefore, both pressure and total amount of gasses have to be taken into account when developing deposition recipes.

### 3.1.2 Deposition parameters and layer types

The precursors gasses employed for the SiC layers deposition are dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>) with this last diluted at 5% in hydrogen (H<sub>2</sub>). As reported in [83], the deposition temperature and the SiH<sub>2</sub>Cl<sub>2</sub> to C<sub>2</sub>H<sub>2</sub> gas flow ratio ratio (*GFR*) strongly influence the structure of deposited the SiC layers. By changing these values it is possible to obtain amorphous SiC (a-SiC) or polycrystalline SiC (poly-SiC) layers. The data shown in Table 3.1 were used as starting point in the optimization of these two types of layers as described in detail in Chapters 4 and 5. In addition, the poly-SiC layers were in-situ doped. For this we employed ammonia (NH<sub>3</sub>) diluted at 5% in H<sub>2</sub> as precursor to obtain nitrogen-doped poly-SiC layers (poly-SiC:N). Details on the deposition and optimization of these layers are reported in Chapter 6.

The above mentioned SiC layers where characterized for their suitability as electron transparent windows, as structural microchannel material or microheater material for the nanoreactor. In the following sections the characterization techniques and related methods employed are described.

GFR	Deposition Temperature (°C)				
$\left( {^{\mathrm{SiH}}_{2}\mathrm{Cl}_{2}}/{^{\mathrm{C}}_{2}\mathrm{H}_{2}} \right)$	860	820	780	760	740
3.0	poly.	poly.	amorphous	-	-
4.0	poly.	poly.	amorphous	-	( <del>-</del>
5.0	-		-	2	-

poly.

poly.

poly.

Table 3.1: Crystallinity of SiC layers as a function of temperature and ratio of the precursor gasses (GFR) at 80 Pa pressure. Adapted from [83].

### **3.2** Characterization techniques and tools

poly.

Several techniques were employed for the characterization of the SiC layers deposited with the aforementioned LPCVD furnace. The basic principle of each technique is here briefly introduced and a somewhat more extensive description is given for the techniques employed for the assessment of the chemical composition, the structural and morphological features, and the mechanical properties.

### 3.2.1 Chemical composition and structure

poly.

### 3.2.1.1 Ion beam analysis techniques

6.0

The elemental composition and its variation along the thickness (depth profiling) of the SiC layers were accurately determined by means of ion beam analysis (IBA) techniques. In IBA, high energy ions are accelerated towards the sample to be analyzed. The impinging ions interact with both the electrons and the nuclei of the atoms composing the sample. These interactions result in the loss of energy and trajectory modifications of the particles. Also, they may result in the generation of new particles, x-rays,  $\gamma$ -rays etc. IBA relies on the analysis of these phenomena to determine the elements present in a sample together with their amount and distribution. Different IBA techniques exist. For our samples Rutherford backscattering spectrometry (RBS), elastic backscattering spectroscopy (EBS), and elastic recoil detection (ERD) were employed.

In RBS and EBS the energy and the number of the ions that are scattered back form samples are analyzed. The scattering events between the impinging ions and the nuclei of the atoms in the sample are elastic and result in trajectory change and loss of energy. The amount of energy lost depends on the mass of the target atom; the lighter the atom the higher the energy loss. This permits to discern between atoms with different mass. In addition, the energy loss also depends on the depth at which the atom is located. The further the atom is from the surface, the higher the energy loss. In their path inward and outward the sample, the ions interact with the electrons of the atoms giving rise to excitation and ionization events and and thus progressively losing energy. The stopping power of the electrons depends on the material and is a function of energy. If this process is repeated for many ions, a profile of the amount of atoms versus depth along the thickness of the sample is generated (Fig. 3.2). The amount of backscattered particles from any given element is proportional to its areal concentration, thus enabling quantitative characterization. In RBS and EBS the energy of each ion that scatters back from the sample at specific angles is analyzed by, solid state detectors. The beam energy and the setup configuration (sample tilt, detector angles) is optimized for each experiment. For each detector a spectrum (counts vs. energy) is built. These spectra are then analyzed to extract the composition of the sample and the depth profiles of its elements. The analysis is made by fitting the spectra using a dedicated simulation software. The simulation is based on the knowledge of the scattering cross-sections of the given atoms and the stopping powers. The elemental amounts obtained by the analysis of the IBA spectra are always expressed in atoms/cm<sup>2</sup>.

The elastic scattering events on which both RBS and EBS are based, take place when the impinging particle has a smaller mass compared to that of the target atoms (Fig. 3.2). If the mass of the impinging particle is larger than that of the target atom, the latter can be recoiled out of the sample (Fig. 3.2). This phenomenon is at the base of ERD. In this technique the charged particles are directed towards the sample with a glancing angle and the recoiled atoms collected at a specific angle by a detector. The detectors equipped with a stopper foil, to stop the (heavier) beam ions that are scattered under the same forward angle. Despite this technique offers lower depth resolution compared to REBS and EBS, it is widely employed as it enables the detection of light elements such as H. More details on the IBA techniques described above can be found in [84–87].

RBS and ERD were employed to characterize the a-SiC layers. For both methods a He+ beam of 2 MeV was employed. The RBS spectra were acquired under channeling conditions which means that the c-Si (100) substrate was aligned with the ion beam. This significantly reduces the contribution of Si substrate and increases the sensibility to the target atoms at



Figure 3.2: (left) Schematics illustrating the working principle of RBS and ERD techniques. Adapted from [88, 89]. (top-right) Energy lost by an ion with an initial energy  $E_0$  that scatters from depth t. First, in its path inside the sample, the ion looses energy due to electronic stopping ( $\Delta E_{in}$ ). When the ion hits the nucleus of an atom it elastically scatters loosing again energy ( $\Delta E_s$ ). Finally, in its way out the ion further loses energy due again to electronic stopping ( $\Delta E_{out}$ ). Therefore, the final energy of the backscatterd ion once out of the sample is  $E_1 = E_0 - \Delta E_{in} - \Delta E_{out}$ . From [84].(bottom-right) Example of an RBS spectrum of a sample consisting of a Ni layer on top of a Si layer. From [84].

a certain depth. These are in fact in the shadow of shallower atoms, thus the probability to be hit by a projectile is lower. The beam was aligned perpendicularly to the sample surface such that the channeling took place along the (100) axis. The two detectors available in the setup were placed at a scattering angles of 170° and 100°. The ERD spectra were instead obtained under 15° glancing incidence and with the detector was placed at 25° recoil angle. This last was equipped with a Mylar stopper foil of 9  $\mu$ m.

The characterization of the poly-SiC and polySiC:N layers was performed by EBS. This technique was chosen above RBS because it offers better depth profiling for thick layers and better sensitivity in the determination of C and Si atoms. For the EBS measurements, the He<sup>+</sup> beam was set to 2.9 MeV. In this case we wanted to avoid channeling effects, therefore the sample was tilted by  $4^{\circ}$  in both the horizontal and the vertical plane. The detectors were placed at angles similar to those employed for the acquisition of the RBS spectra.

All the IBA measurements and analysis were performed by Detect99<sup>1</sup> using a 3.5 MV singletron by HVEE. The spectra were interpreted by means of RUMP simulations [90]. Extensive effort was placed in the optimization of the measurement and interpretation of the spectra. In particular, the determination of the cross-sections for the analysis of the EBS data was rather demanding. A detailed description of these procedures is out of the scope of this thesis. Thus, in Chapters 4, 5, and 6 we will present only the obtained results.

### 3.2.1.2 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive technique employed for the determination of the crystalline structure of materials. In this technique, a sample is irradiated with x-rays of a certain wavelength  $\lambda$  with a variable angle of incidence  $\theta$ . Each atom composing the material will scatter the incident X-rays generating spherical x-ray waves. If the atoms are regularly arranged, as it is the case for crystalline solids, these waves will interfere destructively in most directions and constructively in only a few directions. Considering an array of atoms regularly arranged in crystalline planes with a certain distance d, as illustrated in Fig. 3.3, the constructive interference is achieved when  $2dsin\theta = N\lambda$ , where N is an integer. This condition is known as Bragg's diffraction. Each material with its own specific crystalline structure will exhibit a specific diffraction pattern. This consists of a series of peaks, each with a certain intensity and width, positioned at different angle values  $(2\theta)$ . By comparing the peak positions to tabulated values (using a stick pattern) it is possible to determine the crystallographic orientation of the sample under study. The intensity and width of the peaks can be interpreted or analyzed to extract qualitative or quantitative information on the crystalline structure. The peaks are fitted to extract parameters such as their maximum intensity, area, and full width half maximum (FWHM).

As shown in Fig. 3.3 a typical x-ray diffractometer consists of an X-ray source, a sample stage and a detector mounted on a goniometer system. A monochromatic x-ray radiation is usually obtained by filtering the radiation generated by the electron bombardment of a copper (Cu) electrode in a vacuum tube. The sample is placed on the stage and the x-ray source and

<sup>&</sup>lt;sup>1</sup>www.detect99.nl

detector moved to achieve an angular scan of the sample. More details on the XRD techniques can be found in [91,92].



Figure 3.3: Brag diffraction and schematic of an x-ray diffractometer.

The poly-SiC and poly-SiC:N layers were submitted to XRD analysis to study their structure. Scans were recorded using the PANalytical X'pert Pro MRD system setup. The geometry was parallel beam, while the X-ray radiation used was a Cu-K $\alpha$ , obtained at 40 kV and 40 mA. After alignment of the sample (z,  $\theta$ ,  $\Omega$ ), diffraction patterns were recorded between 5° and 90° (2 $\theta$ ), step size 0.02°, with a step time of 20 seconds. Omega was fixed at 5°. Data evaluation was done with the Bruker program EVA and using the ICDD PDF-44 database. All patterns were background-subtracted, meaning that the contribution of air scatter and possible fluorescence radiation was removed.

#### 3.2.1.3 Transmission electron microscopy

Transmission electron microscopes (TEMs) enable physical and chemical characterization of samples with extremely high resolution and accuracy. The physics behind the functioning as well as technology of TEMs are extremely complex, details can be found in [16]. Here the working principle, touched on in Chapter 1, is described together with some essential details on the microscope. In a TEM a beam of electrons with energies between 100 and 400 keV is accelerated towards the specimen to be characterized. As illustrated in Fig. 3.4 when impinging on the sample a wide variety of interactions take place. The trajectory and the energy of the impinging electrons will be modified. Part will pass through the specimen experiencing elastic or inelastic scattering, and part will pass nearly unchanged. The transmitted electrons are properly processed and collected to obtain an image or structural information of the specimen. At the same time, the beam-sample interaction will result in the generation of X-rays, photons and secondary



Figure 3.4: Signals generated when a high-energy beam of electrons interacts with a thin specimen. Most of these signals can be detected in different types of TEM. From [16].

electrons. Typically, the generated X-rays are collected to perform chemical analysis.

For imaging and structural analysis, the TEMs can be operated in several modes depending on the way the electron beam is modified before and after impinging on the specimen. The modification of the beam is achieved by means of electromagnetic lenses and apertures. As shown in Fig. 3.5 these elements are all contained into which is referred to as TEM column. The electron-gun, responsible for the generation and acceleration of the electrons, is located at the top of the column. A set of condenser lenses placed immediately after the electron-gun enable controlling the diameter of the electron-beam. Approximately in the central part of the column, the electron-beam passes through the specimen, located, by means of a TEM holder, between the lower and upper objective lenses and more specifically between their polepieces (see Fig. 3.5). These lenses allow for the focusing and positioning of the electron beam on the sample. In the lower part of the column another set of lenses provide the magnification and focusing of the image into a viewing screen or on a computer display via a CCD detector or a TV camera. For the reasons explained in Chapter 1, TEM column is kept at high vacuum in the  $10^{-5}$  -  $10^{-6}$  Pa (  $10^{-6}$  -  $10^{-7}$  mbar) range.

TEM images were acquired for the inspection and characterization of a-SiC layers. For imaging this layer, cross-section samples were prepared by mechanical grinding and argon ion-milling. Then, high-resolution TEM images were acquired in a Philips CM-300UT microscope. The same microscope was employed for the inspection of a-SiC electron transparent windows and for their performance assessment. When needed, analysis of the images was performed with ImageJ software.



Figure 3.5: TEM microscope and schematic showing the main elements located inside its column.

### 3.2.2 Surface properties

### 3.2.2.1 Scanning electron microscopy

Scanning electron microscope (SEM) is a well-known tool enabling the observation at high magnification of materials and structures. In this thesis, SEM was employed to obtain high resolution images of the surface of the LPCVD SiC layers and of the fabricated MEMS structures.

SEM uses the electrons, whose wavelength is shorter than that of visible light) as a probe thus allowing resolutions down to a few nanometers. The electron source (electron-gun) is typically a field-emission gun or a filament. The electrons are accelerated with energies in the range 0.2-30 keV into a system of electromagnetic lenses and apertures that create a highly-focused beam on the sample. A system of magnetic coils deflects the beam in the xand y-direction for scanning the sample. The scanned area can be squareor rectangular-shaped with a maximum side length in the order of few mm. The electron beam focused on the sample causes the emission of electrons, X-rays, and photons. Typically the secondary electrons emitted by the sample are collected by a properly positioned detector and processed to build an image of the sample. As the intensity of the generated secondary electrons varies with the angle of the incident electrons the morphology of the sample can be reproduced as gray-scale image. As for TEMs to prevent damaging the electron source and allow the formation of a focused electron beam, the SEM needs to operate at very low pressures ( $<10^{-5}$  Pa,  $10^{-6}$  mbar). For inspection samples are loaded on a motorized inside the vacuum chamber of the microscope. The stage enables the displacement of the sample in the three main spatial directions (x, y, z) as well as its rotation. The part of interest of the sample can thus be imaged by accurate positioning it under the electron beam. In addition, the motorized stage allows the tilting of the sample, thus enabling the acquisition of 3D, rather than only surface (top-view), images.

High resolution SEM (HR-SEM) images of the surface of poly-SiC and poly-SiC:N layers were acquired using an extreme high resolution SEM (FEI Verios-460L) operated in immersion mode. The acceleration voltage was set to 10 kV and the filament current to was varied between 25 to 50 pA to obtain optimal imaging conditions. Samples of  $1.5 \times 1.5$  mm were inspected. Top view and of 45° tilted view of the surface of the SiC layers were acquired at various magnifications. These HR-SEM images allowed for both qualitative and quantitative analysis of the surface morphology. The approach employed for the quantitative analysis is here explained. Through the use of a specific image processing and analysis software (ImageJ) an estimation of the size of the horizontal section of the grains was obtained. The analysis was conducted on HR-SEM images acquired with 0° tilt angle (top view) and with a horizontal field of view (HFV) of 4  $\mu$ m. The employed procedure is illustrated with an example in Fig. 3.6. As first step the contrast of the HR-SEM image of the surface was enhanced. Then, by means of an algorithm searching for the maximum brightness points in the image, the apex of each grain was identified (Fig. 3.6 (a)). Following, the grain boundaries defining the individual grains were found by another algorithm searching for the minimum brightness points in the surroundings of each identified apex. This procedure allowed building a map of the grain boundaries as the one shown in Fig. 3.6 (b). The surfaces enclosed by the grain boundaries correspond to the horizontal cross-sections of the grains. The software calculated the areas of each of these surfaces together with their distribution (Fig. 3.6 (c)). The mean value of the distribution was employed as an estimation of the average cross-section area,  $G_{A_{av}}$ . Finally, under the assumption that found area is enclosed into a circle its diameter was employed an estimation of the average width of the grains  $G_{W_{av}}$ .



Figure 3.6: Illustration of the procedure employed for the estimation of the average grain width using a HR-SEM image of the poly-SiC surface. (a) Top view HR-SEM image acquired with a HFV of 4  $\mu$ m, the apex of each grain is identified and marked. (b) Map of the grain boundaries extracted from the HR-SEM image. (c) Distribution of the areas enclosed by the grain boundaries.

### 3.2.2.2 Atomic force microscopy

Atomic force microscopy (AFM) is a technique used for the quantitative characterization of the surface morphology (imaging and measuring) of a wide variety of materials with a resolution that can reach the nanometer scale. AFM uses a mechanical probe to sense the surface of a sample. The probe consists of a cantilever with a very sharp tip at its free-swinging end, protruding from a support plate. When the tip is brought into proximity of the sample surface, forces between the tip and the surface atoms lead to a deflection of the cantilever. Depending on the operation mode, these forces can be mechanical contact force, van der Waals forces, electrostatic forces, capillary forces etc. The vertical deflection of the cantilever is monitored by means of an optical system (optical lever). A laser beam is focused at back of the cantilever and its reflection collected by a photodetector. The movement of the laser spot on the photodetector gives an amplified measurement of the movement of the probe (sensitive to nanometer level movements). The sample surface is scanned by the probe along closely spaced lines in an area that is generally square shaped, by moving the sample using a piezoelectric tube scanner. This enables movements in x, y and z directions with extremely high precision. A feedback system is employed to keep the distance constant (close contact) and consequently, the force between the tip and the sample surface. The feedback system uses the signal from the photodetector to adjust the height (z direction) of the sample to keep the same probe-sample distance. The amount of z displacement corresponds to the sample topography.

Depending on the nature and the surface morphology of a sample, different operation modes can be employed for the scanning. For our measurements the AFM was operated in tapping mode. In ambient conditions, most samples develop an extremely thin liquid layer at the surface (humidity meniscus). This makes difficult to keep the probe tip close enough to the sample while preventing the tip from sticking to it. The tapping mode solves this problem. A schematic of the tapping mode operation is shown in Fig. 3.7. In this mode the cantilever is driven to oscillate near its resonance frequency by means of an additional small piezoelectric actuator. When the tip comes close to the surface the forces acting on it cause the amplitude of the oscillation to decrease. The height (z) necessary to maintain the amplitude of the cantilever oscillation to a certain value (set-point) corresponds to the sample topography.

Apart from the operation mode, also the probes are important to obtain correct scanning of a surface. A wide variety of probes differing for construction material and geometry and fabricated by means of microfabrication techniques are available. Typical probes are made of monocrystalline Si. The back side of the cantilever is usually covered by a gold layer to increase the reflection of the laser beam. The tip of the probe is extremely sharp with a radius of curvature at the apex varying between 5 and 20 nm. In some cases, a coating is applied to the tip to improve its wear resistance



Figure 3.7: Schematic illustration showing the working principle of an AFM operated in tapping mode. From [93].

and response to the sample surface. AFM probes are disposable and are replaced when the tip is damaged (wear) or contaminated or when the cantilever is broken.

The main advantage of AFM compared to SEM is the possibility of numerically processing the acquired data. These are triplets of x, y, z values, expressing the measured height value z as a function of x, y pairs corresponding to the plane coordinates. The post processing of these data generates a 3D image of the scanned surface. Also, the data can be analyzed to obtain a quantitative characterization of the surface features.

The AFM setup employed for the characterization of the surface morphology of the SiC layers was a NTEGRA Aura AFM. For this measurement,  $1.5 \times 1.5$  mm samples were diced and glued on an Invar disk using a silver-based conductive adhesive. Details on the scanning area, resolution and probes employed are given in Chapters 4, 5, and 6. Post processing and analysis of the data were performed by means of the data visualization and analysis software Nova by NT-MDT and Gwyddion. Post processing of the raw data was first performed to achieve a 3D reconstruction of the surface morphology. The tilt from each of the single scanned lines was removed by subtracting a first order polynomial. If needed the tilt was then removed from the entire set of data by the subtraction of a second order surface (typically a plane). These operations also lead to a height shift such that the minimum recorded height was set to zero. Afterward, the post-

processed data were analyzed to extract quantitative information on the surface morphology. The amplitude parameters extracted and employed for our analysis are reported and defined here below.

- $Z_{MAX}$ : height of the highest peak in the scan.

 $-Z_A$ : average surface height which, defined as:

$$Z_A = \frac{1}{NM} \sum_{x=1}^{N} \sum_{y=1}^{M} Z(x, y)$$

 $-S_Q$ : RMS surface roughness, representing the deviation of the surface height from the average surface height  $Z_A$  and defined as:

$$S_Q = \sqrt{\frac{1}{NM} \sum_{x=1}^{N} \sum_{y=1}^{M} (Z(x,y) - Z_A)^2}$$

 $-S_Z$  is the maximum height of the average profile obtained by averaging all the scanned lines.

More details on the amplitude parameters defined above and on additional parameters can be found in [94].

#### 3.2.2.3 Contact angle measurement

Contact angle measurements were performed to investigate the wettability of the SiC layers. The method consists in delivering a small amount of liquid onto the surface of the layer and measuring the angle formed between the surface of the layer and the liquid-air interface (see Fig. 3.7). The value of the angle depends on the properties of both the solid and the liquid. The balance between the cohesion forces acting within the liquid molecules (e.g. hydrogen bonds and van der Waals) and the adhesion forces (e.g. electrostatic, and mechanical) acting between the liquid and the solid surface, determine the contact angle. The liquid can spread on the solid surface forming a thin film and giving rise to a very small contact angle. This indicates a high wettability of the surface. Alternatively the liquid can form a droplet (sessile drop) characterized by a large contact angle and indicating a low wettability. Generally a very rough distinction is made considering a surface hydrophilic for  $\theta < 90^{\circ}$ , and hydrophobic for  $\theta > 90^{\circ}$ .

Several methods exist to measure the contact angle. We employed the static sessile drop method. This relies on acquiring a side view image of the liquid droplet shortly after its formation, and determining the contact angle by means of a dedicated software implementing a fitting. The measuring setup was a Dataphysics OCA 20 Contact Angle System, consisting of a computer controlled dispensing unit allowing the delivery of a precise amount of liquid onto the layer surface. This last is positioned on a stage interposed between a camera and a light source. The stage can be moved horizontally and vertically to position the droplet on the optical axis and for focusing. The intensity of the light can be regulated to tune the contrast of the image of the side view of the droplet. Once such an image is acquired this can be processed to extract the contact angle.



Figure 3.8: (a) Contact angle measurement setup. (b) Profile a water drop on a hydrophilic surface and measurement of the contact angle.

### 3.2.3 Thickness

The thickness of the SiC layer was determined using three different techniques: spectroscopic ellipsometry, optical reflectometry and contact profilometry. The first two techniques provided indirect measurement of the thickness, while with the last a direct measurement was obtained. To obtain an accurate determination of the thickness of the SiC layers the most suited technique was selected depending on the features of the layer and the capabilities/limitations of the technique itself.

Each of these techniques presented advantages and disadvantages in terms of ease, speed, precision, and accuracy of the measurement. In addition, the morphological and optical properties of the poly-SiC layers influenced each of the techniques in a different way.

### 3.2.3.1 Spectroscopic ellipsometry

Ellipsometry is an optical characterization technique employed to determine the optical and structural properties of thin multi-layer structures. The working principle is illustrated in Fig. 3.9. A light beam with a known polarization is directed to the sample that needs to be characterized. The interaction of the beam with the layers of the sample results in a reflected beam which polarization is different compared to that of the incident beam. The polarization change is strictly related to the physical and optical properties of the layers. An ellipsometer determines this change of the polarization by measuring with extremely high accuracy two quantities,  $\Psi(0^{\circ} \leq \Psi \leq 90^{\circ})$  and  $\Delta(0^{\circ} \leq \Delta \leq 360^{\circ})$  [95]. They are related to features of the layers, like thickness, optical constants, crystallinity, etc. The procedure needed to obtain these quantities is the following:

<u>Measurement</u>:  $\Psi$  and  $\Delta$  are measured as a function of the light beam wavelength angle of incidence and/or polarization state.

Modelling: a mathematical model is specifically built for the measured sample. The model usually contains known parameters: the angle of incidence, the wavelength and the polarization state of the incident light beam, together with the number of layers constituting the sample. The model also contains the unknown physical parameters such as: layer(s) thickness and optical constants. This model has to be such that  $\Psi$  and  $\Delta$  can be accurately calculated starting from a certain set of physical parameters. The mathematical model is based on Snell's law, Fresnel's equations and thin film interference equations. If one or more layers consist of a composite material, equations for calculating the effective complex dielectric function can be included into the mathematical model.

<u>Fitting</u>: the unknown physical parameters are varied and data ( $\Psi$  and  $\Delta$ ) are generated until finding a set of optimized parameters that yield the generated data to closely match the measured data. Complex mathematical algorithms are employed for this task.

Evaluate fitting: the set of parameters found is analyzed to establish that these are unique, physically reasonable and not strongly correlated. If these criteria are met it is possible to conclude that the constructed model probably represents the physical reality of the sample. In this step a number of statistical quantities that help to evaluate the accuracy and precision of the fit results, are calculated. At this point the model can be modified if unsatisfactory results are obtained; either because statistics show the results are not unique or because the features in the experimental data, are not adequately described by the model.

Variable angle spectroscopic ellipsometry (VASE) was employed to determine the thickness of the a-SiC layers. The instrument employed was a Woollam M2000UI. The ellipsometric spectra were acquired at 7 different angles between  $45^{\circ} - 75^{\circ}$  (step of 5°), in the spectral range between 245

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Figure 3.9: (a) Schematic illustration of the principle of spectroscopic ellipsometry. (b) Data analysis procedure. From [96].

nm and 1690 nm. The procedure and the model employed for the fitting of the data are described in Chapter 4. VASE measurements were performed also on poly-SiC and poly-SiC:N layers. However, due to the morphology, structure and electrical properties of these layers, the modelling and fitting resulted very difficult. Different techniques were employed to measure the thickness of these layers.

### 3.2.3.2 Optical reflectometry

Optical reflectometry allows fast and precise measurements of the thickness of a thin layer. This technique was employed to obtain an estimation of the thickness and their uniformity across the wafer of the poly-SiC and poly-SiC:N layers.

Optical reflectometry is based on the interference analysis of the light reflected from a thin layer, or a stack of thin layers, laying on a substrate. A light beam of variable wavelength is focused on the sample and the light reflected by the sample is made interfere with it. The intensity of the resulting light measured as a function of the wavelength gives rise to an interference reflectance pattern (Fig. 3.10). This is a function of the optical constants and thicknesses of the layers composing the sample. The reflectance pattern is recorded by a PC and analyzed to obtain the thickness of the layer. This can be unambiguously and precisely determined only if the optical constant of the layer under measurement, as well as the thicknesses and optical constants of all the other layers in the stack are known. A mathematical model including these parameters is then used to fit the measured interference reflectance pattern to obtain the unknown thickness.

The system employed for our measurements was a Leitz MPV-SP. Measurements were carried out on poly-SiC and poly-SiC:N layers deposited directly on a Si wafer. The optical constants employed in the model where
those for stoichiometric SiC already available in the system.



Figure 3.10: Example of measured data acquire by optical reflectometry and the corresponding fitting.

#### 3.2.3.3 Contact profilometry

The thickness of the poly-SiC and poly-SiC:N layers was also measured by contact profilometry as this method provided a direct measurement of the thickness.

In contact profilometry a diamond-tipped stylus is employed to sense the height variation at the surface of a sample, such as those caused by steplike boundaries or irregularities. The stylus is brought into contact with the sample and pressed against it with a certain force. The force is selected according to surface hardness to ensure good contact and damage-free measurements. The surface is scanned by moving the sample beneath the stylus along a given direction. A high precision motorized stage moves the sample according to the programmed scan-length and speed. The stage is also employed for pre-positioning the sample such that the desired measuring point is under the stylus. The vertical movement of the stylus is translated into an electrical signal by a linear variable differential transformer (LVDT) to which it is connected. The LVDT is an electromechanical transducer that scales an AC reference signal proportionally to the changes in the vertical position of the stylus. This signal is then conditioned and converted to a digital format by means of a high precision A/D converter. These data are stored in computer memory for display and analysis. Profilometry measurements are very accurate, repeatable and offer resolution down to a few

nanometers. The resolution varies with the range of the step height variation that needs to be measured, and can range from few nanometers to a few hundreds of microns. The scan length instead ranges from tens of microns to a few tens of millimeters. The horizontal resolution and the accuracy with which the profile of the surface features is reproduced depend on the shape of the stylus tip. Typical tip radiuses range from 0.2 to 25  $\mu$ m.

For our measurements we employed a Veeco DekTak 8 profilometer using a stylus tip with a radius of 5  $\mu$ m. Test structures were fabricated by patterning the poly-SiC and poly-SiC:N layers grown on top of a SiO<sub>2</sub> layer (Fig. 3.11). Photolithography and dry etching were employed for the patterning. The SiO<sub>2</sub> was utilized as landing layer during the etching and then completely removed by wet etching in BHF 1:7.



Figure 3.11: Test structure fabricated for the contact profilometry measurement and illustration of the measurement working principle.

#### 3.2.4 Mechanical and electrical properties

#### 3.2.4.1 Wafer curvature measurement

A solid is under stress when its atoms are displaced from their equilibrium position by a force. In a thin film, which is not submitted to a mechanical load, the stress is due to the constraint exercised by the Si substrate on which they are deposited or grown. This is much thicker than the films and will impede the expansion or contraction of the film thus generating stress. The origin of contraction or expansion can be thermal or intrinsic. Thermal ( $\sigma_{th}$ ) and intrinsic ( $\sigma_i$ ) stresses are often referred to as residual stresses and the total residual stress of a layer is given by their sum ( $\sigma_{r-t} = \sigma_{th} + \sigma_i$ ). Thermal stress arises from the mismatch between the coefficient of thermal expansion (CTE) of the thin film and that of the substrate. Deposition or growth processes are in fact typically performed at high temperatures. After cooling down to room temperature, the film and the substrate can have different dimensions. Intrinsic stress instead, arises during the formation process of the thin film. Intrinsic stress is distinct from thermal stress in that it is present already at the deposition temperature [97]. The mechanisms which generate intrinsic stress include events as grain growth, defect annihilation, etc. [97]. For example, the formation of grains which enlarge during growth would increase the lateral dimension of a film. More details on the origin of stress in thin films can be found in [97–99].

When the final lateral dimension of the film is larger than that of the Si wafer the stress is compressive. In the opposite case the stress is tensile. When the thin film is present only on one side of the Si substrate, this last will curve downwards or upwards depending on the stress of the film being compressive or tensile, respectively (see Fig. 3.12).



Figure 3.12: Effect on the curvature of a wafer for a layer with tensile or compressive residual stress. From [100].

The amount of stress can be determined by measuring the wafer curvature before and after the film is formed. The theory behind this technique was developed by Stoney who proposed an equation relating the wafer curvature to the film stress  $\sigma$  (Pa):

$$\sigma = \frac{E_s h_s}{6(1-\nu_s)h} \left(\frac{1}{R} - \frac{1}{R_0}\right) \tag{3.1}$$

where  $E_s$  is the elastic modulus (Young's modulus) (Pa),  $\nu_s$  the Poisson's ratio,  $h_s$  the wafer thickness (m), h the film thickness (m),  $R_0$  the wafer radius of curvature without the film (m), R the wafer radius of curvature with the film (m).

Wafer curvature measurements are typically performed by laser-based optical systems. The working principle is illustrated in the schematic of Fig. 3.13. A laser beam scans the wafer by means of a sliding mirror along one axial direction passing by its center. The angle of the deflected beam is detected and employed to obtain the bow of the wafer, the radius of curvature is then obtained by fitting the bow. Usually the bare Si-wafer results practically flat giving a  $R_0 = \infty$ . To obtain the radius of curvature R of the wafer with the thin film, first its bow is measured and then this is subtracted from the one of the bare wafer. The resulting bow is fitted to obtain the R. The data are collected from the optical system by means of a computer and analyzed using a dedicated software.



Figure 3.13: Schematic of the laser-based wafer curvature measurement technique.

The system employed for our wafer curvature measurements was a TEN-COR FLX-2908 (dual-laser) capable of detecting curvature radiuses down to  $1.2 \cdot 10^{-4} \text{ m}^{-1}$ . To determine the stress of each of the deposited SiC layers, wafer curvature measurements were performed multiple times for three orthogonal orientations, i.e. at 0°, 90° and 180° with respect to the main flat of the wafer. Before each deposition the curvature of the bare Si wafers was measured. To increase the precision in the stress calculation the individual thickness of each of the Si wafers was measured. After the deposition the SiC layer was removed from the backside of the wafer by plasma etching and then the curvature measured. The stress was calculated by first averaging the values obtained from each of the multiple measurements for each orientation. Then the resulting average values for each of the three orientations were also averaged.

#### 3.2.4.2 Nanoindentation

Nanoindentation was employed to obtain the elastic modulus and the hardness of the poly-SiC layers.

Nanoindentation is a widely employed technique for the mechanical characterization of materials. The most typical parameters that can be extracted from nanoindentation measurements are the elastic modulus and hardness of a sample. In this technique a very hard tip, typically made of diamond, is pressed against the sample surface for a certain depth and then retracted. During both penetration (loading) and retraction (unloading) the displacement of the tip is measured as a function of the applied force. The obtained force-displacement curve is then analyzed to extract the mechanical parameters of the sample.



Figure 3.14: Schematic of a nanoindenter and typical load-depth curve.

For our measurements an Agilent MTS Nanoindenter XP G200 was employed. This instrument performs continuous stiffness measurement (CSM) [101, 102]. In this method a small harmonic force f with frequency  $\omega$  is applied above the nominal loading force F. This allows to perform a continuous measurement of contact stiffness  $S_m$  as a function of the indentation depth h, with advantages in terms of accuracy speed and thermal drift [102]. The relationship between the reduced elastic modulus and the measured contact stiffness is given by [101, 103]:

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A_c}} S_m \tag{3.2}$$

Where  $A_c$  is the elastic contact area between the tip and the indented surface of the sample. This is described by a fitted contact area function, which also accounts for tip wear and blunting. The reduced elastic modulus includes both material and tip contributions. The elastic modulus of the material under study can be extracted by using the method proposed by Oliver and Pharr [101]. However, this original method was developed for monolithic materials and the extracted material properties are not accurate for thin films on a substrate having a different elastic modulus than that of the film. To correct for the substrate contribution, King's model can be used. This applies a correction factor,  $e^{-\frac{\beta t}{r}}$ , to determine the thin film properties [104],

$$\frac{1}{E_r} = \frac{1 - \nu_{tip}^2}{E_{tip}} + \frac{1 - \nu_{film}^2}{E_{film}} \left(1 - e^{-\frac{\beta t}{r}}\right) \frac{1 - \nu_{sub}^2}{E_{sub}} \left(e^{-\frac{\beta t}{r}}\right)$$
(3.3)

where t is the thickness of the film. The correction terms include the squared projection distance r, defined as  $r = \sqrt{A_c}$ . For very thick films  $r/t \longrightarrow \infty$ , the substrate contribution is null, while for very thin films  $r/t \longrightarrow 0$  the reduced elastic modulus depends practically only on the substrate. The parameter  $\beta$  is dependent on the punch geometry and on the ratio r/t [104]. This parameter can be conveniently described by the empirical fitting function [104, 105]:

$$\beta = m_1 + m_2(r/t) + m_3(r/t)^{\frac{1}{2}} + m_4(r/t)^{\frac{1}{3}}$$
(3.4)

For our punch geometry, the function parameters are  $m_1$ ,  $m_1$ ,  $m_1$  and  $m_1$  are respectively; 0.3783, -0.005609, 0.3474 and 1.1970 [105].

Finally the hardness H was calculated as  $H = F_{max}/A_c$ , where  $F_{max}$  is the peak indentation load.

#### 3.2.4.3 Four point probe resistivity measurement

The sheet resistance  $R_S$  of the poly-SiC, and poly-SiC:N layers was obtained by four point probe measurements. The sheet resistance is defined as  $R_S = \rho/t$ , where  $\rho$  is the resistivity of the layer and t its thickness. Once  $R_S$  was measured, the  $\rho$  of our layers was calculated using the thickness obtained with the techniques described above. Both  $\rho$  and  $R_S$  resulted useful in the characterization of the poly-SiC poly-SiC:N layers. Also, these quantities were employed in the design of the MEMS nanoreactor.

In four-point probe measurements four aligned contact probes equally spaced with a certain distance S are employed (Fig. 3.15). The four probes are brought into close contact with the layer surface. A current I is then forced to flow through the layer by using the most external probes, while the voltage difference V at the middle probes is measured. This last is measured at high impedance, such that the current flow through these probes is negligible. This makes negligible the voltage drop across the parasitic and contact resistances associated with these probes. Therefore, the measured Vcorresponds to the voltage drop across the portion of layer spanning between the middle probes. This value and the injected current I are employed to calculate the sheet resistance as  $R_S = (V/I) \times G$ . Where G is a correction factor taking into account the geometry of the sample and the associated current paths. In our case, where the thickness of the layer is much smaller than its width (the diameter of the wafer, 10mm),  $G = \pi/ln(2) = 4.5324$ .

The system employed for the measurements was a CDE Res Map 178

station interfaced with a computer and a dedicated software. The station is capable of measuring sheet resistances between  $2 \times 10^{-3}$  and  $5 \times 10^{6} \Omega/\Box$ , with an accuracy of about  $\pm 0.5\%$ . The measurements can be carried out directly on wafers. By performing a certain number of measurements across the wafer surface a uniformity map of the RS can be obtained. This information is useful to investigate the uniformity of both doping and thickness of a layer. To ensure electrical isolation from the substrate, the RS of the poly-SiC and poly-SiC:N layers was measured on test wafers where a thermal oxide layer was grown prior the deposition (Fig. 3.15).



Figure 3.15: Schematic illustration of the four point measurement performed on the poly-SiC and poly-SiC:N layers.

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# CHAPTER 4

# LPCVD a-SiC for Electron Transparent Windows

## 4.1 Introduction

In this chapter we investigate the properties of a-SiC layers deposited by LPCVD. By varying the parameters of the deposition process, three different a-SiC layers were obtained. These were extensively characterized to validate the fulfillment of the requirements indicated for the electron transparent windows (section 2.3.1) and thus to verify their suitability as alternative material for this element of the nanoreactor. With this aim the relation between process parameters and material properties was determined and the deposition conditions to obtain ultra-thin continuous, uniform, a-SiC layers were found. The performance of the fabricated windows using the best a-SiC layer were then tested focusing on transparency and resistance to the TEM electron beam.

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# 4.2 Deposition and characterization of LPCVD a-SiC layers

# 4.2.1 LPCVD deposition parameters

The a-SiC layers were deposited in a hot-wall LPCVD furnace using as precursor gasses dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>) diluted at 5% in hydrogen (H<sub>2</sub>) (section 3.1). Depositions were carried out on p-type silicon (Si) wafers with a diameter of 100 mm, a thickness of 525 (±25)  $\mu$ m and a (100) orientation. The native oxide present on the surface of the Si wafers was not removed prior to each deposition. This provided an amorphous substrate for the growth of the a-SiC layers. On some wafers a 200 nm thick SiO<sub>2</sub> layer was thermally grown prior to the a-SiC deposition. This was needed for the continuity tests performed on the a-SiC layers. Therefore, all the depositions were done on silicon wafers coated with a SiO<sub>2</sub> resembling the fabrication process of our application.

To ensure amorphous layers all the depositions were performed at a fixed temperature and pressure of 760 °C and 80 Pa, respectively (section 3.1.2). Precursors flows were varied to achieve gas flow ratios (*GFRs*) of 2, 3 and 4. As shown in Table 4.1, these were obtained by increasing the SiH<sub>2</sub>Cl<sub>2</sub> flow and decreasing the one of dilute  $C_2H_2$ , while keeping the total gas flow constant. This resulted in a significant variation of the H<sub>2</sub> flow and in a very small variation (< 1 sccm) of the  $C_2H_2$  flow. Deposition times were tuned to achieve layers with thicknesses of 20 nm and 40 nm for each gas combination. The tuning was done by running test depositions.

#### 4.2.2 a-SiC layers characterization

The deposited a-SiC layers were characterized using various techniques described in section 3.2. The results obtained from each of the performed characterizations are reported and discussed in the following subsections. This analysis allowed the identification of the most favorable deposition conditions to obtain an a-SiC layer suitable to be employed as electron transparent windows.

#### 4.2.2.1 Chemical composition

The three deposited a-SiC layers were characterized by RBS to obtain the depth profile of their elemental composition. This technique was complemented by ERD to detect the presence of hydrogen (H) and quantify its amount. These characterizations were performed on the 40 nm thick layers deposited on the untreated Si wafers.

The obtained RBS spectra are shown in 4.1 (a)-(c). Analysis of these spectra indicates that the layers are mainly composed by Si, carbon (C), oxygen (O), and, in a very small amount, chlorine (Cl). The ERD spectra shown in 4.1 (d) reveals also the presence of H. For all layers the RBS spectra show a peak in the O profile near channel 365. This O is located at the interface between the Si and the a-SiC layer and is related to the presence of the native oxide of the Si wafer. The thickness of the native oxide was measured by ellipsometry before each deposition obtaining a value of  $1.6 \pm 0.2$  nm. This contains approximately  $3.5 \times 10^{15}$  atoms/cm<sup>2</sup> of Si and  $7.1 \times 10^{15}$  atoms/cm<sup>2</sup> of O. By subtracting these two quantities from the overall Si and O amounts determined by RBS, we obtained the effective Si and O amounts contained in the a-SiC layers. In Table 4.2 are reported the elemental concentrations expressed in percent for each of the a-SiC layers. These were calculated by taking into account the effective Si and O amounts as above, the overall C amount obtained by RBS, and the H amount obtained by ERD. These results indicate that all the layers are non-stoichiometric (a-SiC<sub>x</sub>); carbon-rich with a Si-to-C ratio that slightly increases with the GFR. The elemental amounts obtained by the analysis of the RBS and ERD spectra were determined with a relative accuracy of 3% for the Si, 4% for the C, 6% for the O, 5% for the Cl, and 5% for the H.

The O present in the layers is mainly incorporated during the LPCVD deposition. The O sources are probably impurities such as  $H_2O$  and  $O_2$  present in the gas bottle containing the dilute  $C_2H_2$ . This is supported by the fact that the O concentration decreases as the *GFR* increases and therefore as the flow of dilute  $C_2H_2$  decreases. In addition, RBS characterizations performed on additional samples deposited using dilute  $C_2H_2$  of lower purity showed much higher O concentrations (~ 15%).

For all the a-SiC layers the oxygen profile shows a peak located near channel 400 which indicates a higher O concentration at the surface of the layers. This might be caused by an oxidation phenomenon that takes place during the unloading of the wafers from the LPCVD furnace after the deposition. The unloading is in fact performed in ambient atmosphere at 700 °C, and at this temperature the O present in the air can oxidize the surface. Unfortunately, decreasing the unloading temperature and/or unloading the samples in a reducing atmosphere was not possible with our furnace. The formation of C-O (gas) during the oxidation process could explain the lower C concentration detected at the surface. Analysis of the ellipsometric measurements allowed estimating a thickness of about 2 nm for the part of the layer containing the extra oxygen. The total amount of oxygen contained

Table 4.1: Gas flows employed for the LPCVD deposition of the three a-SiC layers performed at a fixed temperature of 760 °C and a pressure 80 Pa.

$\frac{GFR}{(\mathrm{SiH}_2\mathrm{Cl}_2\ /\ \mathrm{C}_2\mathrm{H}_2)}$	$\begin{array}{c} \mathrm{SiH_2Cl_2} \\ \mathrm{(sccm)} \end{array}$	$\begin{array}{c} \mathrm{C_{2}H_{2}} \ (5\% \ \mathrm{in} \ \mathrm{H_{2}}) \\ (\mathrm{sccm}) \end{array}$	Total gas flow (sccm)
2.0	46	454	500
3.0	65	435	500
4.0	83	417	500

Table 4.2: Elemental composition and relative concentrations of the three  $a-SiC_x$  layers as determined by RBS and ERD analysis. The contribution of the native oxide has been removed. The given error margins are one sigma value. The ratio between the Si and C concentrations is reported in the last column.

$\frac{GFR}{(\mathrm{SiH}_2\mathrm{Cl}_2\ /\ \mathrm{C}_2\mathrm{H}_2)}$	Si (%)	C (%)	O (%)	Cl (%)	H (%)	Si/C (%)
2.0	$36.3 \pm 1.1$	$54.1 \pm 2.2$	$5.9\pm0.3$	$0.40 \pm 0.02$	$3.3 \pm 0.2$	$0.67 \pm 0.05$
3.0	$39.1 \pm 1.2$	$51.9\pm2.1$	$5.5\pm0.3$	$0.50\pm0.02$	$3.0\pm0.1$	$0.76\pm0.05$
4.0	$42.2\pm1.3$	$50.4\pm2.0$	$4.1\pm0.3$	$0.40\pm0.02$	$2.9\pm0.1$	$0.84\pm0.06$

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Figure 4.1: RBS spectra and simulations of the three a-SiC layers (a-c) and the corresponding ERD spectra (d). The contribution to RBS spectra of the silicon substrate has been removed in the channel range 250-430. The elements in the layers are carbon (C), silicon (Si) oxygen (O), chlorine (Cl) and hydrogen (H), see Table 4.2 for the amounts. The layers are composed of three sub-layers. Oxygen peaks are visible at the interfaces of the central sub-layer, indicating the presence of native oxides. The main a-SiC layer is sandwiched between these oxides. C and O content decrease with *GFR* while Si content increases. For the layer deposited with a *GFR* of 4.0, low energy tails are visible at the Si and C spectral features. The ERD spectra indicate the presence of H, this decreases as the *GFR* increases.

in this surface was obtained by simulating the surface O peak. The obtained amounts were about  $6.3 \times 10^{15}$ ,  $6 \times 10^{15}$  and  $4.5 \times 10^{15}$  atoms/cm<sup>2</sup> for *GFRs* of 2, 3 and 4, respectively. By subtracting these quantities from the total O amounts, we obtained an estimation of the O incorporated only during the deposition. This corresponds to a concentration of 4.4, 3.9 and 2.9 % for *GFRs* of 2, 3 and 4, respectively. These values are slightly lower compared to those reported in Table 4.2. However, the Si and C relative concentrations and therefore the Si-to-C ratios are not affected if this new values are taken into account. A small gradient in the O signal is visible around channel 375. This reveals that during the deposition some extra oxygen is incorporated in the first part of the layers. This amount is very small. The cause of this is not well understood. For what concerns the H, its concentration decreases with the *GFR*. This behavior appears to be related to the decrease of the dilute  $C_2H_2$  flow and therefore to the one of the H<sub>2</sub> dilution gas. The Cl concentration is very low, and is probably a residue of the dichlorosilane precursor. Finally, in the RBS spectrum of the layer deposited with a *GFR* of 4.0 low energy tails in the C and Si peaks are visible. As shown by the AFM analysis reported later in 4.2.2.7, the tails indicate the presence of Si and C atoms located out of the layer surface in the shape of hillocks.

#### 4.2.2.2 Thickness and uniformity

Prior RBS characterization the a-SiC $_x$  samples were submitted to spectroscopic ellipsometry measurements (section 3.2.3.1). As suggested by the RBS analysis reported above, a three-layer model was built to perform the fitting of the ellipsometric data and eventually obtain the thickness of the a-SiC<sub>x</sub> layers. The model employed is shown in Fig. 4.2. It consist of a Si substrate, a  $SiO_2$  layer modeling the native oxide, a Cauchy layer modeling the main part of the a-SiC<sub>x</sub> layer, and a SiO<sub>2</sub> layer modeling the oxidized surface of this last layer. This last is an approximation as the oxidized surface layer also contains C as shown by the RBS characterization results and as later confirmed by the etching tests performed in HF-based solutions (section 4.2.2.5). This approach was adopted after the unsuccessfully modeling of the surface layer using a Cauchy layer or an effective medium approximation (EMA) layer. Most probably, the suitability of the  $SiO_2$ layer is due to the fact that the amount C contained at the surface is low or very low. For the fitting the acquired ellipsometric data were limited to wavelengths above 1100 nm. In this region the Cauchy layer is suited even in the case of layer with non-zero absorbance. The thickness of the native oxide was set to 1.6 nm. This value was obtained from ellipsometric measurements made on the Si wafers prior the deposition of the a-SiC $_x$ layers. The thickness of the Cauchy layer as well as its parameters were set to variable. For the first fitting the thickness of the top  $SiO_2$  layer was set to zero. This allowed to obtain an estimation of the total thickness of the deposited a-SiC<sub>x</sub> layer. Afterward the thickness of the top layer was also set to variable. A reasonable fit for all the parameters involved was found

when the thickness of this last layer converged to a value of about 2 nm.

To investigate the thickness uniformity the spectra were acquired at five different points on the wafer surface, i.e. in the center and at 3 cm from it in four orthogonal directions. All the layers resulted highly uniform showing thickness variations with a relative standard deviation (SD) of less than 1% (see Table 4.4). The high thickness uniformity was also indicated by the uniform color of the layers.



Figure 4.2: Top: model employed for fitting the ellipsometric data. Bottom: example of measured and fitted data acquired for the layer of 40 nm deposited with a GFR of 3.0.

#### 4.2.2.3 Density

For all the a-SiC<sub>x</sub> layers a mass density of  $2.74 \pm 0.03$  g/cm<sup>3</sup> was calculated using the data obtained from the analysis of the RBS spectra and using the thicknesses obtained by ellipsometry. This value is slightly lower compared to that of LPCVD SiN<sub>x</sub> (2.9-3.1 g/cm<sup>3</sup>) [78]. In addition, taking into account the atomic numbers of the constituents (Z<sub>C</sub>=6 < Z<sub>N</sub>=7 < Z<sub>Si</sub>=14) and their relative amounts <sup>1</sup>, windows with the same thickness made of a-SiC<sub>x</sub> should introduce less electron scattering and allow better transparency of windows made of SiN<sub>x</sub> [58].

<sup>&</sup>lt;sup>1</sup>a-SiC<sub>x</sub> contains less Si compared to  $SiN_x$ , which is silicon-rich

#### 4.2.2.4 Residual stress

The residual stress  $(\sigma_r)$  was determined by performing wafer curvature measurements on the a-SiC<sub>x</sub> layers of 40 nm. The minimum measurable stress for these layers with our setup was about 32 MPa (section 3.2.4.1).

The stress resulted tensile for all the layers with a magnitude that increased with the GFR from about 0.7 up to 1.1 GPa. Moderate tensile stress is desirable as it enables the fabrication of flat freestanding membranes and therefore of windows that do not buckle even when exposed to elevated temperatures. A layer possessing high stress, like the one deposited with GFR = 4.0, is instead not suitable to the fabrication of mechanically robust windows.

#### 4.2.2.5 Chemical resistance

The etch rate of the a-SiC<sub>x</sub> layers was measured for both wet and dry etching. As wet etchants we tested different chemicals, typically employed in microelectronics and MEMS technology, that is: hydrofluoric acid, silicon iso-etch, phosphoric acid and potassium hydroxide, see Table 4.3. For the dry etching we employed two different plasma etchers. The first machine was a reactive ion etching (RIE) (ALCATEL GIR 300) using a gas mixture of  $CF_4/SF_6/O_2$ , and an RF power of 60 W. The second was an inductively coupled plasma (ICP) RIE (Trikon Omega 201) using a gas mixture of Cl2/HBr, with an ICP power of 500 W and RF power of 40 W. The etch rate tests were performed on the a-SiC<sub>x</sub> layers of 40 nm deposited on untreated Si wafer. The etch time was 3 hours for the wet etch tests except for the silicon iso-etch where the etch time was 2 hours. For the plasma based etch tests, a time of 30 s was set. In all the cases the decrease in thickness caused by the etch was measured by ellipsometry.

The measured etch rates are reported in Table 4.3. In general all the a-SiC<sub>x</sub> layers show very high resistance to all the chemicals employed. Etch rates lower than 0.3 nm/h are measured in hydrofluoric and phosphoric acids. Therefore, a-SiC<sub>x</sub> layers can be considered inert in these chemicals. Etch rates lower than 2 nm/h are measured in a 33 wt.% KOH solution. The layer deposited with GFR of 4.0 is the most resistant to this chemical. Slightly higher etch rates, up to 3 nm/h, are measured in Si iso-etch. After this test an elevated number of pinholes was observed in the layers deposited with a GFR of 3.0 and 4.0. Due to the pinholes peel-off of the layer took place during the etching. No pinholes or defects and peel-off were instead observed for the layer deposited with GFR of 2.0. The observed etch rates are extremely low, thus showing the inertness of this material. However, due to its higher O and Si content we expect that the etch rates of the

2-nm thick surface layer are to some extent higher than those of the main part of the a-SiC<sub>x</sub> layer. This could have influenced the values presented in Table 4.3. The a-SiC<sub>x</sub> layers can be instead dry etched. The the measured etch-rates are reported in Table 4.3. For both plasma etchers, there was practically no differences between the etch-rates of the three a-SiC<sub>x</sub> layers. The etch-rate obtained with the ICP-RIE etcher is about three times higher than the one obtained using the RIE.

Table 4.3: Etch rates measured for the  $a-SiC_x$  layers in different wet and dry etchants typically employed in microelectronics and MEMS fabrication technology.

Etchant	Etch rate $(nm/h)$				
Lichand	GFR = 2.0	GFR = 3.0	GFR = 4.0		
BHF 7:1	0.11	0.11	0.16		
HF 40%	0 (< 0.01)	0 (< 0.01)	0 (< 0.01)		
HNO <sub>3</sub> /HF 68:1 (Si iso-etch)	1.2	2.97	1.75		
H <sub>3</sub> PO <sub>4</sub> 85% @ 157°C	0.29	0.26	0.28		
KOH 33% @ 85°C	1.8	1.7	1.1		
RIE: $CF_4/SF_6/O_2$	$2.6 \times 10^{3}$	$2.6 \times 10^{3}$	$2.6 \times 10^{3}$		
ICP-RIE: Cl <sub>2</sub> /HBr	$8.9 \times 10^3$	$8.9 \times 10^3$	$8.9 \times 10^3$		

#### 4.2.2.6 Layer continuity

The continuity of the a-SiC<sub>x</sub> layers of both 20 and 40 nm was investigated by evaluating the density of pinholes. For this test the a-SiC<sub>x</sub> layers deposited on the thermally oxidized wafers were employed. These were immersed for 2 hours in hydrofluoric acid 40% (HF 40%). As reported later in this paper all the a-SiC<sub>x</sub> layers are inert in HF 40%. Therefore, where a pinhole was present the underlying SiO<sub>2</sub> was etched by the acid making the pinholes visible to an optical microscope inspection. After patterning a photoresist mesh on the surface of the wafer, the density of pinholes was obtained by counting their number in an area of  $4 \times 4$  cm<sup>2</sup> with the aid of an optical microscope.

The continuity test revealed that all the layers were continuous. These contained only few of pinholes randomly distributed across the surface of the wafer (Fig. 4.3). Pinholes density slightly increased with the *GFR* and decreased with the thickness. The low pinhole density indicates that the layers have a low defect density thus making them suitable for the fabrication of mechanically strong windows. The high quality of the a-SiC<sub>x</sub> layers



was expected as a result of the LPCVD deposition process.

Figure 4.3: Optical microscope images showing some pinholes and the photoresist mesh. In the magnified image the pinhole is clearly visible as a dark spot. The circular undercut caused by the HF etch in the underlying oxide is also visible.

#### 4.2.2.7 Surface morphology

Atomic force microscopy (AFM) was employed to determine the surface morphology and roughness of the a-SiC<sub>x</sub> layers of 40 nm. The AFM scans were performed using titanium nitride (TiN) coated silicon tips (NSG30)on an area of 5×5  $\mu{\rm m}$  and with a resolution of 512 x 512 lines . Analysis of the AFM scans (Fig.4.4) show that the layer deposited with a GFR of 2.0 is very smooth with a root mean square surface roughness,  $S_Q$ , of 0.24 nm. No spikes or hillocks are detected all over the scan area. On the contrary, the layer deposited with a GFR of 3.0 presents a moderate number of hillocks having a maximum height and width of about 28 nm and 110 nm, respectively. For this layer the  $S_Q$  measured on an area without hillocks is 0.28 nm, while the one measure on the whole surface is 0.9 nm. The layer deposited with a GFR of 4.0 shows an elevated number of hillocks (maximum height and width of about 150 nm and 290 nm, respectively). For this layer the SQ measured on an area without hillocks is 0.67 nm, the one measured on the whole surface is 24.6 nm. The hillocks explain the tails present in the RBS spectrum of this last layer (Fig. 4.1). At present, we cannot explain the reasons behind the hillocks formation. However, we suspect that this phenomena might indicate the transition from an amorphous to a polycrystalline layer [83].



Figure 4.4: 3D images, obtained from the AFM scans, showing the surface morphology of the three a-SiC<sub>x</sub> layers. The surface of the layer deposited with *GFR* of 2.0 is uniform and presents no hillocks. On the surface of the layer deposited with a *GFR* of 3.0 a moderate number of hillocks reaching a maximum height of 28 nm is present. The surface of the layer deposited with a *GFR* of 4.0 shows an elevated number of hillocks reaching a maximum height of 150 nm.

#### 4.2.3 Summary of the properties and layer choice

The characterization results of the three  $a-\operatorname{SiC}_x$  layers are summarized in Table 4.4. They indicate that layer deposited with a *GFR* of 2.0 is the better choice as electron transparent window material. This has the lowest pinhole density and the lowest intrinsic stress. Finally, it is the only layer possessing the smooth surface required for a window layer.

Properties	a-SiC <sub>x</sub> layers				
	GFR = 2	GFR = 3	GFR = 4		
SD thickness (%)	0.55	0.53	0.85		
Continuity @ 20 nm $(pinholes/cm^2)$	4.3	8.6	11.3		
Continuity @ 40 nm $(pinholes/cm^2)$	0.25	1.2	2.5		
$\sigma_r (GPa)$	$0.67 {\pm} 0.04$	$0.92 {\pm} 0.06$	$1.12 {\pm} 0.06$		
$S_Q @ 40 \text{ nm} (nm)$	0.24	0.9	24.6		

Table 4.4: Properties of the a-SiC<sub>x</sub> layers.

# 4.2.4 Additional characterization of the chosen $a-SiC_x$ layer

Additional characterizations were performed on the a-SiC<sub>x</sub> (x = 1.49) layer obtained with a *GFR* of 2.0 to ensure its suitability as alternative fabrication material for electron transparent windows. Moreover, to determine its growth rate and the thinnest continuous a-SiC<sub>x</sub> layer five additional depositions were performed. The resulting layers had thicknesses comprised between 6 and 50 nm and were obtained by tuning the deposition time between 50 and 200 minutes.

#### 4.2.4.1 Amorphous structure verification

TEM cross-sections of the a-SiC<sub>x</sub> layer obtained with a GFR of 2.0 were acquired to verify its amorphousness. These also allowed to assess the validity of the thicknesses obtained by fitting the ellipsometric data with the proposed approach.

A TEM cross-section of this layer is shown in Fig. 4.5. The Fast Fourier Transform of this image shows no diffraction spots, confirming the desired amorphousness. The thicknesses determined from TEM cross sections match those determined by ellipsometry thus validating the model employed.

#### 4.2.4.2 Wettability

The wettability was investigated by contact angle measurements on the 20 nm thick layer. The measurement was performed right after deposition



Figure 4.5: High resolution TEM image showing the cross-section of a the  $a-SiC_x$  layer deposited with a *GFR* of 2.0. The crystalline structure of the Si substrate is visible, while no ordered structure is visible in the  $a-SiC_x$  layer. The Fourier transform of the  $a-SiC_x$  layer (inset) confirms its amorphousness.

and after a dip in BHF 7:1 (buffered hydrofluoric acid) for 1 min. The contact angle was again measured after one year while the wafer was stored in a clean room atmosphere, before and after a cleaning step in fuming  $HNO_3$ . For comparison the same test was extended to a  $SiN_x$  layer deposited by LPCVD.

Contact angle measurements show that right after deposition the a-SiC<sub>x</sub> layer is totally hydrophilic (no measurable contact angle). The same is true right after a BHF dip. The contact angle measured after one year of storage in clean room environment was about 18°, indicating a slightly hydrophobic surface. However, after the HNO<sub>3</sub> cleaning step the surface turned back to totally hydrophilic. The change in surface wettability during storage may result from the collection of airborne contaminants such as hydrocarbons. Analogous results were obtained for the SiN<sub>x</sub> layer. The wettability of the a-SiC<sub>x</sub> layer deposited with a *GFR* of 2.0 makes it suited for its application as electron transparent window.

#### 4.2.4.3 Surface roughness

An additional AFM scan was performed on the 40 nm thick a-SiC<sub>x</sub> layer over a reduced scan area of 1x1  $\mu$ m. This reveals an RMS surface roughness of 0.22 nm, slightly lower compared to the one determined on a larger 5×5  $\mu$ m area. This value is also lower than that of commercially available SiN<sub>x</sub> electron-transparent windows which is around 0.6 nm. The extremely low roughness of the a-SiC<sub>x</sub> layer deposited with a GFR of 2.0 makes it suited for its application as electron transparent window.

#### 4.2.4.4 Growth rate

The layer thickness as a function of deposition time is plotted in Fig. 4.6. Fitting the experimental data with a second order polynomial equation shows that the growth in this thickness range can be considered almost linear, as the second order coefficient is very small. The growth rate is small enough ( $\sim 0.2 \text{ nm/min}$ ) to grow very thin layers with a good control of the thickness. The fitting suggests an incubation time of about 25 minutes before the layer starts growing. However, this value is just a rough estimation. In order to better understand the growth dynamics in the early stages more studies are required which unfortunately are out of the scope of this thesis.



Figure 4.6: Layer thickness as a function of deposition time, for the layer deposited with a GFR of 2.0. A second order polynomial equation is employed to fit the data. The growth is almost linear and the growth rate is low enough to allow the deposition of very thin layers with a controllable thickness. The fitting suggests the presence of an incubation time before the layer starts growing.

#### 4.2.4.5 The thinnest continuous layer

To estimate the minimum achievable thickness for this layer, the continuity test was extended to the additional layers with increasing thickness deposited with a GFR of 2.0 (Table 4.5).

The results of the continuity test indicate that the pinhole density increases as the thickness decreases (Table 4.5). For the layer of 15.3 nm the pinhole density is still very low, indicating that this layer is continuous. As the thickness decreases to  $\sim 13$  nm the pinhole density drastically increases revealing already a poor continuity. Finally, the layer of  $\sim 6$  nm is highly discontinuous. This layer, in fact, peeled-off as a consequence of the complete etch of the underlying SiO<sub>2</sub> layer by the 40% HF. This might indicate that at this thickness the layer either contains an enormous amount of pinholes or that it is not yet closed suggesting an island growth mode. These results indicate that for the fabrication of electron transparent windows layers of at least 15.3 nm must be employed.

Table 4.5: Measured pinhole density for a-SiC<sub>x</sub> layers of increasing thickness deposited with a GFR of 2.0.

Layer thickness (nm)	Pinohole density $pinholes/cm^2$
6.1	Discontinuous layer / peel-off
12.9	$1.6 \times 10^{3}$
15.3	12.7
21.2	4.3
30.7	1.06
41.4	0.25
50.5	0

## 4.3 a-SiC<sub>x</sub> electron transparent windows

#### 4.3.1 Design and fabrication

The a-SiC<sub>x</sub> layer obtained with a GFR of 2.0 was integrated in a microfabrication process to achieve window devices. This allowed to investigate the possibility of fabricating windows made of this layer, and to test the properties of the a-SiC<sub>x</sub> layer in a TEM microscope, namely transparency and electron beam resistance. A schematic of the cross-section of the window device is shown in Fig. 4.7. It consists of a  $1-\mu$ m thick SiN<sub>x</sub> free-standing membrane,  $1\times 1$  mm wide, embedding an array of 41 circular windows with a diameter of 4  $\mu$ m. The SiN<sub>x</sub> membrane serves as a strong and relatively rigid support for the windows [36]. The a-SiC<sub>x</sub> window layer is 16 nm thick, but because of its small diameter, has a strength comparable

to that of the large membrane [59].



Figure 4.7: 3D Illustration and schematic cross-section of the window device fabricated to test the properties of the selected  $a-SiC_x$  in a TEM microscope. The  $SiN_x$  support membrane integrates electron transparent windows made of  $a-SiC_x$ . The schematic cross-section of the window device shows the different layers employed in the fabrication together with their thickness. The dimensions of the membranes and windows are also indicated.

A schematic of the fabrication process followed to realize the window device is shown in Fig. 4.8. For the fabrication we employed p-type Si wafers as a substrate with a diameter of 100 mm and (100) crystal orientation. The fabrication started by growing 200 nm thermal SiO<sub>2</sub> necessary for the as etch stop layer during the release of the support membrane (Fig. 4.8(a)), followed by the LPCVD deposition of 16 nm of a-SiC<sub>x</sub> (Fig. 4.8 (a)). This thickness was selected to have a window layer that is thin but still continuous (section 4.2.4.5). For comparison, we also prepared some wafers with windows of 15-16 nm of LPCVD SiN<sub>x</sub>. The a-SiC<sub>x</sub> was then covered by 300 nm of LPCVD SiO<sub>2</sub> made from TEOS (tetraethyl orthosilicate) and by 1  $\mu$ m of LPCVD SiN<sub>x</sub> (Fig. 4.8 (a)). The SiO<sub>2</sub> served as an etch stop layer during the etching of the SiN<sub>x</sub> membrane necessary for the definition of the windows. For this step circular openings were defined on the SiN<sub>x</sub> by lithography and plasma etching (Fig. 4.8 (b-c)). A square-shaped opening was defined on the backside of the wafer by lithography and plasma etching. The stack consisting of  $SiN_x$ ,  $SiO_2$ , a-SiC<sub>x</sub> and thermal  $SiO_2$  layers was removed in a single etching step stopping on the Si surface (Fig. 4.8 (d)). This allowed to release of the support  $SiN_x$  membrane by etching the Si substrate in a 33 wt.% KOH solution (Fig. 4.8 (e)). Finally, the  $SiO_2$  stop layers sandwiching the thin a-SiC<sub>x</sub> layer where removed in a BHF solution thus achieving the desired freestanding windows (Fig. 4.8 (f)).



Figure 4.8: Schematic cross-section of the fabrication sequence of the window device. (a) Formation of the layer stack needed for the fabrication of windows and support membrane. (b) Patterning of the openings in the  $SiN_x$  and  $SiO_2$  layers for the formation of the windows. (d) Patterning of the opening at the backside for the release of the support membrane layer. (e-f) Release of the support-membrane and windows by KOH and BHF, respectively.

Optical and SEM images of the fabricated window device are shown in Fig. 4.9. These images demonstrate the feasibility of the fabrication process.

The window layer appears flat, confirming that the material possess tensile residual stress.



Figure 4.9: (a) Optical image of the device showing the freestanding  $SiN_x$  support-membrane. (b) SEM image the array of  $a-SiC_x$  windows integrated in the  $SiN_x$  support-membrane. (c) Close up of a window with a particle on it. Here the low acceleration voltage employed (0.8 kV) makes the window visible. The window layer is flat.

#### 4.3.2 TEM windows testing

#### 4.3.2.1 Mechanical integrity and strength

The mechanical integrity of the a-SiC<sub>x</sub> windows was first verified by both optical and SEM microscopy, and then by leak-rate measurements. In total 32 devices were tested. The leak test was performed using a vacuum setup capable of creating a pressure difference of 10<sup>5</sup> Pa across the supportmembrane of the device. The setup (see Fig. 4.10) consists of a vacuum chamber with a volume of about 2  $\ell$ , provided with a rotary pump and a venting N<sub>2</sub> line. A pressure sensor interfaced with a digital pressure gauge is also connected to the chamber. The window device is mounted at the top-side of the chamber in a housing provided with a small hole. The leak tight connection of the device to the chamber is achieved by means of an O-ring present around the hole. The device is gently pressed against the Oring by means of a clamping system. To test the window device the vacuum chamber is first pumped to a base pressure of 0.1 Pa. Then, after closing vacuum pump valve, the rise of the pressure shown at the pressure gauge is monitored as a function of time.



Figure 4.10: Schematic of the vacuum setup employed to verify the integrity of the a-SiC<sub>x</sub> windows. It consists of a vacuum chamber equipped with a pressure sensor. The device under test is mounted in the housing present at the top of the chamber. This is then pumped down to 0.1 Pa. Once  $V_p$  is closed the pressure rise is monitored to detect leaks in the devices.

All the devices tested showed a leak rate of  $\sim 3.4 \times 10^{-4}$  mbar·l/s which is the background leak recorded for the vacuum setup with a dummy device with no windows. This indicates that the windows and the support membrane are intact and that they are capable of withstanding the applied pressure of 10<sup>5</sup> Pa. This means that the a-SiC<sub>x</sub> layer of 16 nm is strong, and points towards a low density of material defects. The same test performed with devices integrating low-stress SiN<sub>x</sub> windows reveals that only about one half of the devices are leak-tight. In this case leaky devices lead to a rapid increase of the pressure of the chamber. This indicates that windows made of SiN<sub>x</sub> are more fragile compared to the a-SiC<sub>x</sub> ones. This can be due to an unintentional reduction of the SiN<sub>x</sub> layer thickness during windows fabrication. The higher chemical resistance of the a-SiC<sub>x</sub> ensures a more reliable control of the window thickness and thus a better final yield.

#### 4.3.2.2 Transparency

The transparency of the a-SiC<sub>x</sub> windows was tested by acquiring high resolution TEM images of gold nanoparticles. The microscope employed was a Philips CM-300UT TEM equipped with a field emission gun operated with an accelerating voltage of 300 kV. A drop of ethanol with in suspension gold nanoparticles of 10 nm in diameter (BBInternational) was dispensed on the support SiN<sub>x</sub> membrane. TEM images were acquired after the complete evaporation of the ethanol. The images were analyzed by fast Fourier transform (FFT) using ImageJ software. This allowed us to determine the smallest visible lattice spacing, which is a measure of the achievable resolution and thus of the transparency.

TEM inspection of the windows revealed the presence of the nanoparticles thus demonstrating the wettability of the a-SiC<sub>x</sub> layer also for ethanol. An atomic-resolved TEM image of a gold nanoparticle is shown in Fig. 4.11. The image shows the lattice fringes of the nanoparticle superimposed to the amorphous pattern of the a-SiC  $_{x}$  window. The 2D FFT transform of this image (inset in Fig. 4.11) indicates that the smallest resolved lattice fringes have a spacing of 0.12 nm. This measurement is close to the resolution limit of the TEM microscope, meaning that the  $a-SiC_x$  window introduces a negligible resolution loss and confirming that the  $a-SiC_x$  windows are transparent to the electron beam. During the imaging experiments on the  $a-SiC_x$ window, no motion of the particles is observed. On the contrary, when using  $SiN_x$  windows some particles can suddenly jump out of the electron beam area. This phenomenon can be caused by electron charging effects induced by the beam. This observation could indicate that a  $SiC_x$  is a better electrical conductor then  $SiN_x$ . The conductivity of the a-SiC<sub>x</sub> could be attributed to the carbon excess present in the material. Unfortunately, a quantitative measurement of conductivity in TEM is not straightforward.



Figure 4.11: TEM image of a gold nanoparticle on an a-SiC<sub>x</sub> window. The image shows the lattice fringes of the nanoparticle and the amorphous patterns of the window. The 2D fast Fourier transform of the image is shown in the inset. The outer bright points (red circles) in the FFT correspond to the smallest resolved lattice fringes, which have a spacing of 0.12 nm. This resolution is close to the resolution limit of the TEM microscope, showing that the a-SiC<sub>x</sub> window has a negligible effect on the resolution.

#### 4.3.2.3 Beam resistance

The resistance to electron beam damage was investigated in the same TEM. The time needed to create a hole in a window (survival time) was measured as a function of the electron flux. To acquire high resolution images, fluxes below 10<sup>7</sup> e/nm<sup>2</sup>·s are typically required. The survival time of the windows was measured by applying electron fluxes from  $10^6$  to  $10^{10}$  $e/nm^2$ . The survival time of a-SiC<sub>x</sub> and SiN<sub>x</sub> windows measured as a function of the electron flux, is plotted in Fig. 4.12. The TEM image of a window before and after the formation of a hole is shown in Fig. 4.13. Windows made of  $a-SiC_x$  are more resistant compared to the  $SiN_x$  ones. At the highest flux employed, a  $SiC_x$  survival time is about 3 times longer. As the flux decrease the difference in the survival time increases. Around  $3.5 \times 10^7$  e/nm<sup>2</sup> s the a-SiC<sub>x</sub> windows survive about 9 times longer. The survival time at lowest flux employed  $(5 \times 10^6 \text{ e/nm}^2 \cdot \text{s})$  is around 7 minutes for the  $SiN_x$  windows. By contrast, applying  $6x10^6 \text{ e/nm}^2 \cdot \text{s}$  to the a-SiC<sub>x</sub> does not cause any damage even after 60 minutes. This could suggest the presence of a flux threshold value below which the  $a-SiC_x$  windows are not damaged. The results reported in [60] suggest that sputtering can be the driving mechanisms of the hole formation into for  $SiN_x$  windows. Assuming that the same mechanism applies to  $a-SiC_x$  windows, then its higher beam resistance can be explained as a higher resistance to sputtering and therefore, the presence of stronger chemical bonds. On the other hand, thermal conductivity could also play a role as a  $SiC_x$  is likely to have a higher electrical conductivity than  $SiN_x$ . The superior beam resistance of a  $SiC_x$  may represent an important difference for acquiring good TEM pictures. This is especially useful during *in-situ* experiments, when long exposures to the electron beam are required. In addition the possibility of employing higher electron fluxes can be helpful when the influence of the electron beam on a certain phenomenon needs to be identified and quantified.



Figure 4.12: Comparison of the survival times for  $a-\operatorname{SiC}_x$  and  $\operatorname{SiN}_x$  windows as a function of the electron flux (double-log scale). The  $a-\operatorname{SiC}_x$  windows withstand the electron beam 3 to 9 times longer than the ones made of  $\operatorname{SiN}_x$ (lines have been drawn to guide the eye).



Figure 4.13: TEM images of an  $a-SiC_x$  window (a) without and (b-c) with a hole. The hole is created by focusing the TEM electron beam onto the window for a time which is long enough.

### 4.4 Conclusions

Three, non-stoichiometric, amorphous silicon carbide layers were deposited by LPCVD using SiH<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> as precursor gases. The characterizations performed on these layers allowed to identify the most suitable layer to be used as electron transparent window material. The reported experiments showed that this layer is uniform and continuous down to a thickness of 15.3 nm. It possesses high chemical inertness, moderate tensile stress, low roughness, and is hydrophilic. Using this layer we fabricated electron transparent windows embedded on a freestanding membrane. Tests performed on these windows demonstrated that the a-SiC $_x$  has a good electron transparency and an elevated resistance to the TEM electron beam. TEM images with atomic-scale resolution down to at least 0.12 nm were acquired. Beam survival times which are 3 to 9 times longer compared to those of  $SiN_x$  were measured. In addition, compared to  $SiN_x$  the a-SiC<sub>x</sub> suffers less from electrical charging and has a better chemical resistance to the HF based wet etchants needed to release the windows. This last enables to a more robust and reproducible fabrication process. The proposed  $\operatorname{a-SiC}_x$  layer can thus be advantageously employed for the fabrication of electron-transparent windows.

In the next chapter we explore the use of SiC as alternative material for the nanoreactor channel.

# CHAPTER 5

# LPCVD Poly-SiC for Nanoreactor Microchannels

## 5.1 Introduction

In this chapter we investigate the properties of poly-SiC layers deposited by LPCVD. By varying the parameters of the deposition process six different poly-SiC layers were deposited. As SiC in general fulfills many of the requirements indicated for the microchannels (section 2.3.2) we characterized the poly-SiC layers to identify the deposition conditions under which low-stress stoichiometric layers are obtained. In addition, some properties which are useful during the design and fabrication of microchannels and free-standing structures were also determined. In particular the surface morphology, the wettability, the electrical conductivity and the elastic modulus were investigated. Also, the correlation between properties and polycrystalline structure of the different poly-SiC layer was underlined. Finally, the most suited poly-SiC layer was employed in the fabrication of surface micromachined channels. This allowed to verify the suitability of this layer for the fabrication of microchannels capable of withstanding elevated pressures. In addition, the microchannel fabrication process included a newly developed sealing technique proposed to improve the fabrication of nanoreactors.

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# 5.2 Deposition and characterization of LPCVD poly-SiC layers

## 5.2.1 LPCVD deposition parameters

The poly-SiC layers were deposited in a hot-wall LPCVD furnace using as precursor gasses dichlorosilane  $(SiH_2Cl_2)$  and acetylene  $(C_2H_2)$  diluted at 5% in hydrogen  $(H_2)$  (section 3.1). As substrate we employed p-type silicon (Si) wafers having a diameter of 100 mm, a thickness of  $525 \pm 25$  $\mu$ m, and (100) orientation. To allow subsequent characterizations of the layers, the depositions were performed on both bare and thermally oxidized wafers. The thickness of the thermal oxide (SiO<sub>2</sub>) layer was 200 nm.

As suggested by the results reported in [106–108] by altering the stoichiometry of poly-SiC layers a modification of their mechanical properties (i.e. stress and elastic modulus) can be achieved. A previous study performed by our group [83] using the same LPCVD system reports on the dependence of the stoichiometry of poly-SiC layers with the GFR. We performed several depositions by varying the GFR, according to the gas flows values reported in Table 5.1. GFRs comprised between 4.0 and 6.5 where obtained by increasing the SiH<sub>2</sub>Cl<sub>2</sub> flow and decreasing that of the dilute  $C_2H_2$ . The amount of these variations was such to keep constant the total gas flow at 500 sccm for all the depositions. Due to its high dilution the absolute variation in the C<sub>2</sub>H<sub>2</sub> flow resulted very small compared to that of SiH2Cl2. The flows and the corresponding relative concentrations of the precursor and dilution gasses are reported in Table 5.2. In this table is also reported the calculated gas molar ratio (GMR) defined as the ratio between the silicon (Si) and carbon (C) atoms present in the gas mixture. All the poly-SiC layers were deposited at fixed temperature and pressure of 860 °C and 80 Pa, respectively. Finally, deposition times were tuned between 50 and 150 min to achieve layers having all with a similar thicknesses close to 500 nm.

#### 5.2.2 Poly-SiC layers characterization

The deposited poly-SiC layers were characterized using various techniques described in section 3.2. The results obtained from each of the characterizations performed are reported and discussed in the following subsections. This analysis allowed the identification of the most favorable deposition conditions to obtain a poly-SiC layer suitable as construction material for the microchannel of the nanoreactor.

Table 5.1: Gas flows ratios and corresponding gas flows employed in the LPCVD depositions of the six poly-SiC layers. The layer identifier is reported in the first column. In the last column the deposition time for each layer is reported .

Layer ID	$GFR \\ {\rm (SiH_2Cl_2/C_2H_2)}$	$\begin{array}{c} \mathrm{SiH_2Cl_2} \\ \mathrm{(sccm)} \end{array}$	$\begin{array}{c} \mathrm{C_2H_2} \ (5\% \ \mathrm{in} \ \mathrm{H_2}) \\ (\mathrm{sccm}) \end{array}$	Total gas flow (sccm)	Deposition time (min)
I-1	4.0	83	417	500	150
I-2	4.5	92	408	500	125
I-3	5.0	100	400	500	110
I-4	5.5	108	392	500	90
I-5	6.0	115	385	500	50
I-6	6.5	123	377	500	50

Table 5.2: Gas flows of the precursor and dilution gasses employed in the deposition of the six poly-SiC layers. The relative concentration of each gas in the total gas mixture is also indicated. In the last column is reported the calculated gas molar ratio.

Layer ID	$GFR \\ ({}^{\mathrm{SiH}_2\mathrm{Cl}_2/\mathrm{C}_2\mathrm{H}_2})$	$SiH_2Cl_2$ (sccm) - (%)	$C_2H_2$ (sccm) - (%)	H <sub>2</sub> (sccm) - (%)	$\frac{GMR}{\left( {^{\mathrm{Si}}}^{(gas)}/\mathrm{C}^{(gas)} \right)}$
I-1	4.0	83 - 16.60	20.85 - 4.17	396.15 - 79.23	2.00
I-2	4.5	92 - 18.40	20.40 - 4.08	387.60 - 77.52	2.25
I-3	5.0	100 - 20.00	20.00 - 4.00	380.00 - 76.00	2.50
I-4	5.5	108 - 21.60	19.60 - 3.92	372.40 - 74.48	2.75
I-5	6.0	115 - 23.00	19.25 - 3.85	365.75 - 73.15	3.00
I-6	6.5	123 - 24.60	18.85 - 3.77	358.15 - 71.63	3.25

Layer ID	$GFR \\ \left( {{{_{{\rm{SiH}}_2}{\rm{Cl}}_2}/{\rm{C}}_2}{\rm{H}}_2} \right)$	$GMR \\ \left( \frac{\mathrm{Si}^{(gas)}}{\mathrm{C}^{(gas)}} \right)$	Si (%)	C (%)	Si/C
I-1	4.0	2.00	49.28	50.72	0.972
I-2	4.5	2.20	49.84	50.16	0.993
I-3	5.0	2.50	49.80	50.20	0.992
I-4	5.5	2.75	50.65	49.35	1.026
I-5	6.0	3.00	51.73	48.27	1.072
I-6	6.5	3.25	53.26	46.74	1.139

Table 5.3: Relative Si and C concentrations for the six poly-SiC layers. The Si to C ratio is reported in the last column to indicates the stoichiometry of the layers.

#### 5.2.2.1 Chemical composition

The chemical composition of the six different poly-SiC layers was obtained by EBS (section 3.2.1.1). For each of these layers the relative concentrations of silicon (Si) and carbon (C), together with the calculated Si to C ratio (Si/C) are reported in Table 5.3. These data are also plotted in Fig. 5.1 as a function of the GFR. The Si concentration increases as the GFRincreases whereas the C concentration decreases. This was expected since an increase in the GFR corresponds to an increase in the concentration of the Si precursor and in a decrease of the C one. Layer I-1, deposited with the lowest GFR, is slightly carbon-rich. As the GFR is increased to 4.5 and 5.0 the relative concentrations of Si and C become very close to each other, such that layers I-2 and I-3 can be practically considered stoichiometric. By increasing the GFR to 5.5 the relative Si concentration further increases and the C one decreases causing layer I-4 to be slightly silicon-rich. Finally, layers I-5 and I-6 deposited using respectively a GFR of 6.0 and 6.5, are clearly silicon-rich. As indicated by the GMR the gas mixture is very rich in Si atoms for all the depositions. However, the Si/C values obtained by EBS indicate that all samples are relatively close to stoichiometry. This might suggest that the reaction in the gas phase of the Si precursor or its adsorption at the surface is slower compared to the one of the C precursor.

#### 5.2.2.2 Surface morphology

The surface morphology of the SiC layer was studied by combining high resolution SEM images and AFM scans. These techniques are as described in detail in sections 3.2.2.1 and 3.2.2.2. Here below some information on


Figure 5.1: Concentration of silicon (Si) and carbon (C) contained in the SiC layers as a function of the gas flow ratio (GFR). The Si to C ratio is also plotted as a function of the GFR.

the acquisition of these data are first given, then the results are presented and analyzed for both techniques.

High resolution SEM (HR-SEM) images of the top view and of  $45^{\circ}$  tilted view of the surface of the SiC layers were acquired at two different magnifications corresponding to a horizontal field of view (HFV) of 2  $\mu$ m and 1  $\mu$ m. The SEM images allowed for both qualitative and quantitative analysis of the surface morphology. In particular, a quantitative estimation of the size of the horizontal section of the grains was obtained through the use of a specific image processing and analysis software (section 3.2.2.1).

The AFM scans were made on  $2 \times 2 \mu m$  surfaces. The AFM scans were not straightforward due to the morphology of the surface and the hardness of the layers. Four types of probes were employed in the attempt of scanning the surface. These were: NSG30 equipped with uncoated silicon tip having a curvature radius of 10 nm, NSG30 equipped with titanium nitride (TiN) coated silicon tip with a curvature radius of 35 nm; NSC05\_20° equipped with a whisker-type tip made of carbon having a curvature radius of 10 nm; DCP20 equipped with a diamond coated silicon tip with a curvature radius of 70 nm. Thanks to their small tip curvature radius the best results in terms of resolution were obtained using the NSG30 and the NSC05\_20° probes. However, their tips were damaged and in some cases torn apart during the first part of the scan. This impeded to perform complete scans, thus making the measurements unusable for analysis. The reason behind the tip failure was most probably the high surface roughness coupled with the presence of sharp peaks and the hardness of the poly-SiC layers. On the other hand the DCP20 probes allowed to perform an entire scan of the surface without observing tip damage and significant scanning artifacts. However, for the samples with the highest surface roughness also these probes were damaged before the scan of the entire surface could be completed. Moreover, for all the layers it was observed that consecutive scans on the same sample caused a small progressive decrease in the RMS surface roughness  $S_Q$ , thus indicating a progressive tip consumption.

Figures 5.2 and 5.3 show the HR-SEM images of the top view of the surface of the poly-SiC layers acquired with a HFV of 2  $\mu$ m and 1  $\mu$ m, respectively. A 45° tilted view acquired with a HFV of 2  $\mu$ m is also included. For all the layers these images show the presence of grains thus revealing the polycrystalline structure of the SiC layers. The polycrystalline structure was expected as a consequence of the deposition conditions. The deposition of poly-SiC layers using same precursors, a similar furnace, and similar deposition parameters has been reported in [106, 109–111]. More in detail the results reported in [106] and [111] show poly-SiC layers with a surface morphology totally similar to those reported here. For those layers the vertical columnar growth has been demonstrated by means of TEM crosssections [111]. The same observation is valid for the poly-SiC layers reported in [106], obtained under different deposition conditions as those employed here. Based on these results we can assume a columnar microstructure also for the layers described in this thesis. Under this assumption the features visible at the surface correspond to the tips of the columnar grains, and the shape of the base of the tips corresponds to the shape of the horizontal crosssection of the column. By observing the HR-SEM images we notice that size and morphology of the grains change with the GFR. Samples deposited with GFRs ranging from 4.0 to 5.5 appear more similar to each other. As the GFR increases above 5.5 an abrupt change in the morphology is observed. These observations are confirmed by the data obtained by the grain analysis of the HR-SEM images and that of the AFM scans are reported in Table 5.4.

For the discussion we can first focus on samples deposited with GFRs ranging from 4.0 to 5.5. Sample I-1 (GFR = 4.0) shows pyramid-shaped features with a hexagonal base of variable size. In addition, small pyramid-shaped grains, also with variable size, are present on the tip of the main grains. For this sample the grains are immediately distinguishable due to the presence of well-defined and clearly visible grain boundaries. A few clustered grains composed by two or more grains are also present. The grains composing the cluster appear compressed together. The shape of the

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Figure 5.2: High resolution SEM images of the surface of the poly-SiC layers I-1, I-2 and I-3. Each column contains three different images corresponding to the same layer. The first two images show to the top and the 45° tilt views acquired with an HFV of 2  $\mu$ m. The last image shows a top view acquired with an HFV of 1  $\mu$ m.

grains taking part to the cluster results deformed and their grain boundaries appear less visible because less deep and/or wide. Therefore, the grain boundaries may be used as an indication of the compression between the grains. As reported in Table 5.4. for sample I-1 an average grain width  $G_{W_{av}}$ of 72.1 nm, a RMS surface roughness  $S_Q$  of 14.5 nm, and a max peak height  $Z_{MAX}$  of 109.1 nm were obtained. The 3D surface reconstruction obtained from the AFM scan of this sample is shown in Fig 5.4 (a). By comparing this with the corresponding 45° tilted HR-SEM image shown in Fig. 5.2 it is possible to observe how the surface reconstruction shows much less features and how the grains appear less resolved. This is a consequence of the convolution between the tip of the AFM probe and the surface features. The curvature radius of the scanning tip is in fact relatively large causing loss of resolution and making difficult to reach the grain boundaries. This is



Figure 5.3: High resolution SEM images of the surface of the poly-SiC layers I-4, I-5 and I-6. Each column contains three different images corresponding to the same layer. The first two images show to the top and the 45° tilt views acquired with an HFV of 2  $\mu$ m. The last image shows a top view acquired with an HFV of 1  $\mu$ m.

the reason why it was not possible to perform a satisfactory grain analysis using the AFM scans thus requiring the acquisition of HR-SEM images. By increasing the *GFR* the  $G_{W_{av}}$  and the  $S_Q$  progressively increases as also does the average surface height  $Z_A$ . The variations in the grain width and in the height of their tips are also visible from the 3D surface reconstructions shown in Fig. 5.4. For sample I-4 (*GFR*=5.5) the estimated  $G_{W_{av}}$  is 108.9 nm and the  $S_Q$  is 34.3 nm which compared to sample I-1 correspond to an increase of about 51% and 136%, respectively. In addition, by increasing the *GFR* from 4.0 to 5.5 the grains result more compressed together (crowding) and more difficult to discern. This is visible in the HR-SEM images showing the less defined grain boundaries and the increased occurrence of clustered grains. In particular, in the HR-SEM images acquired with the 45° tilt for sample I-4 the grains appear highly packed and connected to each other.

Table 5.4: Data obtained from the grain analysis of the HR-SEM images and from the analysis of the AFM scans for each of the six poly-SiC samples. In the table are reported: the average projected area of the grains  $G_{A_{av}}$ , the average grain width  $G_{W_{av}}$ , the max peak height  $Z_{MAX}$ , the average surface height  $Z_A$ , the RMS surface roughness  $S_Q$ , and the maximum height of the average profile  $S_Z$ .

Layer ID	$\begin{array}{c} GFR \\ \left( {{{_{{\rm{SiH}}_2}{\rm{Cl}}_2}/{\rm{C}}_2}{\rm{H}}_2} \right) \end{array}$	$G_{A_{av}}$ (nm <sup>2</sup> )	$G_{W_{av}}$ (nm <sup>2</sup> )	$Z_{MAX}$ (nm)	$Z_A$ (nm)	$S_Q$ (nm)	<i>S<sub>Z</sub></i> (nm)
I-1	4.0	3969	72.1	109.1	50.1	14.5	$70\pm5$
I-2	4.5	5500	83.7	134.4	56.5	19.4	$83\pm5$
I-3	5.0	7079	94.9	146.6	72.3	24.6	$106\pm5$
I-4	5.5	9320	108.9	208.8	100.1	34.3	$135\pm5$
I-5	6.0	4821	78.3	98.3	44.2	12.2	$56 \pm 5$
I-6	6.5	4365	74.5	67.8	34.3	9.5	$46\pm5$

Finally, the HR-SEM images show an increase in the sharpness and height of the grain tips. The increase of average height of the tips could be a direct consequence of the mutual compression of the grains, as these would find more space to grow in the vertical direction. In addition it is possible to observe how the hexagonal base of the features appears less and less regular as the GFR increases. Also in this case the mutual compression of the grains might be the cause. The mutual compression of the grains might be a direct consequence of the formation of larger grains.

As already mentioned above when the GFR is increased above 5.5 the surface morphology undergo an abrupt change. Before describing their surfaces, it must be noted that the SEM images of these last two samples are not as sharp as those acquired for the samples described above. The change in the image quality was not related to the instrument but to the surface itself. All the samples were in fact inspected in the same experimental session and under the same conditions and the inspection repeated in a separate session to exclude instrument related problems. The loss of contrast and resolution is probably the result of electron charging. This points towards a change in the way the probing electrons distribute and diffuse into the sample and thus in change of the polycrystalline structure. Sample I-5 deposited with a GFR of 6.0 shows a lumpy surface composed by irregularly shaped and sized grains with their rounded tips pointing in random directions. The description of this surface is not straightforward. The grains appear as the result of the combination of many other small grains with shapes that are more round compared to those of the samples with GFRs



Figure 5.4: 3D reconstruction of the surface of the six poly-SiC layers obtained from the AFM scans. The same false-color scale has been set for all the samples. In these images the changes in the surface morphology of the layers are visible. The image corresponding to sample I-4 shows tip artifacts caused by failure of the AFM tip during the last part of the scan.

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up to 5.5. After a careful inspection of several SEM images (not shown here) it was still possible to discern the presence here and there of features with a hexagonal shape. For this sample both the  $G_{A_{av}}$  and the  $S_Q$  are significantly lower than those of sample I-4. In a similar way for sample I-6 a further decrease in the mean  $G_{A_{av}}$  and  $S_Q$  is observed. Nevertheless, for this sample the surface features seem to have a more regular shape which by a closer look appear to have a hexagonal shape. These grains are surrounded by small grains and appear more separated from each other as suggested by the clearly visible grain boundaries. In general the modifications in the size and morphology of the grains can be a consequence of the changes in the growth dynamics and at the same time a consequence of the modification in the crystal structure induced by the variations in the deposition conditions. The crystal structure of the poly-SiC layers was therefore also investigated and the results correlated to the above surface analysis in the next section.

#### 5.2.2.3 Polycrystalline structure

The crystallinity of the poly-SiC layers was investigated by XRD spectroscopy (section 3.2.1.2). The analysis of the XRD spectra shown in Fig. 5.5 reveals that all the poly-SiC layers have a 3C type crystallographic structure (fcc lattice). All the spectra show the typical peak pattern of the 3C polytype. The most intense peak is positioned at  $2\theta = 35.6^{\circ}$  and corresponds to the 3C-SiC crystallographic planes with 111 orientation. This indicates that 111 is the preferred orientation of the atomic planes of the grains of the poly-SiC layers. Also, peaks of medium intensity corresponding to 220 and 311 oriented 3C-SiC crystallographic planes are present at  $2\theta = 60^{\circ}$  and  $2\theta = 71.8^{\circ}$ , respectively. Apart from the main peaks described above low intensity peaks typical of the 3C structure are also present in the spectra. A peak located at  $2\theta = 75.5^{\circ}$  and corresponding to 3C-SiC 222 planes is present in all the spectra. Moreover, in the spectra of the samples deposited with GFRs equal or higher than 5.5, a peak associated with 3C-SiC {200} planes is visible at  $2\theta = 1.4^{\circ}$ . This peak is instead extremely weak in the spectra of the remaining samples.

In order to evaluate possible changes in the crystallographic orientation the intensity I of these last two peaks was compared to that of the peak corresponding to {111} planes. The ratios  $I_{(111)}/I_{(220)}$  and  $I_{(111)}/I_{(311)}$  are reported in Table 5.5. These values indicate that as the *GFR* increases the relative number of planes with 220 and 311 orientation increases meaning that the crystals are differently oriented with respect to the surface and thus suggesting changes in the poly-SiC crystallographic structure. This is valid up to sample I-5 where the ratios  $I_{(111)}/I_{(220)}$  and  $I_{(111)}/I_{(311)}$  reach a mini-



Figure 5.5: XRD Spectra of the six poly-SiC layers. The peaks corresponded to the 3C-SiC phase are labeled and their and their position indicated by the stick pattern on the  $2\theta$  axis. The peak corresponding to Si {311} is also indicated.

mum. A small increase in these values is then found for sample I-6 where they become comparable to those of sample I-4. The full width half maximum (FWHM) of peaks  $\{111\}$  and  $\{311\}$  is reported in Table 5.5. These values also change with the *GFR*. Samples I-1, I-2 and I3 have comparable FWHM while this slightly increases for sample I-4. A significant increase in the FWHM of  $\{311\}$  peak is observed for samples I-5 and I-6. The increase in the peak width generally indicates an increase in the crystalline disorder meaning a distorted atomic arrangement inside the crystals due to local

Layer ID	$GFR \\ \left( {{{_{\rm{SiH}_2}{\rm{Cl}_2}/{\rm{C}_2}{\rm{H}_2}}} \right)$	$I_{\{111\}}/I_{\{220\}}$	$I_{\{111\}}/I_{\{311\}}$	FWHM {111}	FWHM {311}	
I-1	4.0	43.39	46.22	0.423	0.707	
I-2	4.5	29.14	23.55	0.421	0.666	
I-3	5.0	32.22	24.69	0.433	0.696	
I-4	5.5	13.63	18.10	0.507	0.784	
I-5	6.0	6.05	11.03	0.68	1.268	
I-6	6.5	11.02	18.33	0.8	1.92	

Table 5.5: Intensities of the peaks corresponding to  $\{220\}$  and  $\{311\}$  crystallographic planes relative to that of the peak corresponding to  $\{100\}$  planes. The FWHM of  $\{111\}$  and  $\{311\}$  peaks are reported in the last two columns.

defects. Moreover, it can indicate a shorter length order, meaning that the crystals forming the grains are smaller.

The results described above can be correlated to the results obtained from the surface morphology and compositional analysis discussed in subsection 5.2.2.1 and 5.2.2.2, respectively. Sample I-1 shows the most regular and well defined grains while already for samples I-2 and I-3 the grain structure and morphology appear more elaborated. This is consistent with the increase in the relative intensity and in the FWHM described above. The same observation is valid for sample I-4. For this sample three additional peaks are visible. These are located at  $2\theta \approx 29.4^{\circ}$ ,  $2\theta \approx 41^{\circ}$ , and  $2\theta \approx 55.7^{\circ}$ . The origin of the first peak is not clear, while the second one might indicate the existence of 6H-SiC (hexagonal lattice) crystallographic planes thus partially justifying the changes in the surface morphology. The third peak is very sharp and has medium intensity. This peak could indicate the presence of strained Si  $\{311\}$  planes which are typically located at 56.13° ( $\theta$ shift due to strain). This is consistent with the fact that this layer contains Si in excess and shows an elaborated surface morphology. Furthermore, the bump present around this peak might again be due to the presence of Si in excess in the layer but this time arranged in a disordered fashion, e.g. amorphous. Another explanation for this bump could be the presence of small and/or disordered SiC crystals arranged with a 24-R (rhombohedral lattice) crystallographic structure. The existence of 24R-SiC phase is as also suggested by the shoulders present at the left and right sides of the 3C-SiC {111} peak.

As for sample I-4 the XRD spectra of sample I-5 shows a peak related to the Si in excess. However, compared to the one of sample I-4 this peak results shifted  $(2\theta \approx 57^{\circ})$  and widened. This might indicate that the Si in excess is now rearranged in a less ordered fashion. In any case, the excess of Si in samples I-4 and I-5 is most probably the cause of the increased disorder in their atomic network suggested by the enlargement of the main peaks and by their surface morphology. It is interesting to notice how the sample I-5 presents a very irregular surface morphology and how the XRD pattern of this sample has the lowest values of the  $I_{\{111\}}/I_{\{220\}}$ ,  $I_{\{111\}}/I_{\{311\}}$  ratios.

Sample I-6 exhibits a peak located at  $2\theta \approx 56.1^{\circ}$  clearly indicating the presence of Si 311 planes. This peak springs out of a bump which can be explained in a similar way as for of sample I-4. The spectrum of sample I-6 is the one showing the widest peaks indicating also in this case that the SiC atomic network is heavily distorted by the presence of the extra Si.

Additional features are also present in the spectra of samples I-1 and I-2. Two wide peaks located at  $2\theta \approx 54.5^{\circ}$  and  $2\theta \approx 64.5^{\circ}$  together with a weak but sharp peak located at  $2\theta \approx 32^{\circ}$  are visible in the XRD spectra of these samples. These peaks might reveal the coexistence of a very disordered 24-R-SiC phase together with the existing 3C phase. This is also suggested by the presence of a shoulder at the left side of the 3C 111 peak and a weaker shoulder at its right. These features are instead absent in the spectrum of sample I-3. Supposing that the wide peaks are the consequence of the C in excess present in these samples, then we would conclude that sample I-3 is very close to stoichiometry as also indicated by the compositional analysis (section 5.2.2.1). Therefore, it is maybe not a coincidence that its XRD spectrum has no additional peaks or features.

Finally two additional features positioned at  $2\theta \approx 18^{\circ}$  and  $2\theta \approx 84^{\circ}$  are almost always present in all the XRD spectra. The origin of these is not clear however we suspect that these are originated by the Si substrate.

#### 5.2.2.4 Thickness, uniformity and growth rate

The thickness of the poly-SiC layers must be accurately determined as this value is required for the determination of important properties, e.g. residual stress, resistivity, elastic modulus and growth rate. Also, for determining the residual stress the average thickness across the wafer is needed. Both optical reflectometry, and contact profilometry (sections 3.2.3.2 and 3.2.3.3) were employed for determining the thickness of the layers. The acquired measurements were corrected to obtain useful thickness values to be employed for the calculation of the layer properties. The corrected data are presented below together with the employed correction procedure.

Optical reflectometry was employed for the fast and precise measurements of the thickness in several points on the wafer. This allowed to de-

termine the uniformity of the layer thickness across the wafer surface. This was expressed as by the average thickness value  $t_{r-av}$ , and the one-sigma standard deviation value  $SD_r$ . These data are reported in Table 5.6. The  $SD_r$  ranges roughly between 2% and 6%, indicating that the film deposition is reasonably uniform. However, reflectometry measurements resulted not accurate due to the not perfect model available for fitting the data. The available model is in fact based on optical constants which are slightly different from those of our poly-SiC layers. Therefore, the thickness of the poly-SiC layers was also measured by profilometry. This technique is in its turn extremely time consuming and therefore less suited for uniformity measurements. For this reason profilometry measurements were carried out only on four different test structures (section 3.2.3.3) in the center of the wafer and the average value of these measurements calculated. The resulting thickness  $t_{p-c}$  , is reported in Table 5.6 for each layer. These data can be compared to the thickness measured in the center by reflectometry  $t_{r-c}$ . The mismatch between the two measurements is not only a consequence of the inaccuracy of the optical measurement but also of the surface morphology of the layers. To understand this it is useful to model each poly-SiC layer as a stack of two layers as shown in the schematic drawing of Fig. 5.6. The bottom layer has a flat surface, the top layer is instead discontinuous in the horizontal direction and represents the rough surface.



Figure 5.6: Schematic drawing describing the model employed for the calculation of the corrected thickness of the poly-SiC layers. The poly-SiC layer is composed by a two layers one flat and a discontinuous layer representing the rough surface.

For correcting the thickness measurements we assumed that the top layer corresponds to the 3D surface reconstruction obtained by AFM. In the reflectometry measurements the discontinuous layer adds up to the flat one with a thickness which in first approximation is equivalent to the average height of the surface  $Z_A$ . This because the rough layer can be in first approximation considered as mixture at 50% of air and poly-SiC itself. Instead, in the profilometry measurement the discontinuous layer contributes with a thickness that can be approximated with the maximum height of the average profile  $S_Z$ . This because the curvature radius of the profilometry tip is huge compared to the size of the surface features and thus we can assume that the tip scans the surface by running above only the highest surface points.

Based on these considerations we calculated a corrected value for the center thickness measured by profilometry as follow. First, the thickness of the flat part of the stack  $t_f$  was obtained by subtracting  $S_Z$  (Table 5.4) from the thickness obtained by profilometry. Second, the average height of the surface  $Z_A$  (Table 5.4) was added to the  $t_f$  to obtain the corrected thickness at the center,  $t_{p-c-cor}$ . The obtained values are reported in Table 5.6 together with their corresponding errors. These were overestimated after taking into account the inaccuracy and imprecisions of the measurement techniques involved. By comparing the  $t_{p-c-cor}$  with  $t_{r-c}$  we notice that the difference is very small for layers I-2 and I-3. These layers in fact gave the best match with the available model during the fitting of the optical data. The difference is slightly larger for layers I-1 and I-4 and very large for layers I-5 and I-6. These last two layers are in fact those which are less stoichiometric due to the excess of Si (section 5.2.2.1). Each of the average thicknesses measured by reflectometry,  $t_{r-av}$ , was then corrected by multiplying it by a correction factor CF calculated as  $CF = t_{p-c-cor}/t_{r-c}$ . The obtained values,  $t_{r-av-cor}$ , with the associated corrected standard deviation are reported in Table 5.6.

The corrected average thickness values were divided by the corresponding deposition time to obtain the average growth rate for each layer. In Fig. 5.7 the growth rate is plotted as a function of the *GFR*, here the standard deviation of the corrected average thickness was employed to calculate the error bars. The growth rate increases with the *GFR*, the increase is modest for *GFR* values comprised between 4.0 and 5.0 going from about 3.6 to 5.0 nm/min. Afterward, the growth rate increases significantly by almost doubling its value when GFR = 5.5, and finally reaching 11.1 nm/min when GFR = 6.5.

It is interesting to notice that the layers with C in excess or close to stoichiometry share a similar growth rate as well as crystalline structure and surface morphology. On the other hand, the abrupt change in the growth rate when the GFR is increased from 5.0 to 5.5 is associated to a change in crystalline structure and surface morphology.

Layer ID	$GFR \\ (SiH_2Cl_2/C_2H_2)$	$t_{r-av}$ (nm)	$SD_r$ (nm)	$SD_{r-rel}$ (%)	$t_{r-c}$ (nm)	$t_{p-c}$ (nm)	$t_{p-c-cor}$ (nm)	$t_{r-av-cor}$ (nm)
I-1	4.0	567	16	2.8	552	543	$526 \pm 7$	$540 \pm 16$
I-2	4.5	512	23	4.5	491	514	$489\pm7$	$509\pm23$
I-3	5.0	531	30	5.6	502	542	$511 \pm 7$	$541\pm32$
I-4	5.5	720	30	4.2	690	695	$660\pm7$	$689\pm27$
I-5	6.0	547	13	2.4	533	495	$483\pm7$	$494 \pm 12$
I-6	6.5	628	12	1.9	616	553	$541\pm7$	$552\pm11$

Table 5.6: Thickness data determined by optical reflectometry and profilometry measurements for the six different poly-SiC layers. The corrected values for the center and for the average thicknesses are reported in the last two columns.



Figure 5.7: Variation of the growth rate and of the total residual stress of the poly-SiC layers as a function of the GFR.

#### 5.2.2.5 Residual stress

The residual stress of the poly-SiC layers was obtained by using the wafer curvature measurement method (section 3.2.4.1). The thickness of the layers employed in the calculation of the residual stress was the corrected average thickness calculated above  $(t_{r-av-cor})$ . The calculated residual stress is reported in Table 5.7 and plotted in Figure 5.7 as a function of the *GFR*. Here the error bars take into account the errors in the values used to calculate residual stress; i.e. film thickness, radius of curvature and substrate thickness. The stress of the layers is tensile and it decreases from about 1.35 GPa to 0.3 GPa as the *GFR* is increased from 4.0 to 5.0. The stress of the layer deposited with a *GFR* of 5.5 is close to or below  $\pm 3$  MPa that is the minimum stress measurable with our setup considering the thickness to about 130 MPa. Finally, for a *GFR* of 6.5 the stress decreases again reaching a value close to 16 MPa. A similar trend in the stress of poly-SiC layers as the amount of SiH<sub>2</sub>Cl<sub>2</sub> is increased has been reported in [106] and [107].

In order to explain the results above we recall that the total residual stress is given by the sum of the thermal stress and the intrinsic stress that is  $\sigma_{rt} = \sigma_{th} + \sigma_i$ , (see section 3.2.4.1). The thermal stress arises from the difference in the coefficients of thermal expansion (CTE). For both Si and 3C-SiC the CTE are temperature dependent and their difference increases with the temperature [112, 113]. At room temperature the CTE of Si (100) is  $2.6 \times 10^{-6} \text{ °C}^{-1}$  while that of 3C-SiC is  $3.2 \times 10^{-6} \text{ °C}^{-1}$ . At 1000 °C

the CTEs are  $4.5 \times 10^{-6}$  °C<sup>-1</sup> and of 3C-SiC is  $5.1 \times 10^{-6}$  °C<sup>-1</sup> for Si and 3C-SiC, respectively. The average values between RT and 1000 °C for Si and 3C-SiC are about  $3.9 \times 10^{-6}$  °C<sup>-1</sup> and  $4.5 \times 10^{-6}$  °C<sup>-1</sup>, respectively. This means an average CTE mismatch of about 15%. This difference would cause the poly-SiC layers to have a tensile stress. On the other side the intrinsic stress arises from the mismatch between the lattice constants of the Si and that of the poly-SiC. The lattice constant of Si (100) is 5.43 Å while that of stoichiometric 3C-SiC is 4.36 Å which translates into a mismatch of about 24%. This difference would as well cause the poly-SiC layers to have a tensile stress. However, the intrinsic stress also depends on the presence of defects such as dislocations (e.g. staking faults) and voids in the grains [97]. In addition, the presence of grain boundaries can strongly influence the stress as it is the case for poly-Si layers. Discerning the contribution of each of these factors is not straightforward and requires extensive characterizations of the crystallographic structure of the layers which are out of the scope of this thesis. Nevertheless, here we propose a possible qualitative explanation for the behavior of the stress of the poly-SiC layers. Recalling that from the analysis of the HR-SEM images we concluded that the grains result more packed as the GFR is increased from 4.0 to 5.5 then we could explain the decrease in the tensile stress for samples I-1 to I-4 as the result of a compressive force arising from the increased packing the of poly-SiC columnar grains. This in fact would progressively compensate the tensile residual stress and eventually lead to a stress close to zero as it is the case for layer I-4. Following the above reasoning we would expect that as the GFR is further increased the residual stress would turn into compressive. However, this does not happen and for layer I-5 the stress is slightly tensile. This behavior is probably justified by the significant change in the polycrystalline structure of this layer which, compared to I-4, presents smaller grains and therefore and a higher density of grain boundaries (sections 5.2.2.2 and 5.2.2.3). This confirms the important role of the grain boundaries in the definition of the stress level. For sample I-6 the stress goes back to a value close to 0. In this case the changes in the crystalline structure caused by the incorporation of the extra Si (sections 5.2.2.1 and 5.2.2.3) needs to be taken into account to explain this behavior.

#### 5.2.2.6 Electrical resistivity

Despite we are mainly interested in the mechanical properties of the poly-SiC layers it is also useful to verify its electrical resistivity. The idea is to evaluate if constrains could arise in case these layers need to be employed in conjunction with electrically conductive layers (section 2.3.3). For this

Layer ID	$\begin{array}{c} GFR \\ \left( {{{_{{\rm{SiH}}_2}{\rm{Cl}_2}}/{\rm{C}_2}{\rm{H}_2}} \right) \end{array}$	$\sigma_{rt}$ (MPa)	$G_{W_{av}}$ (nm)	Si/C	$ ho \ (\Omega \cdot cm)$
I-1	4.0	$1347 \pm 110$	72.1	0.972	$118.8 \pm 1.1$
I-2	4.5	$827\pm81$	83.7	0.993	$28.8\pm1.1$
I-3	5.0	$277\pm34$	94.9	0.992	$7.5\pm0.1$
I-4	5.5	$0\pm3$	108.9	1.026	$3.0\pm0.02$
I-5	6.0	$149 \pm 15$	78.3	1.072	$70.6\pm0.7$
I-6	6.5	$16\pm5$	74.5	1.139	> 270

Table 5.7: Table reporting the stress values measured for the poly-SiC layers. Other relevant properties of the layers which can influence the stress are also included in the table . In the last column the resistivity with its standard deviation is reported.

reason the resistivity  $\rho$  of the poly-SiC layers was determined. The fourprobe measurements system described in section 3.2.4.3 was employed to measure the sheet resistance of the layers at the center of the wafer  $R_{S-c}$ . The resistivity was then calculated as:  $\rho = R_{S-c}/t_{p-c-cor}$ .

The resistivity values obtained are reported in Table 5.7, these are in the order of  $10^0 - 10^2 \Omega \cdot cm$ . Unexpectedly, these values are many orders of magnitude lower than the calculated resistivity of intrinsic monocrystalline 3C-SiC, that at room temperature is roughly  $1 \times 10^{15} \Omega \cdot cm$ . As reported in [114] and [115] such low resistance values can be the result of unintentional nitrogen (N) doping.  $N_2$  is in fact present as an impurity in the gas mixture employed for the deposition. In particular the source of N<sub>2</sub> was identified as the dilution gas  $(H_2)$  of the  $C_2H_2$ . A rough calculation of the concentration of N present in the poly-SiC layers points to values in the order of  $1 \times$  $10^{15} - 1 \times 10^{16}$  atoms/cm<sup>3</sup>. These values were calculated considering the 3C-SiC as monocrystalline. However, due to the polycrystalline structure the concentration of N could be as high as  $1 \times 10^{16} - 1 \times 10^{17}$  atoms/cm<sup>3</sup> which is in line to what measured by Dunning et al. [114] on a similar 3C-SiC layer. The resistivity and conductivity of the six poly-SiC layers are plotted in Fig 5.8 as a function of the GFR. The resistivity of the poly-SiC decreases from a value of 118.8  $\Omega \cdot cm$  for the sample deposited with a *GFR* of 4.0 down to 3.0  $\Omega \cdot cm$  for the sample deposited with a *GFR* of 5.5. As the *GFR* is increased above 5.5 the resistivity suddenly increases. For the layer deposited with a GFR of 6.0 a resistivity of 70.6  $\Omega \cdot cm$  is measured. Finally, for sample deposited with the highest GFR resistivity drastically increases. This value was not measurable as it was higher than the instrument limit which is  $5 \times$  $10^6 \ \Omega/\Box$ , meaning that the resistivity of sample I-6 is higher than 270  $\Omega \cdot cm$ .

The behavior of the resistivity as a function of the *GFR* can be explained by taking into account the crystalline structure of the samples. In general the electrical properties of polycrystalline semiconductor are strongly influenced by the grain boundaries. The defects present at the grain boundaries act as trap for majority carriers and give rise to potential barriers which limit the current flow within grains thus increasing the resistivity.

The resistivity decrease observed when the GFR is increased from 4.0 to 5.5 can therefore be explained by the decrease in the density of grain boundaries caused by the increase of the grain size. Following the same reasoning the resistivity of sample I-5 increases again as does the density of grain boundaries. It is worth to note that the resistivity of this sample has a value comprised between that of sample I-1 and I-2 as it is its grain size. Finally, the resistivity of sample I-6 drastically increases. This is probably due to a further decrease in the grain size. However, this might not be the only cause as the conduction is further disturbed by an increase in the carriers scattering due to the disordered crystalline structure of this sample. This is highlighted by the peak broadening of the XRD spectra of this sample. Another factor that could be taken into account to explain the resistivity variation with the GFR is the decrease in the concentration of gas source of the unintentional doping (see Table 5.2). However, as the change in the flow is small its effect might be secondary compared to those of the grain boundaries.



Figure 5.8: Graph showing the variation of the resistivity and conductivity of the poly-SiC layers as a function of the *GFR*. For GFR = 6.0 the values corresponding to the limit of the measurement setup are plotted as indication.

#### 5.2.2.7 Wettability

Contact angle measurements showed that all the poly-SiC layers are hydrophilic. The water drop dispensed on the surface of these layers immediately spread over the surface giving a value close to 0 as contact angle.

#### 5.2.2.8 Mechanical properties

The elastic modulus of the poly-SiC films was determined by nanoindentation (section 3.2.4.2). Four nanonoindentaions per sample were performed and the collected data averaged before the analysis. The elastic modulus and the hardness were determined with the method described in section 3.2.4.2. For the calculations we employed  $E_{sub} = 130$  GPa,  $\nu_{sub} = 0.28$ ,  $E_{tip} = 1.2$  TPa,  $\nu_{tip} = 0.2$ , and  $\nu_{film} = 0.168$ .

The high surface roughness of the poly-SiC layers influenced the acquired data. The problem is that in the presence of surface features the actual contact area differs from the calibrated one  $A_C$  (section 3.2.4.2). This is true especially for the first part of the indentation measurement. Therefore, only the data acquired with an indentation depth between 200 and 300 nm were employed in the analysis. The higher limit of this range was chosen to stay as far as possible from the substrate and thus to reduce its influence. As suggested in [116], a measure of the layer strength which is independent from the contact area  $A_C$  and thus from the surface roughness, is given by the following parameter:

$$\frac{H}{E_r^2} = \frac{4}{\pi} \frac{P}{S_m} \tag{5.1}$$

where H is the hardness and  $E_r$  is the reduced elastic modulus (section 3.2.4.2). The  $H/E_r^2$  parameter is a measure of the resistance to plastic penetration and as such a measure of resistance to permanent damage. Therefore, it can be used as indication of strength [116]. However, it needs to be said that this parameter is more accurate when the thin film and the substrate are elastically homogeneous (same stiffness) [116]. This is not the case for poly-SiC films on Si substrates. However, as the poly-SiC layers share the same substrate and composition, the parameter above is still useful to provide a qualitative comparison between the different poly-SiC layers.

The obtained values for the elastic modulus  $E_{film}$ , the hardness  $H_{film}$ and the  $H/E_r^2$  parameter are reported in Table 5.8. All the layers have comparable values. However, we can observe that layers I-1, I-5 and I-6 possess the highest  $E_{film}$ . Also, these layers have the highest  $H/E_r^2$ values indicating that they have the highest resistance to permanent damage caused by plastic penetration. The layer with the lowest elastic modulus and  $H/Er_r^2$  are I-2 and I-4, with the former having also the lowest hardness. The values extracted for elastic modulus of our poly-SiC layers are comparable to those measured for similar layers and reported in [117].

Table 5.8: Table reporting the mechanical parameter extracted for the poly-SiC layers. Other relevant mechanical and structural properties of the layers are also included in the table.

Layer ID	E <sub>film</sub> (GPa)	H (GPa)	$H/E_r^2$ (nm <sup>2</sup> /mN)	$\sigma_{rt}$ (MPa)	$G_{W_{av}}$ (nm)	Si/C
I-1	$384 \pm 8$	$25.5\pm2.4$	$630\pm16$	$1347 \pm 110$	72.1	0.972
I-2	$326\pm6$	$20.6\pm2.3$	$587\pm6$	$827\pm81$	83.7	0.993
I-3	$379 \pm 12$	$23.3\pm2.0$	$608 \pm 15$	$277\pm34$	94.9	0.992
I-4	$347\pm9$	$27.5\pm2.4$	$590 \pm 31$	$0\pm3$	108.9	1.026
I-5	$402 \pm 27$	$27.7\pm2.9$	$640 \pm 42$	$149\pm15$	78.3	1.072
I-6	$456\pm29$	$26.1\pm2.7$	$620\pm15$	$16\pm5$	74.5	1.139

# 5.2.3 Poly-SiC layer choice

One of the most important parameters to be considered for the choice of the poly-SiC layer is the stress. This material is in fact meant to work as the structural free-standing layer of the microchannel. Therefore, a layer possessing slightly tensile stress, is preferred. In this respect I-3 and I-5 are the most suited layers. However, to reduce the deformation of the channel when this is exposed to high temperatures the tensile stress cannot be too low. In this respect I-3 is a better choice. In addition, despite I-5 would allow easier processing due its smoother surface, and despite its slightly better mechanical properties it shows a less ordered crystalline structure and it is less stoichiometric. This might result in a lower chemical resistance which is unfavorable during microfabrication and operation. Based on these considerations, I-3 appears to be the best choice.

# 5.3 Poly-SiC surface micromachined channels

The selected poly-SiC layer was employed in the fabrication of surface micromachined channels. This allowed verifying its suitability as structural layer for surface micromachined nanoreactors. At the same time we explored the feasibility of a new technique for the sealing of the surface micromachined channels. This technique, specifically developed for SiC layers, solves the problems typically related to the conventional sealing as explained in more detail in section 5.3.1.1.

# 5.3.1 Microchannel Design

The motivations behind the use of surface micromachining for the fabrication of the channel of the nanoreactor have been indicated in sections 2.3.2 and 2.4.3. The schematics of Fig.5.9 illustrate the typical geometry of the surface micromachined channel of the nanoreactor together with its main features.

The microchannel has an effective length L, a width W and a height h, with L >> W >> h; e.g. L = 10 mm,  $W = 400 \ \mu$ m, and  $h = 2 \ \mu$ m. The microchannel is provided with through-silicon inlet and outlet openings having a square truncated-pyramid shape. The top layer of the microchannel integrates an array of pillars, evenly distributed with a spacing s. These prevent the collapse of the top layer during sacrificial etching. Moreover, they provide a distributed anchoring of the top layer creating a mechanically robust microchannel able to withstand elevated pressures.

#### 5.3.1.1 Conventional fabrication and sealing

The fabrication of the microchannel described above is achieved by sacrificial etching. This technique consists in the removal of the layer (sacrificial layer) laying below the top structural layer (in our case the ceiling) of the microchannel. This allows the formation of the hollow space which corresponds to the flow region of the microchannel. The schematic of Fig. 5.10 describes the conventional fabrication process of the surface micromachined channel of the nanoreactor. In this schematic the steps required for the fabrication of the bottom membrane and of the electron transparent windows have been omitted for simplicity. As first step, a TEOS layer with a thickness of 1  $\mu$ m is deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) to form the sacrificial layer. This layer is then locally etched down to the Si substrate to create a molding structure for the formation of the pillars (Fig. 5.10 (a)). A layer of 700 nm of  $SiN_x$  is then deposited by LPCVD to form the ceiling of the channel and the pillars at the same time. Afterward small circular apertures are patterned into the ceiling to form the access holes necessary to bring the etchant into contact with the sacrificial layer (Fig. 5.10 (b)). The sacrificial layer is then removed by wet etching using BHF 1:7 (Fig. 5.10 (c)). In Fig 5.11 (a), a SEM image of a surface micromachined channel with an h=5.0  $\mu$ m is shown. In this image the array of pillars and access holes are visible. In order to achieve a hermetic



Figure 5.9: Schematics describing the typical geometry of the surface micromachined channel of the nanoreactor. The main elements such as pillars and inlet/outlet openings are depicted. The top view of the microchannel is shown in (a) while the cross-sections along the support pillars and flow region are shown in (b) and (c), respectively.

microchannel the access holes needs to be sealed. This is typically done by depositing an additional layer on top of the structural layer. This last step is critical as it can cause several problems. As illustrated in Fig. 5.10 (d\*), by employing a conformal layer for the sealing this would enter the channel having a dramatic effects on the transparency of the windows (see section 2.3.1 ). This problem is typical of layers deposited by LPCVD which are therefore not suited for sealing the channel of the nanoreactor. If instead a non-conformal layer is employed for closing the access holes, the internal coating can be confined in a very limited area close to the access holes (see Fig. 5.10 (d)). Layers deposited by PECVD are suited to achieve this kind of sealing as this technique allows tuning the conformality of the layers by tuning the deposition parameters. Nevertheless, in order to achieve the sealing with this approach very thick layers are required. As shown in Fig. 5.10 (d), a thick layer may cause the deformation of the ceiling by mechanical stress [118]. Also, it can increase the topography [80], and reduce the transparency of the channel (see section 2.3.2). To eliminate these effects the scaling layer can be removed everywhere except in the surroundings of



Figure 5.10: Schematics illustrations describing the fabrication of the channel of the surface micromachined nanoreactor.(a) Deposition of the sacrificial layer and patterning to achieve the molding structure for the pillars. (b) Deposition of the structural layer and patterning to create the access holes. (c) Wet etching of the sacrificial layer through the access holes. (d\*) Access holes are sealed by conformal coating. This approach causes internal deposition which is not suited for the nanoreactor. (d) To solve this problem the access holes are sealed by a thick non-conformal coating. (e) The mechanical deformation and reduced transparency consequence of the elevated thickness are solved by patterning the sealing layer.

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the access holes thus forming cylindrical plugs with a height corresponding to the thickness of the sealing layer [80]. This approach has been adopted for the sealing of the microchannel of the nanoreactor.

In the design phase of the nanoreactor the height of the plugs has been minimized to avoid the formation of a high topography at the surface of the channel. The diameter of access holes has been therefore chosen to be as small as possible within the constraints imposed by the fabrication process. The access holes where designed to have a diameter of 1.5  $\mu$ m. Experimentally it was found that a thickness for the sealing layer of about 2.0  $\mu$ m is required to achieve the sealing [80]. Nevertheless, the subsequent fabrication steps, the possible spreads in the diameter of the access holes, and the spreads in the thickness of the sealing layer impose to use larger thickness values ranging between 2.3  $\mu$ m and 2.7  $\mu$ m. SEM images of the plugs of the conventional surface micromachined nanoreactor are shown in Fig 5.11. In these images is possible to see the high topography of the plugs. This high topography array causes several problems during the fabrication steps necessary for achieving a complete nanoreactor. In the next section we describe an alternative sealing technique which avoids the use of an additional layer and therefore of high topography plugs. As it will be explained this technique exploits the stiction phenomenon and the high the mechanical strength and chemical inertness of poly-SiC.



Figure 5.11: SEM images of a surface micromachined channel and its elements. (a) cross-section of a non-sealed microchannel showing the array of pillars and access holes. (b) View under an observation angle of  $45^{\circ}$  of the structural layer and the plugs. (c) Cross-section of a plug made of 2.3  $\mu$ m PECVD SiN<sub>x</sub> and covered by 200 nm LPCVD SiN<sub>x</sub>. This plug is sealing an access hole with an effective width of 1.35  $\mu$ m [80].

#### 5.3.1.2 The self-sealing microchannel concept

In microfabrication, stiction is a well-known problem that limits the applicability of wet etching for the release of microstructures with relatively large areas and low stiffness [119]. During the drying, which follows the sacrificial etch, capillary forces can bring compliant free-standing structures into contact with the underlying surface. There, adhesion forces may exceed the mechanical restoring force of the deformed structure, leading to permanent adhesion.

Stiction, however, may also be advantageously exploited to achieve structures that self-seal. For example, stiction-induced sealing of parylenebased structures has been demonstrated in [120–123]. Also, the stictionbased sealing of a polysilicon channel has been demonstrated by Tas et al. [124]. Their channel, however, had dimensions in the submicron range and the permanent sealing of the channels was achieved after an annealing at elevated temperatures (1100 °C).

Here we propose to exploit the stiction phenomena to achieve the sealing of the micromachined channel of the nanoreactor. The idea is illustrated in Fig 5.12. The sacrificial and structural layers are patterned to achieve to create a portion of the structural layer adjacent to the microchannel area without supporting pillars Fig 5.12 (a). During the drying step following the sacrificial etching the unsupported portion of the structural layer can bend down and adhere to the Si surface due to stiction Fig 5.12 (b-d). This way a self-sealing microchannel is achieved and no additional layers are required for the sealing. As shown by the schematic of Fig. 5.12 in this approach the access holes are avoided by using lateral apertures to bring the etchant into contact with the sacrificial layer. If we consider the typical dimensions of the channel of a nanoreactor indicated in Fig. 5.9 then we understand that with this approach the etching time necessary to completely remove the sacrificial layer would be extremely long. To give an idea the estimated time would be of about 25 hours if the same materials and the chemicals used for the fabrication of the conventional nanoreactor would be employed. Moreover, during this long etch the  $SiN_x$  structural layer would be completely etched. These problems make this approach unfeasible. However, using SiC would allow to implement the proposed approach. The outstanding chemical inertness of SiC allows to employ highly concentrated HF solution which would drastically shorten the time required to the completely remove of the sacrificial layer while leaving the SiC layer intact. In addition the superior mechanical properties of SiC would allow achieving a mechanically strong structural layer capable to bend without cracking.

# 5.3.1.3 The self-sealing microchannel design

In Fig. 5.13 the design of the proposed self-sealing microchannel is shown together with its geometrical dimensions. The microchannel dimensions are: L = 5.4 mm,  $W = 430 \ \mu$ m, and  $h = 1 \ \mu$ m. The through-silicon inlet and outlet openings have a side-length of 158  $\mu$ m on the side of the



Figure 5.12: Principle of the proposed stiction-induced sealing technique. (a) The structural layer has a non-supported portion (no pillars) located at the edges of the microchannel area. (b) the sacrificial layer is removed by wet etching through lateral apertures along the channel. (c) During the evaporation of the rinsing liquid, capillary forces drive the bending of the non-supported portion of the structural layer towards the Si substrate. (d) A sealed microchannel is achieved when the structural layer touches and adheres to the Si surface.

microchannel and a side-length of 900  $\mu$ m on the back side.

The top layer of the microchannel integrates an array of circular pillars with a diameter of 5  $\mu$ m, evenly distributed with a spacing  $s = 20 \ \mu$ m. To prevent the microchannel collapse by stiction during the drying after the sacrificial etching, this spacing was chosen smaller than the critical length for square plates clamped at the edges. The pillars were designed to anchor the top layer to the bottom Si substrate. This pillar system allows high robustness, stiffness and a well-defined channel height of the microchannel under pressure [80, 125]. Moreover, it prevents the detachment and loss of the top layer during the sacrificial etching and the subsequent drying of the rinsing water. For a robust and effective anchoring the pillars were designed to extend downwards and insert into the Si substrate. This solution was implemented after results of preliminary tests show that during the sacrificial etch non-anchored pillar detach during the sacrificial etch [126].

To achieve the proposed stiction-induced sealing, the top layer was designed to extend beyond the pillars/channel area. This extension forms a lateral sealing wing able to bend and adhere to the bottom Si surface during the drying phase. Fig. 5.13 shows a cross-section of the free standing



Figure 5.13: Schematics drawings of the self-sealing microchannel: (a) top view, (b) section AA' crossing the pillars along the flow direction, and (c) section BB' crossing along the flow region. (d) cross-section showing details of the poly-SiC structural layer and of the free-standing sealing wing.

sealing-wing. The s-shaped profile was designed to reduce the gap between the sealing-wing and the Si surface from 1  $\mu$ m to 0.2  $\mu$ m. The reduced gap allows for a decrease in the elastic strain energy stored inside the structure when stiction occurs (see by Eq. 11 in [127]), making the seal more robust and allowing for a shorter sealing wing.

The top-sealing layer can be fabricated using the selected poly-SiC layer (I-3). This possesses very good mechanical strength and low tensile stress, thus making it suitable not only as structural material, but also as sealing layer. To achieve a certain mechanical robustness a thickness of 900 nm was selected for this layer.

Silicon oxide was selected as sacrificial layer. Its thickness was designed to be 1  $\mu$ m in the channel area and 200 nm in correspondence of the adhesion area of the sealing wing. As will be shown later in section 5.3.2 this was made to obtain the s-shaped profile for the sealing-wing. The sacrificial layer was deposited by PECVD using Tetra-Ethoxy-Silane (TEOS) as precursor. AFM scans where performed to determine the surface roughness of this layer before and after the thinning required to get the thickness of 200 nm. The measurements were carried out with the setup described in section 3.2.2.2 using an NSC05\_20° tip. An area of  $1 \times 1 \mu m$  was scanned with a resolution of 512  $\times$  512 lines. The as-deposited 1  $\mu$ m thick TEOS had an RMS surface roughness,  $S_{O}$ , between of 0.47 and 0.55 nm. Once thinned down to 200 nm the  $S_Q$  decreased to values between 0.32 and 0.38 nm. This is advantageous as it allows to obtain a very smooth bottom surface for the poly-SiC layer and thus a very strong adhesion of the sealing wing [128]. For the same reason the sealing-wing was designed to adhere directly to the Si substrate which is well-known to be extremely smooth ( $S_Q$  is typically 0.1-0.2 nm [70]). Moreover, smooth adhering surfaces helps achieving an effective sealing by preventing leak paths. Another advantage of using TEOS oxide is that this material can be rapidly etched in hydrofluoric acid (HF), which is very selective to both poly-SiC and Si.

The critical dimensions of the sealing-wing were calculated by approximating it as a single-clamped plate. The pull-in and peel lengths were found using Eqs. 14 and 15 reported in [127]. For these calculations the following values were employed: E = 380 GPa (section 5.2.2.8),  $\nu = 0.168$  [117],  $\gamma_l = 73 \times 10^{-3}$  J/m<sup>2</sup> (DI water at 20°C),  $\theta_{C1} = 65^{\circ}$ ,  $\theta_{C2} = 0^{\circ}$ ,  $\gamma_s = 79 \times 10^{-3}$ J/m<sup>2</sup>. The value for  $\theta_{C2}$  was obtained by contact angle measurements performed on a poly-SiC layer exposed to the same HF etching step required for the fabrication of the microchannel. The value of  $\gamma_s$  was estimated experimentally by observing the stiction of circular plates as a function of their radius and gap and by using the theory for the peel-radius derived in [127]. The calculated pull-in and peel lengths were 14.9  $\mu$ m and 15.3  $\mu$ m, respectively. These values are very close to each other. However, the minimum length of the sealing-wing necessary to achieve stiction was determined by the larger of the two that is the peel length. The length sealing wing was designed to largely exceed this value. A total length of 128  $\mu$ m was chosen, which is about 8 times the peel length value. This choice was made to create a stronger adhesion and ensure an effective sealing also in the presence of surface defects and/or small particles, thus making the sealing approach more robust.

# 5.3.2 Microchannel fabrication

The schematic cross-sections describing the fabrication sequence of the microchannel device is shown in Fig. 5.14. Double-side polished p-type Si wafers with (100) orientation, 100 mm diameter and a thickness of  $525 \pm 25$  $\mu m$  were employed as substrate. Fabrication started with deposition of 1  $\mu$ m thick PECVD TEOS oxide on top of the Si substrate (Fig. 5.14 (a)). Lithography and plasma etching were performed to pattern the TEOS oxide layer. The first patterning is used to thin the TEOS down to 200 nm in the area where the sealing-wing should adhere (Fig. 5.14 (a)). A second patterning is used to create 1- $\mu$ m deep circular depressions with a diameter of 5  $\mu$ m by etching the TEOS oxide down to the level of the Si surface (Fig. 5.14 (a)). These circular depressions serve as mold for the formation of the pillars during the deposition of the top layer of the microchannel. These are obtained by performing an anisotropic etch of silicon with a depth of  $4-5 \ \mu m$  using an inductive-coupled-plasma (ICP) deep reactive-ion etching (DRIE) system (Adixen AMS100). The etching temperature is -10 °C and  $SF_6$  and  $C_4F_8$  are employed as etching and passivation gasses, respectively. Next, the sidewalls of the holes are protected with an extra passivation layer. Finally, a hemispherical cavity at the bottom of each hole is obtained by changing the Si etching to isotropic conditions. During the etching of the Si substrate the surface of the TEOS oxide layer is protected by photoresist. This is needed to preserve the smoothness of its surface.

The top layer of the microchannel is then formed by depositing 900 nm of poly-SiC (Fig. 5.14 (b)). This layer was obtained by setting the deposition parameter of the LPCVD furnace equal to those employed for the deposition of layer I-3 (section 5.2.1). This way a layer with about 0.3 GPa tensile stress could be obtained. The deposition time was tuned to achieve the desired thickness.

The through-wafer inlet- and outlet openings are created by anisotropic etching of the Si substrate using a solution of potassium hydroxide (KOH) 33 wt% at 85°C (Fig.5.14 (c)). During the etching, the poly-SiC at the



PECVD TEOS LPCVD poly-SiC HF acid DI Water

Figure 5.14: Schematic cross-sections showing the main fabrication steps of the microchannel device. The cross-sections are AA' and BB' as indicated in Fig. 5.13. (a) Shaping of the sacrificial layer and anchoring holes formation into Si by dry etching. (b) LPCVD deposition of the poly-SiC top-sealing layer. (c) Formation of the inlet/outlet openings by dry etching the poly-SiC at the backside of the wafer and by subsequent substrate removal in KOH 33 wt%. (c) Patterning of the top-sealing layer at the front side. (d) Removal of the sacrificial layer. (e) and (f) drying of the DI water and bending of the sealing-wing. (g) The sealed microchannel device with its elements.

front side works as protection layer while the same layer at the backside serves as hard mask. In this layer, square openings with side-length of 0.9 mm are patterned and etched in an ICP RIE system (Trikon Omega 201) using a gas mixture of Cl<sub>2</sub> and HBr, with an ICP and RF power of 500 W and 40 W, respectively. The poly-SiC on the front side of the wafer is then patterned to define the top-sealing layer of the microchannel. The sacrificial etch is performed by immersing the wafers in concentrated (40 wt%) HF for about 6 hours to completely remove the TEOS oxide layer (Fig. 5.14 (d)). This chemical was chosen to allow a fast removal of the sacrificial oxide (~ 0.9  $\mu$ m/min) and at the same to preserve the smoothness of the Si (100) surface [129]. After the sacrificial etch the wafers were rinsed in DI water for 5 minutes and dried at room temperature, letting the stictioninduced sealing take place (Fig. 5.14 (e) to (g)). Afterward the wafers are dried by baking them in an oven for 5-10 minutes at 100 °C in ambient air at atmospheric pressure. This step also serves to strengthen the adhesion between the sealing wing and the substrate. Finally, the wafers are diced for testing. For testing purposes, devices consisting in microchannels with no inlet and outlet openings were fabricated on a separate wafer by following the same steps described above except for the anisotropic etch of the Si substrate.

### 5.3.3 Results and discussion

#### 5.3.3.1 Sealing process

The drying and the consequent stiction-induced sealing of the poly-SiC and microchannel was followed *in-situ* by optical microscopy. Images were acquired using a CCD camera connected to the microscope. The formation of interference fringes and discolorations resulting from the thinning of the water layer allowed observing the bending of the sealing wing and its adhesion to the Si surface.

Fig. 5.15 shows a sequence of optical microscope images of the sealing process of the microchannel device. The sequence illustrates the last part of the drying of the rinsing-water and the consequent self-sealing of the microchannel. It is possible to follow the sealing process by observing the changes in the interference fringes and in the coloration at the sealing wing. These are the result of the decrease in the thickness of the water layer and therefore of the decrease of the gap between the sealing wing and the Si surface. The first image of the sequence (Fig. 5.15 (a)) shows the instant when the rinsing water is present under the sealing wing and inside the microchannel, corresponding to the situation depicted in Fig. 5.14 (e).



Figure 5.15: Sequence of optical microscope images showing the stictioninduced sealing of the microchannel. The drying and consequent thickness decrease of the rinsing water drives the bending of the sealing wing toward the Si surface. Changes in the interference fringes and in the coloration at the sealing wing make this process visible (a) to (e). The complete adhesion of the sealing wing to the Si surface is suggested by its uniform dark-green coloration (f). The time elapsed between the first (a) and last (f) image is about 2 minutes.

Here interference fringes are clearly visible on the straight side of the sealing wing. A change of the interference fringes, suggesting a decrease in the thickness of the water layer, is visible in Fig. 5.15 (b). This may indicate an equalization of the water layer thickness along the sealing wing length. In these first two images the dark coloration of the round part of the sealing wing reveals the presence of a very thin water layer under it. Here the most external edge is darker than the rest suggesting that the layer of water there present is extremely thin, or that the edge is already into contact with the bottom Si surface. The coloration at the microchannel side is brighter and some fringes are visible, indicating that this area still did not adhere to the substrate. The elevated speed of the drying in the round side of the sealingwing made it difficult to capture the presence of larger fringes in that area. In Fig. 5.16 (c) and (d) the water layer under the sealing wing is already very thin and no fringes are visible. Here, the water film gives a dark-yellow coloration to the sealing wing. This coloration turns into dark-green as a consequence of a further decrease in the water film thickness. Fig. 5.15 (e) shows how the thinning of the water film proceeds. In this picture the front of the drying water inside the microchannel is also visible. Finally, in Fig. 5.15 (f) the lower part of the sealing wing has a dark uniform coloration suggesting the absence of water under it and therefore its complete adhesion to the Si surface. Compared to the device reported in [126] we did not observe any deformation of the top layer, which resulted in more robustness. This was due to the use of the anchoring pillars replacing the unanchored ones and the macropillar employed in [126].

# 5.3.3.2 Sealing wing adhesion

Once the sealing process was completed the microchannels were submitted to several tests to verify the adhesion of the sealing-wing, the formation of the channel and the effectiveness of the sealing.

The bending of the sealing wing was verified by measuring the out of plane height of the top-sealing layer by using a white light interferometry (WLI) microscope (Veeco Wyko NT3300). For improving the light reflection a 20 nm thin layer of gold was evaporated on top of the microchannel devices.



Figure 5.16: White light interferometer measurement of the rounded region of the sealing-wing. (left) Reconstructed 3D image showing the shape of the sealing-wing. (right) Graph showing the out of plane height measured along the white line in the 3D image. The gray rectangles indicate the averaging regions for the height measurements. The measurement show that the lower part of the sealing-wing is completely adhered to the bottom Si surface.

The profile measurement obtained by WLI microscopy (Fig. 5.16) demonstrates that the height difference between the lower part of the sealing wing and the Si surface is constant with an average value of 0.89  $\mu$ m. This value corresponds to the thickness of the sealing wing thus showing that its lower part is in complete contact with the Si substrate. The average height

difference between the Si surface and the top part of microchannel is 1.86  $\mu$ m corresponding to the sum of the sacrificial layer and the top layer thicknesses. This suggests that a non-collapsed ceiling and a proper flow-space are obtained.

High resolution SEM images of cross-sections of the device were acquired under various observation angles. This allowed verifying the bending and the adhesion of the sealing-wing, the formation of the channel, and the anchoring of the pillars. The microscope employed was a Scanning electron microscope (SEM) Philips XL50. In some cases a 20 nm thin layer of gold was evaporated to decrease charging effects and improve image quality.

The SEM image of Fig. 5.17 (a) shows a cross-section of the external edge of the sealing wing. This appears into contact with the Si surface.



Figure 5.17: 3D sketch of the microchannel device and related SEM crosssection images: (a) external edge of the sealing-wing adhered to the Si surface, (b) top-sealing layer with the embedded anchoring pillars. Here the invertedmushroom shape of the pillar and their setting into the Si-wafer is visible.

In this image particles are visible between the edge of the wing and the Si surface. These are gold agglomerates resulting from the evaporation made for improving the SEM imaging. The position of the particles also confirms the absence of a gap between the scaling wing and the Si surface. In the SEM cross-section of Fig. 5.17 (b) the anchoring of the inverted-mushroom pillars is shown. The image also shows the flow-space of the microchannel. These SEM images confirm the observations made on the optical (Fig. 5.15) and WLI microscope (Fig. 5.16).

#### 5.3.3.3 Effectiveness of the sealing

To verify the effectiveness of the sealing and the stability of the adhesion after a high temperature step, a 300-nm thick layer of low-stress silicon nitride (SiN<sub>x</sub>) was deposited on the tests microchannels fabricated with no inlet and outlet openings. The deposition was performed by LPCVD at a temperature of 760 °C and a pressure of 100 Pa. After this step the microchannels were first inspected by means of an optical microscope to verify their integrity. Afterward, SEM images of cross-sections were acquired to check for the presence of a deposited layer underneath the sealing-wing and/or inside the microchannel.

The SEM images of Fig. 5.18 show the cross-sections of the test devices after the deposition of the  $SiN_x$  layer at 760 °C. The sealing wing is still intact. The  $SiN_x$  layer is visible on top of the sealing wing whereas no deposition seems to be present underneath the sealing wing or inside the flow-space. Also, an accurate SEM inspection of these test devices did not show any crack. These results demonstrate that the adhesion of the sealing-wing is permanent and capable to withstand a high temperature thermal step.

To prove the effectiveness of the sealing we tested the leak tightness of the microchannels. First, a wetting (permeability) test was performed on all the devices presenting no defect at an optical microscope inspection. The test consisted in pouring ethanol on the top part of the microchannels. The seepage of ethanol into the channel would cause a visible color change, thus revealing the presence small cracks and/or defects in the top-sealing layer. During this test the devices were inspected using an optical microscope. No penetration of the ethanol into the channels, neither cracks were observed, indicating the integrity of the top-sealing layer and the complete adhesion of the sealing-wing.

Finally a helium (He) leak test was performed. A dedicated setup was built for this purpose (Fig. 5.19). The device under test was placed in a small vacuum chamber with its inlet and outlet pressed against to O-ring



Figure 5.18: SEM images of the cross-section of the sealing wing after the deposition of 300 nm of  $SiN_x$  by LPCVD. The images show the adhesion of the sealing wing at the external edge (a) and at the microchannel side (b). The  $SiN_x$  layer is visible above the sealing wing whereas no deposition is visible below the sealing wing or in the flow space of the microchannel.

seals. The He pressure at the inlet was set by means of a digital pressure controller (Bronkhorst EL-PRESS P-612CV). The chamber and the outlet were connected to a He leak detector (Leybold Inficon UL-200) consisting of a turbo molecular pump and a mass spectrometer. To test the device for leaks the outlet was kept closed. In this way a uniform pressure, equal to the one set by the pressure controller, was achieved along the microchannel. The leak rate could be monitored down to the system background leak ( $4.0 \times 10^{-9} \text{ Pa} \cdot \text{m}^3/\text{s}$ ). For this test pressures between 200 kPa and 600 kPa were applied, using increasing steps of 100 kPa.

The helium leak test revealed that these devices were also leak-tight down to the background leak of our setup recorded with a dummy device. The channels remained intact and leak tight up to 600 kPa. Pressures above this value caused bursting of the top layer above the inlet. However, the sealing wing remained always intact and adhered to the substrate, thus confirming its robustness.

To understand the failure mechanism of the top layer a finite-element simulation and stress analysis was performed using COMSOL Multiphysics software. The top layer at the inlet area was modelled as a square freestanding membrane with a lateral size of 160  $\mu$ m supported at the edges by



Figure 5.19: Schematic of the vacuum setup employed for the leak detection and flow-rate tests. The microchannel device is fixed into a vacuum chamber. The inlet is pressurized using helium and a pressure controller. Leaks can be detected by keeping the outlet closed and monitoring the He flow coming from the vacuum chamber. Flow rates can be determined by opening the valve at the reactor outlet.

pillars with a diameter of 5  $\mu$ m and a pitch of 20  $\mu$ m. An initial pre-stress of 0.3 GPa was included in the simulation. The deflection of the membrane and the first principal stress distribution for an applied pressure of 650 kPa are shown in Fig 5.20. Stress concentrations points occur at the junctions between the support pillars and the membrane, with values up to 16.8 GPa. This is in agreement with an analysis of similar microchannels made of SiN<sub>x</sub> [125]. Thin membranes of polycrystalline 3C-SiC characterized by bulge testing show fracture strengths between 3.2 GPa and 6.5 GPa [130]. The stress at the pillar junctions largely exceeds these values, thus explaining the rupture of the membrane.

#### 5.3.3.4 Flow and pressure tests

By using the same setup employed for the leak test, it was possible to measure the gas flow-rate into the microchannel as a function of the pressure. To do this the valve connecting the outlet of the microchannel to the leak detector was open. This allowed pumping the outlet down to 30 Pa (which is practically zero in this context). The He flow-rate at the mass spectrometer was recorded for pressures between 200 kPa and 600 kPa using steps of 100 kPa.

The flow rates recorded for six devices as a function of the applied pressure are plotted in Fig. 5.21. The data are compared to curves obtained from the analytical model [131–134]. To investigate the influence of the pillar sustaining structure on the microchannel flow, two different models were considered. In the first model the microchannel was approximated as a tube


Figure 5.20: Finite element analysis of the microchannel membrane located above the inlet aperture. The membrane is square with a lateral size of 160  $\mu$ m, the distance between two adjacent pillars is 20  $\mu$ m. The applied pressure is 650 kPa. (a) 3D view showing the deflection of the membrane. (b) Bottom view showing the first principal stress distribution. In the inset close up of the stress concentrations occurring at the junction between the pillars and the membrane.

of rectangular section with dimensions equal to those of the microchannel (5.4 mm  $\times$  0.43 mm  $\times$  0.001 mm). The theoretical flow rate obtained with this model was about twice the measured one. In the second model the microchannel was approximated as 22 parallel rectangular tubes. This is

the number of spaces between the pillar rows. Each channel had height and length equal to those of the microchannel. For the width we employed the distance between the edges of two adjacent pillars, that is 15  $\mu$ m. This second model gave a better fit of the experimental data, thus suggesting that the pillars significantly affect the conductance of the microchannel. This has to be taken into account in the design of microchannels using the proposed pillar array as sustaining structure.



Figure 5.21: Measured microchannel He flow-rates as a function of the pressure. The experimental data have been fitted using regression analysis. This result is compared with the theoretical flow-rates obtained by modeling the microchannel in two different ways. First, as a 5.4-mm-long rectangular tube with a height of 1  $\mu$ m and a width of 430  $\mu$ m. Second as 22 parallel rectangular tubes each with a length of 5.4 mm, a height of 1  $\mu$ m, and a width of 15  $\mu$ mm. The latter value corresponds to the distance between the walls of two adjacent pillars.

## 5.4 Conclusions

Poly-SiC layers were deposited by LPCVD employing  $SiH_2Cl_2$  and  $C_2H_2$  as precursor gases. The gas flows were varied to obtain six different poly-SiC layers. These were extensively characterized to assess their properties and to identify the most suited layer as alternative construction material for the microchannel of the nanoreactor. The chosen poly-SiC layer was successfully employed for the fabrication of surface micromachined channels. In addition, these were fabricated by using a new technique allowing for an improved sealing. The microchannels were tested for integrity, flow, and strength proving the effectiveness of the proposed sealing technique and the feasibility of microchannels made of poly-SiC. Therefore, the poly-SiC layer can be integrated in the fabrication of the microchannel of the nanoreactor either in the conventional process or in conjunction with the newly developed sealing technique.

In the next chapter we explore the use of SiC as alternative material for the microheater of the nanoreactor.

## CHAPTER 6

# LPCVD Poly-SiC:N for Nanoreactor microheaters

## 6.1 Introduction

In this chapter we present the LPCVD deposition and characterization of poly-SiC:N layers *in-situ* doped by the addition of  $NH_3$  to the gas mixture. By increasing the flow of the doping gas flow, six poly-SiC:N layer with decreasing resistivity were obtained. The chemical, mechanical and electrical properties of these layers were investigated to verify their suitability as heating and sensing material for high temperature microheaters.

The relation between the investigated properties were identified and correlated to the deposition parameters. A poly-SiC:N layer with low resistivity was selected and employed in the fabrication of SiC-based TEM microhot-plates. These devices were extensively tested to assess their performance and prove their suitability for operation in TEM at high temperatures. The causes of the poor stability of the resistance of the poly-SiC:N layers were identified and an annealing step implemented to overcome this problem. The annealed devices were found to be capable of operating in a stable way at temperatures up to 900 °C. The operation of the fabricated TEM microhotplate was demonstrated by *in-situ* observation of the melting and evaporation of gold nanoparticles in a TEM.

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## 6.2 Depositions and characterization of LPCVD poly-SiC:N layers

## 6.2.1 Deposition parameters

The nitrogen doped poly-SiC (poly-SiC:N) layers were deposited in the same hot-wall LPCVD furnace employed for the deposition of the a-SiC and the poly-SiC layers described in Chapter 4 and Chapter 5, respectively. Depositions were carried out on p-type Si wafers having a diameter of 100 mm a thickness of  $525 \pm 25 \ \mu m$  and (100) orientation. To allow subsequent characterization of the layers the depositions were performed on both bare and thermally oxidized wafers. The thickness of the SiO<sub>2</sub> layer was 200 nm. The poly-SiC:N layers were deposited at fixed temperature and pressure of 860 °C and 80 Pa, respectively. As for the undoped poly-SiC,  $\rm SiH_2Cl_2$  and  $C_2H_2$  diluted at 5% in  $H_2$  were employed as precursor gasses. Ammonia  $(NH_3)$  diluted at 5% in H<sub>2</sub> was added to achieve the *in-situ* doping of the layers. For all the depositions the flows of SiH<sub>2</sub>Cl<sub>2</sub> and dilute C<sub>2</sub>H<sub>2</sub> were kept constant at 320 and 80 sccm, respectively. The flow of dilute NH<sub>3</sub> was increased from 0 to 90 sccm with steps of 15 sccm to obtain one undoped reference layer and six layers containing an increasing concentration of doping atoms. The gas flows were selected taking into account the results obtained for the undoped poly-SiC layers (section 5.2) and the maximum gas flow allowed in the furnace (500 sccm @ 80 Pa). All the layers were deposited with a GFR of 5.0 as this value resulted in a poly-SiC very close to stoichiometry, i.e. layer I-3 (section 5.2.2.1). However, compared to the case of layer I-3 the flows were proportionally reduced to accommodate the doping gas while keeping the total gas flow below 500 sccm. Finally, the deposition times were tuned between 50 and 150 min to achieve layers with a thickness close to 600 nm for each gas combination. For some selected gas combinations additional longer depositions were performed to obtain layers with a thickness close to 1  $\mu$ m. These layers were employed to investigate possible thickness dependent variations in the stress as reported in [135], and in the resistivity. The precursors flows and the deposition times employed for the set of samples described above are reported in Table 6.1. In addition, in Table 6.2 we report the flows and the corresponding relative concentrations of the precursor, doping and dilution gasses. The relative concentrations are also plotted in Fig. 6.1 as a function of the  $NH_3$  flow. From this graph we see that as expected the  $\mathrm{NH}_3$  concentration increases. At the same time, the concentrations of SiH<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> decrease, and that of  $H_2$  increase. However, the decrease in the concentration of  $C_2H_2$  is very small due to the fact that this gas is highly diluted.

Layer ID	${{ m SiH}_2{ m Cl}_2}$ (sccm)	${f C_2 H_2}$ (5% in ${f H_2}$ ) (secm)	$\begin{array}{c} \mathrm{NH_3} \ (5\% \ \mathrm{in} \ \mathrm{H_2}) \\ (\mathrm{secm}) \end{array}$	$\begin{array}{c} {\rm Total \ gas \ flow} \\ {\rm (sccm)} \end{array}$	Deposition time (min)
D-0	80	320	0	400	120
D-1	80	320	15	415	80
D-2	80	320	30	430	75
D-3	80	320	45	445	75
D-4	80	320	60	460	75
D-5	80	320	75	475	75
D-6	80	320	90	490	70
D-2-2	80	320	30	430	120
D-4-2	80	320	60	460	120
D-5-2	80	320	75	475	120
D-6-2	80	320	90	490	115

Table 6.1: Gas flows and deposition times employed for the LPCVD deposition of the reference poly-SiC and of the poly-SiC:N layers. The layer identifier is reported in the first column.

Table 6.2: Flows of the precursor, doping, and dilution gasses employed in the deposition of the reference poly-SiC and the poly-SiC:N layers. The relative concentration of each gas in the total gas mixture is also indicated. In the last column is reported the total gas flow injected in the tube.

Layer ID	$SiH_2Cl_2$ (sccm) - (%)	$C_2H_2$ (sccm) - (%)	NH <sub>3</sub> (sccm) - (%)	H <sub>2</sub> (sccm) - (%)	Total (sccm)
D-0	80 - 20.00	16 - 4.00	0.00 - 0.00	304.00 - 76.00	400
D-1	80 - 19.27	16 - 3.86	0.75 - 0.18	318.25 - 76.69	415
D-2	80 - 18.60	16 - 3.72	1.50 - 0.35	332.50 - 77.33	430
D-3	80 - 17.98	16 - 3.59	2.25 - 0.51	346.75 - 77.92	445
D-4	80 - 17.39	16 - 3.48	3.00 - 0.65	361.00 - 78.48	460
D-5	80 - 16.84	16 - 3.37	3.75 - 0.79	375.25 - 79.00	475
D-6	80 - 16.33	16 - 3.26	4.50 - 0.92	389.50 - 79.49	490



Figure 6.1: Variation in the concentrations of precursor, doping and dilution gases as a function of the  $\rm NH_3$  flow for the reference poly-SiC and the poly-SiC:N layers.

## 6.2.2 Characterization

The deposited poly-SiC:N layers were characterized using various techniques described in section 3.2. The results obtained from each of the characterizations performed are reported and discussed in the following subsections. This analysis allowed the identification of the most favorable deposition conditions for obtaining a poly-SiC:N layer suitable as the fabrication material for microheaters.

#### 6.2.2.1 Chemical composition

The chemical composition of the reference poly-SiC layer and the six poly-SiC:N layers was obtained by EBS (section 3.2.1.1). The EBS analysis reveals that all the layers are composed by Si, C and N, except for the reference layer (D-0) which as expected does not contain a detectable amount N (there is however some N due to the unintentional doping as discussed in section 5.2.2.6). The relative concentrations of these elements for each of the seven samples is reported in Table 6.3 and plotted in Fig. 6.2. As expected the reference poly-SiC layer (D-0) is very close to stoichiometry (slightly carbon-rich) as it is the layer I-3 deposited with the same *GFR* analyzed in Chapter 5 (Table 5.3). The poly-SiC:N layers (D-1 to D-6) are instead slightly silicon-rich with a Si to C ratio that increases with the NH<sub>3</sub> flow. As this increases we observe a progressive increase in the concentration of N and a decrease in the concentration of C, while the concentration

Table 6.3: Relative molar concentrations of the elements present in the reference poly-SiC and the six poly-SiC:N layers determined by EBS. In the last three columns the ratios between the concentrations of Si, C and N are also reported.

Layer ID	Si (%)	C (%)	N (%)	$^{Si/C}$	N/Si	N/C
D-0	49.70	50.30	0.00	0.988	0	0
D-1	50.54	49.13	0.33	1.029	0.0065	0.0067
D-2	50.97	48.06	0.96	1.060	0.0189	0.0200
D-3	50.74	47.90	1.36	1.059	0.0268	0.0284
D-4	50.18	47.70	2.12	1.052	0.0422	0.0444
D-5	50.15	47.16	2.69	1.063	0.0536	0.0570
D-6	50.06	46.31	3.63	1.081	0.0726	0.0785

of Si remains almost constant. Therefore, the inclusion of N atoms appears to happen at expenses of C atoms as also suggested in [136]. The increase in the concentration of N with the  $\rm NH_3$  flow appears to be quadratic as revealed by the good fitting of the  $2^{nd}$  order polynomial curve included in Fig. 6.2.



Figure 6.2: Relative concentrations of silicon (Si), carbon (C) and nitrogen (N) contained in the reference poly-SiC and in the six poly-SiC:N layers as a function of the  $NH_3$  flow. The concentration of C decreases while the one of Si remains almost constant. The increase in the concentration of N is well fitted by a quadratic curve.

## 6.2.2.2 Surface morphology

As for the poly-SiC layers, the surface morphology of the poly-SiC:N layers was studied by combining high resolution SEM images and AFM scans. These techniques are described in detail in sections 3.2.2.1 and 3.2.2.2, respectively. Here below some information on the acquisition of these data are first given, then the results are presented and analyzed for both techniques.

High resolution SEM (HR-SEM) images of the top view and of 45° tilted view of the surface of the SiC layers were acquired at two different magnifications corresponding to a horizontal field of view (HFV) of 2  $\mu m$ and 1  $\mu$ m. The SEM images allowed for both qualitative and quantitative analysis of the surface morphology. In particular a quantitative estimation of the size of the horizontal section of the grains was obtained through the use of a specific image processing and analysis software (section 3.2.2.1). Compared to the poly-SiC case the data analysis procedure resulted more difficult as the identification of the apex of the grains was more problematic. This was due to the more rounded shape of the grains and to the lower resolution and contrast of the HR-SEM images. As these samples should be more electrically conductive compared to the undoped ones the loss of contrast and resolution should not result from electron charging effects but from changes in the way the probing electrons distribute and diffuse into the sample. This suggests a different crystalline structure of the poly-SiC:N layers compared to that of the poly-SiC.

The AFM scans were performed on  $2 \times 2 \ \mu m$  surface area. As for the set of undoped poly-SiC samples analyzed in Chapter 5, DCP20 probes equipped with a diamond coated silicon tip with a curvature radius of 70 nm were employed. From the analysis of the AFM scans, amplitude parameters of the surface were obtained (section 3.2.2.2).

The HR-SEM images showing the surface of the reference poly-SiC (D-0) and those of the poly-SiC:N layers (D-1 to D-6) are combined in Figure 6.3. The top views were acquired with a HFV of 2  $\mu$ m and 1  $\mu$ m, while the 45° tilted view was acquired with a HFV of 2  $\mu$ m. As expected, all layers present a polycrystalline structure. The surface morphology of sample D-0 appears very similar to that of sample I-3 deposited using the same *GFR*. Also, as discussed above these two samples are very close in composition. However, the grain analysis and reveals a grain size of about 120 nm for sample D-0 opposed to the 95 nm obtained for sample I-3. Moreover, the surface of this sample is extremely rough with an  $S_Q$  of 36.7 nm opposed to the 24.6 nm obtained for sample I-3. Differences in the growth dynamics might explain the morphological differences between samples D-0 and I-3. A possible cause can be the difference in the speed of the gasses in the reac-

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Figure 6.3: High resolution SEM images of the surface of the reference poly-SiC and of the six the poly-SiC:N layers. For each layer two different magnifications corresponding to HFWs of 2 and 1  $\mu$ m are shown. A 45° tilted view for the HFV of 2  $\mu$ m is also included.

tor tube (see section 3.1.1). Both layer are deposited at the same pressure P = 80 Pa while the total gas flow injected in the tube is different, that is 500 sccm and 400 sccm for sample I-3 and D-0, respectively. Therefore, the

Table 6.4: Data obtained from the grain analysis made on the HR-SEM images and from the analysis of the AFM scans for each of the six poly-SiC:N layers and for the reference poly-SiC layer. In the table are reported: the average projected area of the grains  $G_{A_{av}}$ , the average grain width  $G_{W_{av}}$ , the max peak height  $Z_{MAX}$ , the average surface height  $Z_A$ , the RMS surface roughness  $S_Q$ , and the maximum height of the average profile  $S_Z$ .

Layer ID	NH <sub>3</sub> (sccm)	$G_{A_{av}}$ (nm <sup>2</sup> )	$G_{W_{av}}$ $(nm^2)$	$Z_{MAX}$ (nm)	$Z_A$ (nm)	$S_Q$ (nm)	$S_Z$ (nm)
D-0	0.0	8064	120.2	263.4	124.4	36.7	$156\pm5$
D-1	0.75	16996	147.1	152.4	72.2	22.2	$97\pm5$
D-2	1.5	18140	151.9	109.2	46.6	15.0	$67\pm5$
D-3	2.25	17181	147.9	109.8	43.3	15.1	$65\pm5$
D-4	3.0	14965	138.0	99.1	45.8	12.8	$63 \pm 5$
D-5	3.75	15094	138.6	76.7	35.6	11.5	$51\pm5$
D-6	4.5	22274	119.3	113.9	70.2	16.5	$86~\pm~5$

speed of the gasses is higher during the deposition of sample I-3. As later shown in section 6.2.2.4, the difference in the growth dynamics is also highlighted by the different growth rates which are 4.6 nm/min and 5.5 nm/min for I-3 and D-0, respectively.

The addition of NH<sub>3</sub> causes a dramatic change of the surface morphology. The surface of the doped samples appears smoother compared to that of the undoped reference sample. This observation is confirmed by the results of the analysis of the AFM scans reported in Table 6.4. The RMS surface roughness  $S_Q$ , suddenly decreases upon the addition of  $NH_3$  going from 36.7 nm to 22.2 nm for samples D-0 and D-1, respectively. In addition, the grains of the doped samples show rounded edges and have a not well defined shape. This could be the result of the clustering of grains with different orientation and size. Alternatively, a change in the growth mode from columnar to granular might explain this phenomena, a TEM crosssection would be required to verify this hypothesis. Moreover, the grains of the poly-SiC:N layers have a larger average width compared to those of the reference undoped sample (see Table 6.4). This value only slightly changes with the increase of the NH<sub>3</sub> flow, clearly decreasing only for the sample deposited with the highest doping flow. Finally, AFM measurements show a progressive decrease in the surface roughness with the increase of the NH<sub>3</sub> flow. However, for the sample deposited with the highest doping flow an abrupt increase in the surface roughness is measured.

#### 6.2.2.3 Polycrystalline structure

The crystallographic structure of the reference poly-SiC and of the poly-SiC:N layers was investigated by XRD (section 3.2.1.2). The analysis of the XRD spectra shown in Fig. 6.5 reveals that all the layers have a 3C-type crystallographic structure. The typical peaks of the 3C-SiC polytype are in fact present in all the spectra as indicated by the stick pattern superimposed to the XRD spectra of Fig. 6.4. For samples D-0 and D-1 the most intense peak is positioned at  $2\theta = 35.6^{\circ}$  and corresponds to the 3C-SiC crystallographic planes with {111} orientation. This indicates that {111} is the preferred orientation of the atomic planes of the grains of these layers. Sample D-0 shows peaks with medium intensity corresponding to  $\{220\}$  and  $\{311\}$  3C-SiC crystallographic planes at  $2\theta = 60^{\circ}$  and  $2\theta = 71.8^{\circ}$ , respectively. The relative intensity of these last two peaks increases with the NH<sub>3</sub> flow. Already for sample D-2 the peak intensity of {111}, {220} and {311} planes becomes comparable. Also, the addition of NH<sub>3</sub> results in a sudden increase of the intensity of the peak corresponding to the {200} planes  $(2\theta \approx 41^{\circ})$ . This peak is instead extremely weak for sample D-0. Besides the main 3C-SiC features, all the samples show a small peak at  $2\theta \approx 34^{\circ}$  and a very broad peak positioned at  $2\theta \approx 56^{\circ}$ . The relative intensity of these secondary peaks increases with the  $NH_3$  flow, thus suggesting an increase in the number of atomic planes related to them. As already suggested in section 5.2.2.3, these peaks might indicate the existence of the 24-R-SiC crystalline structure or might be related to the Si in excess present in the samples or both. The large width of the peak at  $2\theta \approx 56^{\circ}$  indicates that these atoms are arranged in a very disordered fashion or that they have a short length order. Therefore, the excess Si atoms can be located at the grain boundaries might be at the origin of this peak.

For the quantitative analysis, the intensity I of the peak corresponding to 111 planes is compared to that of 220, 311, and 200. The ratios  $I_{(111)}/I_{(220)}$ ,  $I_{(111)}/I_{(311)}$  and  $I_{(111)}/I_{(200)}$  are reported in Table 6.5. These values confirm that {111} is the preferred orientation for the atomic planes of the reference poly-SiC layer. However, as also hinted by the HR-SEM images, the addition of the doping gas induces a modification of the grain structure. The intensity of the peaks corresponding to {220}, {311} and {200} orientations drastically increases becoming comparable to that of {111}. The peak intensity ratios reach the lowest values when the NH<sub>3</sub> flow is set to 3.0 sccm (sample D-4). For higher NH<sub>3</sub> flows a small increase is recorded. The equalization of the peak intensities reveals a drastic change in the orientation of the crystallographic planes of the grains. In Table 6.5 is reported the FWHM of these peaks. The FWHM of peak {111} largely



Figure 6.4: XRD spectra of the reference poly-SiC and the doped poly-SiC:N layers. The stick pattern of 3C-SiC is superimposed indicating the expected positioning of the main peaks.

increases upon the addition of the doping gas. Another significant increase is observed when the  $NH_3$  flow is set from 3.0 to 3.75 sccm. The addition of the doping gas also causes a significant decrease of the FWHM of peak {220}. The FWHM of the peak {311} instead increases more progressively. The increase in the peak width might indicate an increase in the crystalline disorder meaning a distorted atomic arrangement inside the crystals due to local defects. Therefore, in this case the broadening of the peaks could be attributed to the inclusion of N atoms in the atomic network thus explaining its distortion or rearrangement. If instead the increase in peak width is interpreted as an indication of a shorter length order (meaning that the crystals composing the grains are smaller) then the addition of N would cause a modified growth of the SiC crystals. In any case the correlation between the XRD spectra and the HR-SEM images is clear. The change in the surface morphology visible when passing from undoped to doped samples suggests

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modifications in the crystallographic organization as also confirmed by the XRD results.

#### 6.2.2.4 Thickness, uniformity and growth rate

As already pointed out in section 5.2.2.4 an accurate determination of the thickness of the layers, and its average value across the wafer is important as these data are required for the extraction of many of the properties of interest. The thicknesses of the reference poly-SiC layer and of the poly-SiC:N layers were measured by optical reflectometry, and mechanical profilometry. The values obtained were corrected by applying the same procedure employed for the poly-SiC layers and described in section 5.2.2.4.

The thickness measured by optical reflectometry in the center of the wafer  $t_{r-c}$ , and the average thickness across the wafer  $t_{r-av}$  are reported in Table 6.6. For the poly-SiC:N layers the relative standard deviation ranges roughly between 1% and 2% indicating that the film deposition is very uniform. The good uniformity was also hinted by the uniform color of the layers. The poly-SiC:N layers are more uniform compared to the reference poly-SiC layer and to the poly-SiC layers analyzed in Chapter 5. The improved uniformity resulting from the addition of NH<sub>3</sub>, is probably due to modifications in the growth mechanisms. This observation is also supported by the abrupt increase in the average growth-rate  $(GR_{av})$  which is observed upon the addition of  $NH_3$ . The  $GR_{av}$ , obtained by dividing  $t_{r-av-cor}$  by the corresponding deposition times for each layer is reported in Table 6.7 and plotted in Figure 6.5. This value increases from about 5.4 to about 8.0 nm/min upon the addition of  $NH_3$  showing no significant variations as the NH<sub>3</sub> flow is further increased. For the reference poly-SiC layer and the first three poly-SiC:N layers the difference between corrected center thickness  $t_{p-c-cor}$  and  $t_{r-c}$  is reasonably small (< 25 nm). However, this difference becomes significant (>125 nm) for the last three layers. This is a consequence of the higher concentration of N present in these layers which contributes to the modifications of the optical constants.

In Table 6.6 we also report the measured thicknesses of four additional layers. These were deposited using the same deposition parameters as those of D-2, D-4, D-5 and D-6 but using a longer deposition times to obtain layers with a thicknesses close to 1  $\mu$ m. Due to the absence of AFM scans and thus of the surface amplitude data necessary to perform the corrections on the thicknesses of these layers,  $t_{r-av-cor}$  and  $t_{p-c-cor}$  were estimated by means of correction factors. These were calculated from the thickness data of the corresponding thinner layers. For example,  $t_{p-c-cor}$  was estimated by multiplying the non-corrected values by correction factors calculated as

Layer ID	NH <sub>3</sub> (sccm)	$I_{\{111\}}/I_{\{220\}}$	$I_{\{111\}}/I_{\{311\}}$	$I_{\{111\}}/I_{\{200\}}$	FWHM {111}	FWHM {220}	FWHM {311}	FWHM {200}
D-0	0	24.47	26.59	222.24	0.445	1.211	0.777	-
D-1	0.75	2.16	3.12	7.66	0.664	0.816	0.816	0.428
D-2	1.5	1.70	2.26	3.92	0.737	0.817	1.011	0.996
D-3	2.25	1.40	1.77	2.41	0.772	0.813	1.075	1.010
D-4	3.0	1.30	1.57	2.00	0.800	0.817	1.046	0.908
D-5	3.75	1.43	1.81	2.96	0.923	0.848	1.048	1.201
D-6	4.5	1.54	1.87	3.03	0.983	0.818	1.048	1.197

Table 6.5: Intensities of the peaks corresponding to  $\{220\}$ ,  $\{311\}$  and  $\{200\}$  crystallographic planes relative to that of the peak corresponding to  $\{100\}$  planes. The FWHM of these peaks are reported in the last four columns.

Table 6.6: Thickness data determined by optical reflectometry and profilometry measurements for the reference poly-SiC layer and the poly-SiC:N layers. The corrected values for the center and for the average thicknesses are reported in the last two columns.

Layer ID	$t_{r-av}$ (nm)	$SD_r$ (nm)	$SD_{r-rel}$ (%)	$t_{r-c}$ (nm)	$t_{p-c}$ (nm)	$t_{p-c-cor}$ (nm)	t <sub>r-av-cor</sub> (nm)
D-0	626	33	5.2	592	647	$615\pm5$	$650\pm33$
D-1	668	14	2.1	659	657	$632\pm5$	$640 \pm 13$
D-2	631	10	1.6	623	618	$597\pm5$	$605 \pm 10$
D-3	631	8	1.3	624	625	$603\pm5$	$610 \pm 8$
D-4	740	12	1.6	727	617	$600\pm5$	$612\pm10$
D-5	737	8	1.1	730	604	$589\pm5$	$594~{\pm}~7$
D-6	686	8	1.2	679	566	$550\pm5$	$556\pm7$
D-2-2	1014	16	1.6	999	983	$958\pm5$	$972 \pm 16$
D-4-2	1106	12	1.1	1097	960	$905\pm5$	$912 \pm 12$
D-5-2	1167	15	1.3	1142	932	$921\pm5$	$941 \pm 15$
D-6-2	1050	13	1.1	1138	924	$840\pm5$	$851 \pm 13$

Table 6.7: Table reporting the average growth rate and the stress and the resistivity obtained for the reference poly-SiC and the poly-SiC:N layers.

Layer ID	NH <sub>3</sub> (sccm)	$GR_{av}$ (nm/min)	$\sigma_{r-av}$ (GPa)	$ ho  imes 10^{-3} \ (\Omega \cdot cm)$
D-0	0	5.4	0	3422
D-1	0.75	8.0	320	68.08
D-2	1.5	8.1	437	20.56
D-3	2.25	8.1	547	9.92
D-4	3.0	8.2	596	4.99
D-5	3.75	7.9	570	3.86
D-6	4.0	7.9	471	3.49
D-2-2	1.5	8.1	436	14.27
D-4-2	3.0	7.6	679	3.73
D-5-2	3.75	7.8	729	2.74
D-6-2	4.0	7.4	621	2.48

the ratio  $t_{p-c-cor}/t_{p-c}$  for each of the corresponding thinner layers. The average growth rate of these layers is reported in Table 6.7 and plotted in Figure 6.5.



Figure 6.5: Variation of the average growth rate and the average residual stress of the poly-SiC:N layers as a function of the  $NH_3$  flow. The plotted data refers to layers with a thickness of 0.6  $\mu$ m and 1  $\mu$ m. The values corresponding to the reference poly-SiC layer of are also plotted. Lines are drawn to guide the eye.

#### 6.2.2.5 Residual stress

The average residual stress  $(\sigma_{r-av})$  of the reference poly-SiC and of the six poly-SiC:N layers was obtained by using the wafer curvature measurement method (see section 3.2.4.1). The thickness of the layers employed in the calculation of  $\sigma_{r-av}$  was  $t_{r-av-cor}$ . The calculated residual stress is reported in Table 6.7 and plotted in Figure 6.5 as a function of *GFR*.

The residual stress of the reference layer D-0 was not measurable as its value was lower than  $\pm 2.2$  MPa . This is the minimum stress measurable with our setup for a layer of 600 nm. The obtained residual stress is different from the one obtained for layer I-3 deposited with the same *GFR* and analyzed in Chapter 5. For this a tensile stress of 0.28 GPa was obtained. We already pointed out that the growth-rate of these two layers is different, that is about 5.7 nm/min for the first and about 4.6 nm/min for the latter. We attributed this to differences in the growth kinetics due to a different dynamic of the gasses in the LPVCD reactor (section 6.2.2.2). On the other hand layers D-0 and I-4 despite having a slightly different stoichiometry and showing a different XRD pattern, they have very similar surface morphology and grain size. Therefore, it might not be a coincidence that these two layers have also similar values for the residual stress. This reinforces what already suggested in section 5.2.2.5 to explain the variation of the stress of the poly-SiC layers with the *GFR*, i.e. the residual stress strongly

depends on the grain structure. Upon the addition of  $NH_3$  the stress suddenly increases. For the poly-SiC:N layer deposited with the lowest  $NH_3$ flow the measured stress is tensile with a value of 0.32 GPa. This value slightly increases almost linearly with the  $NH_3$  flow. The stress reaches its maximum value of 0.57 GPa when the  $NH_3$  flow is set to 3.75 sccm. By further increasing this flow the stress slightly decreases to 0.47 GPa. The sudden change in the stress observed upon the addition of the doping gas is coherent with the morphology change observed in the HR-SEM images and confirmed by the XRD analysis. In a similar way the increase in the stress with the  $NH_3$  flow can be correlated to the crystallographic changes revealed by the XRD analysis. Finally, at the highest  $NH_3$  flows the higher the thickness the higher stress. This suggests the presence of stress gradient as reported for similar layers in [137]. This aspect has not been investigated in this thesis.

#### 6.2.2.6 Electrical resistivity

The sheet resistance  $R_S$  of the reference poly-SiC and the six poly-SiC:N layers was measured using the four-probe system described in section 3.2.4.3. Measurements were carried out in the center of the wafer, and for the doped layers, also in several points on the wafer surface. The center resistivity was then calculated for each layer as  $\rho = R_{S-c}/t_{p-c-cor}$ . These values are reported in Table 6.7 and plotted in Figure 6.6 as a function of the NH<sub>3</sub> flow. The corresponding conductivity values were also calculated and plotted in the same graph.

The reference poly-SiC layer has a resistivity of about 3.7  $\Omega \cdot cm$ . As for the residual stress this value is closer to that of sample I-4 rather than to that of sample I-3. Again these two layers have similar grain size. This is reasonable as the resistivity of a polycrystalline material strongly depends on the density of grain boundaries and therefore on the size of the grains. The addition of the doping gas causes a drastic decrease of the resistivity. For sample D-1 a value of  $70 \times 10^{-3} \Omega \cdot cm$  is measured. As the NH<sub>3</sub> flow is increased, the resistivity further decreases. For the sample deposited with the highest NH<sub>3</sub> flow, a value of  $3.6 \times 10^{-3} \Omega \cdot cm$  is obtained. It is interesting to note how the decrease in resistivity tends to saturate, thus indicating a saturation of the electrically active dopant atoms. Similar results have been reported [136] and [138]. The layers with a thickness of 1  $\mu$ m show an additional decrease in the resistivity of about 15 % compared to the thinner corresponding layer. This decrease, as suggested by the characterization results later discussed in this chapter, is probably due to the longer time spent in the LPCVD furnace causing a larger number of dopants to become active. The uniformity of the measured sheet resistance improved with the increase of the  $\rm NH_3$  flow and slightly worsened as the thickness increased. For example the standard deviation of the sheet resistance of layer D-2 was 8.2 %, this decreased to about 5.0 % for layer D-4 and finally to about 1.1 % for layer D-6. For the thicker layers these values increased to 9.3 %, 5.4 %, and 1.7%, respectively.



Figure 6.6: Variation of center resistivity and conductivity of the poly-SiC:N layers as a function of the NH<sub>3</sub> flow. The plotted data refers to layers with a thickness of 0.6  $\mu$ m and 1  $\mu$ m. The values corresponding to the reference poly-SiC layer are also plotted. A logarithmic scaling is applied to the vertical axes.

To assess the possibility of using the poly-SiC:N layers as a sensor, the variation of its resistance was measured as a function of the temperature by using a dedicated setup. This is shown in Fig. 6.7. It consists of a vacuum chamber connected to a turbomolecular pump and enclosing a high-temperature measurement stage. This is composed by an aluminum nitride heating-chuck and four spring-loaded probes isolated by a quartz perforated plate. The chuck is heated by flowing through it a current provided by a digital current source. The temperature of the chuck is monitored by means of a thermocouple attached to it. The probes are connected to a digital current source and to a digital multimeter enabling the measurement of the resistance of a layer in a 4-points (van der Pauw) configuration. The digital current sources, the multimeter, and the thermocouple are controlled by means of a LabVIEW script running on a PC. This implements a closed loop control on the temperature during the heating up and cooling down

6.2 Depositions and characterization of LPCVD poly-SiC:N layers 153



Figure 6.7: (a) Setup employed for measuring the poly-SiC:N layers resistance as a function of the temperature. (b) High temperature measurement stage. (c) Glowing of the heating-chuck and of the poly-SiC:N samples during a measurement at 700 °C, the probes positioned on the sample and set in place by the perforated quartz plate are also visible.

cycles. Also it records and displays the measured data.

For the measurement the probes are pressed against the surface of a square-shaped sample. A small probing current  $I_p$  is forced into two neighboring probes, while the voltage drop across the other two probes  $V_m$  is monitored as the temperature changes. The sheet resistance, measured as a function of the temperature, is given by:

$$R_S(T) = G \times \frac{V_m(T)}{I_p} \tag{6.1}$$

where G is a geometrical correction factor that varies from sample to sample due to the not perfect positioning of the probes. The correction factor G can be obtained by measuring independently the RS (20°C) with a standard 4-points system, such as the one described in section 3.2.4.3.

The measurements were performed on the poly-SiC:N layers deposited on the thermal oxide. Square shaped samples with a 2 cm side were glued to the heating chuck by using silver paste, to ensure a good thermal contact. For our samples, correction factors G with values comprised between 5.2 and 6.5 were obtained. The measurements were performed from 20 to 700 °C and then back to 20 °C, with a heating up and cooling down rate of 5 min/°C. A hold-time of 5 minutes was set for the highest temperature. The measured resistance values were normalized to the resistance measured at 20°C and fitted with a second order polynomial equation. In this way a temperature-resistance conversion function  $C_{R-T}(T)$  was obtained. This function expresses the relative change of the resistance as a function of the temperature. Consequently, the sheet resistance or resistivity of a layer at any given temperature can be calculated as follow:

$$R_S(T) = R_S(20^\circ C) \times C_{R-T}(T) \tag{6.2}$$

$$\rho(T) = \rho(20^{\circ}C) \times C_{R-T}(T) \tag{6.3}$$

The acquired data are plotted in Fig. 6.8 together with the corresponding fitted  $C_{R-T}(T)$  functions. For all the tested samples, the resistivity decreases as the temperature increases. The temperature coefficient of resistance (TCR) is therefore negative (NTC). The lower the resistivity at room temperature, the larger the decrease and the worst its linearity. For example at 700 °C the resistivity decrease for the poly-SiC:N layer with the highest doping, is about 30%, while for the layer with the lowest doping the decreases is about 55%. Similar results for poly-SiC:N layers deposited using same precursors and a similar LPCVD system are reported in [139]. The same applies to LPCVD poly-SiC:N layers deposited using different precursors [140]. It is known that due to the presence of grains the electrical properties of polycrystalline materials are different from their monocrystalline counterpart. Typically, the high density of defects present at the grain boundaries acts as trapping centers for free carries. The trapped charges give rise to depletion regions of opposites sign in the grains thus creating a potential barrier impeding the movement from grain to grain of the remaining free carries. As the temperature rises, the thermionic emission through the barrier increases thus causing a decrease of the resistivity. As reported in [140] for similar poly-SiC:N layers, the lower the doping the higher the barrier height and the stronger the negative dependence with the temperature. Alternatively the lower the barrier the less the sensitivity to the thermionic emission and thus the change of the resistance with the temperature.

The measurement of our samples presented several problems especially at the highest temperatures. In most of the cases the measurement became noisy with sudden changes in the resistance values. Also, in some cases the contact was lost before reaching the highest temperature or during the cooling down sweep, thus impeding the data acquisition. For the samples that did not suffer from this problem, the data relative to the cooling down sweep laid below those acquired in the heating up. In many cases the difference decreased as the temperature decreases. The origin of these problems was not clear at the moment of the measurement. However, the poor contact between probes and the poly-SiC:N layers at high temperatures was suspected as the cause. More insight on this matter was given by the measurements performed at high temperature on the devices fabricated using the poly-SiC:N layer as heating material.



Figure 6.8: Variation of the normalized resistivity of poly-SiC:N layers having different resistivity. The resistivity decreases as the temperature increases. The higher the resistivity the larger the decrease. The measurement is noisy at high temperature and differences between the forward and backward temperature sweeps are visible. The resistivity decrease is well fitted by a second order polynomial curve.

## 6.2.3 Poly-SiC:N layer choice

For the microheater a low resistivity material is preferred as this allows for flexibility in the design of the microheater. Layers D-4, D-5 and D-6 and the corresponding thicker layers are the most suited in this respect. They also all have comparable surface roughness, very similar polycrystalline structure and stoichiometry. The residual stress of these layers is medium-high. However, as the layer does not need to be employed as a continuous freestanding structure, these values of residual stress are acceptable. Moreover, layer D-6 has the lowest resistivity and a residual stress lower than that of D-4 and D-5. Therefore, this can be considered as the best candidate to be employed as conductive layer of the microheater.

## 6.3 SiC TEM microhotplate

A poly-SiC:N layer with low resistivity was integrated in the fabrication process of a SiC-based TEM microhotplate. This device was realized using one of the poly-SiC layers characterized in Chapter 5 as structural material. Also, the selected a-SiC layer described in Chapter 4 was integrated in the process to realize electron transparent windows. This device was fabricated to verify the suitability of the poly-SiC:N as heating material and asses its performance. At the same, the SiC-based TEM microhotplate allowed to test the integration of all the developed SiC layers as a first step toward the realization of a full SiC nanoreactor described in Chapter 7.

## 6.3.1 Design

The TEM microhotplate consists of a suspended membrane integrating an array of electron transparent windows and a resistive microheater in its center (Fig. 6.9). The membrane is square-shaped with a side length of 1 mm and clamped to a Si chip having a width of 3.3 mm and a length of 10 mm. These dimensions, the positioning of the membrane on the chip, and the arrangement of the microheater wiring were selected to match the layout of the nanoreactor, so to be able to test the microhotplate using the available TEM holders and electronics.

A continuous membrane design was chosen to ensure robustness and to resemble the nanoreactor design. The support-membrane had a thickness of 2  $\mu$ m, achieved by stacking a 1  $\mu$ m thick poly-SiC layer on top of a 1  $\mu$ m thick SiO<sub>2</sub> layer. Both layers had a structural role, with the latter working also as clamping structure for the window (section 6.3.2). Although a thickness of about 300 nm would have been already enough to perform this task. a thicker layer was chosen to increase the strength of the support-membrane without causing excessive power loss. The thermal conductivity of SiO<sub>2</sub> is in fact lower than that of SiC. Also, this layer stack resembled that of the nanoreactor. A 3D sketch of the TEM microhotplate is shown in Fig. 6.9. An array of 126 freestanding electron transparent windows is arranged in six parallel rows in the central part of the membrane. The a-SiC<sub>x</sub> windows are circular with a diameter of 4  $\mu$ m and a thickness of 20 nm. The resistive microheater consists of a poly-SiC:N wire with a meander geometry winding between the window rows. The microheater occupies a square shaped area with a side length of only 0.3 mm in the central part of the supportmembrane. Positioning the microheater far from the Si edges provides good thermal isolation and thus low power dissipation. As explained in section 2.3.3 the power dissipated by the microheater should be kept as low as possible to minimize the image drift in TEM. To ensure electrical isolation a 500 nm thick layer of LPCVD TEOS is interposed between the microheater wire and the support-membrane. This intermediate layer also works as mechanical matching element between the microheater and the membrane, which are made of layers having different stress values. The microheater is connected in four points (A,B,C, and D in Fig. 6.9) to poly-SiC:N wires running diagonally on the support-membrane and extending on the Si substrate. The symmetrical design of the connecting wires was chosen to allow for mechanical strength. Also, the arrangement of the connection points was designed to perform accurate electrical measurements. The connecting wires attached at the points A and D of the microheater (see Fig. 6.9) are employed to provide the driving current. The other two wires attached at points B and C are instead used to perform a high impedance voltage measurement. Sensing of the voltage drop of the microheater only between points B and C is advantageous as the coldest part of the microheater wire, i.e. segments AB and CD, are excluded from the measurement. This enables for an accurate calculation of the temperature in the windows area which is very important for TEM experiments.



Figure 6.9: 3D sketch of the TEM microhotplate showing the arrangement of windows and of the poly-SiC:N wire on the membrane. The microheater is located at the center of the membrane and is connected by the power and sense contact-wires to the on-chip metallized wires. The driving current is flown through the power contact-wires while the resistance between the points B and C is measured by reading the voltage drop at the sense contactwires.

For the same reason the microheater wire should be designed to obtain a temperature which is as uniform as possible between the measuring points. In general, a uniform temperature distribution in a reduced area can be achieved by properly dimensioning and arranging the microheater wire on the membrane. This typically requires very long wires with variable width arranged in a double spiral or meander geometry [141–143]. These designs are feasible when a metal is employed as wire material. The low resistivity of the metal allows to properly dimension and arrange the microheater wire to obtain the required temperature uniformity and at the same time to keep the resistance of the microheater to a reasonably small value. This is a problem when using poly-SiC:N layers, as these have a resistivity which is about three orders of magnitude higher than that of a metal. Long wires would therefore result in microheaters with very high resistance, requiring the power supply electronics to work at very high voltages. The electronic control system of the nanoreactor (section 2.2.1) can deliver a max current of 20 mA with a max voltage drop of 6.5 V across the microheater powering terminals, hence a max power of 130 mW. The metal (Pt) microheater of the nanoreactor consumes about 30 mW at 500 °C [36]. To be able to deliver at least the same power without exceeding the maximum available voltage, the total resistance of the poly-SiC:N wire should be smaller than 1.4 k $\Omega$ . However, considering that the thermal conductivity of poly-SiC is higher compared to that of  $SiN_x$ , the device would possibly dissipate much more thus requiring even a smaller resistance. On the other hand, a layer with high thermal conductivity is a better choice as it helps obtaining a uniform temperature distribution. For this reason, in the design discussed here the poly-SiC:N wire configuration was not optimized to obtain a uniform heat distribution on the membrane. Instead, more attention was directed towards achieving a total resistance at least smaller than 2 k $\Omega$  at temperatures above 500 °C while being able to heat up a square area with a side length of 0.3 mm. A SiC TEM microhotplate design with a lower resistance and thus capable of reaching high temperatures with the available electronics is described in section 6.3.3.4. An optimized version with a uniform heat distribution is instead presented in Chapter 7.

At the moment of the design the lowest sheet resistance available was about 35  $\Omega/\Box$  for a poly-SiC:N layer with a thickness of about 1  $\mu$ m. The microheater wire was then designed to have this thickness as this value was also suited for a reasonably low topography. A width of 35  $\mu$ m was chosen for the microheater wire obtaining a total resistance at room temperature smaller than 2.4 k $\Omega$ . The width of both power and sense contact-wires was designed to gradually increases from 35  $\mu$ m to 240  $\mu$ m when going from the microheater area to the edge of the support-membrane. This was made to minimize their electrical resistance and therefore the voltage drop across them, thus resulting in less heat generated near the edge of the membrane and less total dissipated power. At the same time the funnelshaped geometry helped to minimize the heat loss through the contact wires.

The contact-wires extend outside the support-membrane and end in square shaped contact pads. The path length of these wires is about 3.9 or 5.6 mm depending on their position on the chip. These wires are very long and their resistance would be roughly 270 and 390  $\Omega$ , respectively. Therefore, to avoid that power is lost on these wires a metallization layer was applied. This consisted of a 250 nm thin layer of nickel (Ni). This metal has been shown to form good ohmic contact to poly-SiC:N [144, 145]. The metallization layer drastically reduces the resistance to an estimated value of about 4  $\Omega$ .

The resistances corresponding to the various segments of the poly-SiC:N wire, including the microheater, the contact-wires, and the wiring on the chip, are shown in the schematic of Fig. 6.10. Also, in Table 6.8 the length and the corresponding numbers of equivalent squares of each of the various segments is reported together with the resistance values calculated at room temperature, at 500 °C, and at 700 °C. The portion of the microheater comprised between points B and C is designed to have a number of squares significantly higher compared to the sum of the squares of the power contact-wires (A'A and D'D) and of those of the coldest portion of the microheater (AB and CD). This ensures that even at elevated temperatures, when the resistance decreases, most of the power is dissipated by the microheater.



Figure 6.10: Schematic diagram showing the resistances corresponding to the various parts of the poly-SiC:N microheater wire both on the membrane and on the chip.

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Table 6.8: Geometrical and electrical parameters employed in the calculation of the resistance of the various parts of the poly-SiC:N microheater wire both on the membrane and on the chip. The effective number of squares accounts for the round corners and for the width variation in the contact wires.

Parameters	Wire segment (see Fig. $6.9$ )						
arameters	A'A=D'D	AB=CD	BC	AD	A'D'	Wires on chip	
L (µm)	511.94	260	1711	2232	3255.9	-	
$W(\mu m)$	35-240	35	35	35	35-240	-	
Effective squares	5.43	7.43	40.16	56.22	67.08		
$R_{tot} @ 21 \ ^{\circ}C (\Omega)$	190.05	260.1	1405.6	1967.7	2347.8	$\sim 4$	
$R_{tot} @ 500 \ ^{\circ}C (\Omega)$	190.05*	260.1*	1076.8	1596.8*	1977.1*	$\sim 4$	
$R_{tot} @ 700 \ ^{\circ}C (\Omega)$	190.05*	$260.1^{*}$	979.7	1499.7*	1880.0*	$\sim 4$	
Resistance/s (see Fig. 6.10)	$R_{PC} = R_{SC}$	$R_{CH}$	$R_H$	$R_H + 2R_{CH}$	$R_H + 2R_{CH} + 2R_{PC}$	$R_{PW} = R_{SW}$	

\* Resistance decrease due to temperature not considered.

## 6.3.2 Fabrication

Schematic cross-sections describing the main fabrication steps of the SiC TEM microhotplate are shown in Fig. 6.11. P-type Si wafers with (100) orientation, 100 mm diameter and a thickness of 525  $\pm$  25  $\mu$ m were employed as substrate. As first step, a layer of SiO<sub>2</sub> with a thickness of 1  $\mu$ m was thermally grown on the Si wafer. Then, a 1  $\mu$ m thick poly-SiC layer was deposited by LPCVD. This layer was deposited at 860 °C and 80 Pa as those characterized in Chapter 5. However, the gas flows were tuned to obtain a layer with a tensile stress of about 0.6 GPa. This allowed to compensate the stress of the  $SiO_2$  layer (about - 0.3 GPa) and to obtain a pre-stressed support membrane capable of partially counterbalancing the buckling arising with the temperature. The obtained poly-SiC layer had a thickness of 950  $\pm$  50 nm and sheet resistance about  $120 \times 10^3 \ \Omega/\Box$ . The spread on the thickness takes into account the variation between the various process wafers present in the LPCVD furnace during the deposition. Next, a layer of TEOS oxide with a thickness of 500 nm was deposited by LPCVD. This not only worked as electrical insulator as described in section 6.3.1, but also as landing layer during the etching of the 1  $\mu$ m thick poly-SiC:N deposited on top of it (Fig. 6.11 (a)). As for the layers characterized in section 6.2.1, the poly-SiC:N employed here was deposited at 860 °C and 80 Pa and setting the gas flows of  $SiH_2Cl_2$  and dilute  $C_2H_2$  to 80 and 320 sccm, respectively. However, the gas flow of dilute NH<sub>3</sub> was set to 55 sccm as at the moment of the fabrication this was the known gas flow ensuring the lowest resistivity. For this layer a thickness of 970  $\pm$  30 nm was measured with sheet resistance comprised between 36 and 38  $\Omega/\Box$ . The spread on the thickness and sheet resistance values reflects the variations between the various process wafers present in the LPCVD furnace during the deposition. The poly-SiC:N layer was then patterned by lithography and plasma etch to define the microheater and the contact-wires on both membrane and surrounding silicon chip. The etching of the poly-SiC:N was performed by RIE using an ICP system (Trikon Omega 201). The employed etching recipe used a gas mixture of Cl<sub>2</sub> and HBr, and a power of 500 W and 40 W for the ICP and RF coils, respectively. Using the same etching system and recipe the poly-SiC:N present on the back side of the wafer was completely removed. The TEOS oxide remaining after the etching of the poly-SiC:N on both front and the backside of the Si-wafer was removed by wet etching in a BHF 1:7 solution (Fig. 6.11 (b)). Following the same procedure, circular holes of 4  $\mu$ m in diameter were patterned in the poly-SiC membrane (Fig.6.11 (c)). These served as molding cavities for the electron transparent windows, obtained by depositing 20 nm of the



Figure 6.11: Schematic showing the main steps of the fabrication flow of the SiC TEM microhotplate.

selected a-SiC<sub>x</sub> layer discussed in Chapter 4. This layer was then removed in correspondence of the areas of the contact wires that needed to be metallized (Fig. 6.11 (d)). These areas were defined by lithography and the a-SiC<sub>x</sub> etched using a RIE system (ALCATEL GIR 300) employing a gas mixture of  $CF_4/SF_6/O_2$ , and an RF power of 60 W. A 250 nm thin layer of Ni was then evaporated using a CHA Solution E-beam evaporator and defined by lift-off (Fig. 6.11 (e)). On some devices also a layer of 300 nm of gold (Au) was evaporated on top of the Ni interposing a 10 nm thin chromium (Cr) layer to promote adhesion. Square shaped apertures were opened at the poly-SiC layer at the back side of the wafer by lithography and plasma etch. Also in this case the SiO<sub>2</sub> layer remaining after the dry etch was removed by wet etching with a BHF 1:7 solution. Finally, the Si substrate was removed in correspondence of the square apertures to release the support-

membrane and the integrated windows (Fig. 6.11 (e)). A solution of 33 wt% potassium hydroxide (KOH) was employed to anisotropically etch the Si substrate. Following similar fabrication steps non-suspended microheaters were fabricated without removing the Si substrate. These served as test structures for performing resistance-temperature measurements.

### 6.3.3 Characterization, results and discussion

Images of the fabricated chips integrating the TEM microhotplate and the test microhotplate are shown in Fig. 6.12. Here the suspended poly-SiC:N microheater sustained by the poly-SiC membrane together with the contact wires on the membranes and on the chip are visible. Also, the metallized areas of the poly-SiC:N contact wires can be clearly distinguished. The optical microscope images of Fig. 6.13 show details of the hotplate. In these images the electron transparent windows between the microheater windings are visible in Fig. 6.13 (b) and (c). The windows are not flat due to the thick SiO<sub>2</sub> anchoring layer. This problem can be solved using a thinner layer with a lower stress as PECVD TEOS.



Figure 6.12: Picture showing the chip integrating the microhotplate and the test microheater. The chip on top has nickel metallized poly-SiC:N wires, while the bottom chip has the additional chromium and gold metallization.



Figure 6.13: Optical microscope pictures showing the different elements of the microhotplate together with their dimensions. Wrinkled electron transparent windows are visible in (c).

#### 6.3.3.1 Resistance-temperature dependence

To ensure the accurate operation of the TEM microhotplates, the resistancetemperature dependance for the poly-SiC:N layer employed was measured both on the un-patterned layer and at device level. For the un-patterned layer the method described in section 6.2.2.6 was performed on a test wafer. For the device characterization a dedicated system was employed. A picture of this system is shown in Fig. 6.14. It consisted of a well-type calibration furnace Fluke 9150 capable of reaching a maximum temperature of 1200 °C , and a Keithley 2611 source-monitor unit. These instruments were controlled by a dedicated LabVIEW script running on a PC. The TEM microhotplates were assembled on custom-designed high temperature probes (Xensor Integration design). Pictures of one of these probes are shown in Fig. 6.15. The probe consists of a stripe of ceramic material integrating eight narrow platinum lines. The device was fixed at the tip of the stripe using cement-like (ceramic, boron-nitride based) glue capable of withstanding temperatures up to 800 °C. Wire bonding was employed to connect the contact pads of the microhotplate and those of the test microheater present on the chip to the platinum lines. Gold wires were employed, and only the devices with the gold metallization allowed the bonding. For connecting the probe to the source-monitor unit, thin wires were welded to the platinum lines at the end of the probe. The probe had a width of 0.9 cm and a total length of 27 cm obtained by assembling together two 15 cm long ceramic stripes by using the same glue employed for fixing the device. As for the device, the electrical connection between the stripes was ensured by wire-bonding. Such long probe was required to place the device at the bottom of the heating chamber, that is where the furnace is calibrated. At the same time it allowed placing the tin-welded electric wires far enough from entrance of the heating chamber where really high temperatures are

reached, thus preventing their failure.



Figure 6.14: Pictures of the setup employed for the resistance-temperature characterization of the fabricated microhotplates employing the custom-made high temperature probes.



Figure 6.15: (a) Picture of a custom made high-temperature probe. (b) Detail of the mechanical and electrical connection of two ceramic stripes. (c) TEM microhotplate fixed the tip of the ceramic and connected by gold wires to the metal lines of the stripe.

The temperature was increased stepwise and the resistance measured at the desired temperature. During the temperature rise the resistance of the microheater was continuously monitored in a four-wire configuration. The probing current was selected to be small enough (< 0.5 mA) to prevent selfheating of the suspended microheater. The temperature was increased to the specified value and the resistance measured once the temperature was stable. The temperature stability was ensured by a two steps procedure implemented by the script. First, the script waited for the temperature reading provided by the furnace electronics to be only 0.2 °C off from the set point and then for the resistance variation to be below a certain threshold, for a given time. For our measurement a threshold value between 0.1 and 0.3  $\Omega$  was set for a time of about 5 min. Once the resistance was stable, a current sweep between -1.0 mA and 1.0 mA was performed to obtain the I-V characteristic. Finally, the resistance value was extracted from the I-V data by performing a second order polynomial fit.

The measurements were performed between 100 °C and 800 °C. For most of the probes at the highest temperature the device detached from the tip due to the failure of the ceramic glue. This also resulted in the breaking of the thin gold wires contacting the device. However, some devices survived allowing measurements up to 875 °C. Several probes were measured. The data acquired for two different probes which represent the obtained results are shown Fig. 6.16. For one probe the temperature was first increased up to 700 °C in steps of 100 °C. After the system cooled down to 20 °C this measurement was repeated. However, this time the maximum temperature was increased above 700 °C measuring the resistance also at 750 °C and 800 °C. The acquired data for this probe are plotted in Fig. 6.16 (a). The resistance values measured for the two temperature sweeps overlap almost perfectly up to 700 °C. Contrarily to what shown by the measurements performed on the non-patterned layers, this result demonstrates that the poly-SiC:N is stable at least up to 700 °C. This was also confirmed by additional measurements carried on other probes submitted to consecutive heating and cooling cycles and increasing the maximum temperature at every cycle in steps from 100 to 700 °C. These tests also showed that after reaching 700 °C the variation of the room temperature value of the resistance was in any case below 0.05 %. For the measurement acquired at 750 °C the resistance took a long time to stabilize. At 800 °C the resistance value was definitely unstable presenting a slow increase with the time. The resistance value at this temperature was acquired by manually starting the current sweep. For temperatures above 800 °C the probe was damaged therefore was not possible to acquire more data. The measurement performed on a second probe and plotted in Fig. 6.16 (b) show that the data point of the first and second temperature sweep also have a good overlap up to 750 °C . The variation of the room temperature resistance measured after the first temperature sweep was below 0.1 %.



Figure 6.16: Variation of the resistance as a function of the temperature measured for the custom-made high-temperature probes.

For this probe, when the temperature was raised to 800 °C, the resistance value was acquired as soon as the temperature of the furnace was stable within 0.1 °C. This may explain why in the plot of Fig. 6.16 (b) the resistance measured at this temperature is almost in line with the measurements points acquired at lower temperature. This confirms that the resistance variation is reasonably slow. The temperature was then decreased to 700 °C and then increased up to 875 °C were eventually electrical contact was lost due to the detaching of the device from the probe. This measurement confirmed the increase of the resistance when the devices are submitted to temperatures above 800 °C.

As made for the non-patterned layers in section 6.2.2.6, the resistancetemperature conversion function  $C_{R-T}(T)$  was obtained by normalizing the



Figure 6.17: Comparison between the normalized temperature-resistance measurement of the first high-temperature probe and that of the corresponding non-patterned poly-SiC:N performed in the high-temperature vacuum setup.

data obtained for the first probe up to 700 °C and fitting them with a second order polynomial. These are shown in Fig. 6.17 together with the normalized data measured for a non-patterned layer obtained under the same deposition conditions. The data show a very similar trend and a good overlap up to 200 °C where they start diverging. A big difference is noticed above 600 °C.

#### 6.3.3.2 Characterization in vacuum

To simulate the operation in a TEM, the performance of the TEM microhotplate was evaluated in vacuum using a custom-made setup. This consists of a vacuum chamber connected to a turbomolecular pump and equipped with a pressure gauge and a flange for electric feedthroughs. The vacuum chamber is shown in Fig. 6.18. The device under test is fitted at the bottom plate of the chamber in a specifically sized slot. Needle probes similar to those present at the tip of the TEM holder are used to contact the device. These are connected the electrical feedthroughs by means of wires. For the measurements an Agilent 4165C Semiconductor Parameter Analyzer or a Keithley 2611 source-monitor unit were connected to the electrical feedthroughs. All the measurements were performed at a pressure of about  $1 \times 10^{-3}$  Pa ( $1 \times 10^{-5}$  mbar), which was the minimum pressure achievable with this system. This pressure was low enough to eliminate the heat loss by means of convection. Experimentally it was found that power dissipated by the microhotplates did not decrease significantly already when


Figure 6.18: (a) Picture of the custom-made vacuum chamber employed for the characterization of the TEM microhotplates in high vacuum. (b) Detail of the electrical wiring from the needle probes to electrical feedthrough. (c) Needle probes pressing on the contact-pads of the device located in housing at the bottom of the chamber.

the chamber pressures was below 1 Pa  $(1 \times 10^{-2} \text{ mbar})$ . Therefore, this setup allowed simulating the operation of the device in a TEM where, in absence of gasses, the heat is dissipated only by conduction and radiation.

A stepwise increasing current  $I_D$  was flown through the power terminals of the microhotplate. The current was increased from 1.0 mA to a certain final value  $I_{Df}$  in steps of 1.0 mA with a hold-time of 1 second. The voltage drop at the power and sense terminals of the microhotplate was acquired at each current step. These values were employed to calculate the resistance of the microheater,  $R_H$ , the power dissipated by it,  $P_H$ , and the total power dissipated by the microhotplate,  $P_T$ . Consecutive current sweeps were performed by increasing  $I_{Df}$  from 5.0 mA to 10 mA. The stability of the microheater resistance, was investigated by determining its room temperature value after each current sweep. The I-V characteristic of the microheater was determined by performing a current sweep from -0.1 mA to 0.1 mA while measuring the potential at the sensing terminals of the microhotplate. This small current value was selected to prevent self-heating effects. A linear fitting of the I-V curve was performed to determine its slope and thus the value of  $R_H(20^\circ C)$ .

All the measured devices presented nearly identical behavior. The measurement performed on a device with  $R_H(20^\circ C) = 1379.5 \ \Omega$  are here presented. The variation of  $R_H$  as a function  $I_D$  for each current sweep is plotted in Fig. 6.19. As expected  $R_H$  decreases as  $I_D$  increases, which



Figure 6.19: Variation of the microheater resistance as a function of the driving current for different current sweeps performed with an increasing final current  $I_{Df}$ .

indicates that the temperature of the microheater increases and therefore that the device is functioning as expected. Yet, an unexpected decrease of the  $R_H(20^\circ C)$  was recorded after each current sweep. The  $R_H(20^\circ C)$ determined after each sweep and its variation  $\Delta R_H(20^\circ C)$  expressed as percentage of the initial value are reported in Table 6.9. Up to the sweep with an  $I_{Df}$  of 6 mA the resistance variation is reasonably small, while already for  $I_{Df}$  of 7 mA the decrease exceeds 1 %. The sweep performed at this current was repeated a second time recording a further decrease of the resistance. This means that the phenomena behind the resistance change requires a time longer than 1 second, that is the time the current is applied before the voltage measurement is acquired. The magnitude of the resistance decrease increased for all the following sweeps reaching a value of 12% for an  $I_{Df} = 10$  mA. The variation of the microheater resistance is as also clearly visible in the plot of Fig.6.19.

The lowest resistance reached in each current sweep is reported in Table 6.9 together with its normalized value and the corresponding temperature. This last was estimated using the  $C_{R-T}(T)$  obtained from the calibration of the high temperature probes (section 6.3.3.1). Therefore, under the assumption that the obtained  $C_{R-T}(T)$  is not affected by the decrease of the  $R_H(20^{\circ}C)$  recorded after each sweep. This assumption is reasonable

when the resistance decrease is small enough as it is up to  $I_{Df} = 7$  mA. As expected the higher the  $I_{Df}$  the lower the resistance and the higher the temperature. Also, the data shows the decrease of  $R_H(20^\circ C)$  takes place every time that a certain temperature is exceeded. The decrease is very small up to  $I_{Df} = 6$  mA which corresponds to a temperature of about 642 °C. This is the average temperature of the microheater. As will be shown by the finite element analysis performed for this microhotplate discussed in Chapter 7, the temperature can be locally higher. For a microheater powered with the same current, the finite element analysis predicts a peak temperature of about 690 °C in the center of the membrane. For  $I_{Df} = 7$ mA the decrease of  $R_H(20^{\circ}C)$  is still small but not negligible. In this case the estimated average temperature is 790 °C with a peak temperature of about of 850 °C. The temperature calculated for  $I_{Df} = 8$  mA is 955 °C, this is a rough estimation because it has been obtained by extrapolation of the  $C_{R-T}(T)$  function and also because the resistance decrease might affect the function itself. The same applies for the temperatures calculated for  $I_{Df}$  of 9.0 mA and 10 mA which were in both cases above 1000 °C. The high temperature reached for these last two sweeps is suggested by the large change of the resistance and the large power consumption (see Table 6.9).

The resistance decrease can be attributed to a modification of the poly-SiC:N layer. A possible explanation is that that the amount of active dopants increases as a temperature close to the deposition temperature (860 °C) is reached, thus lowering the resistance. Dopants already present in the grain can be activated, or dopants present at the grain boundaries can diffuse into the grains where they become active, or both. In this process also the current flow may play a role. This last hypothesis would explain why a decrease in the resistance, although small, is already recorded at temperatures much lower than 860 °C. This could also explain why a time of only 1 second is already enough to produce a measurable resistance decrease. During the calibration of the high-temperature probes the recorded resistance variations were not significant at least up to 700 °C. For this measurement the currents below 0.5 mA were employed. This current is much lower compared to the 6.0 mA flown through the microheater when the first resistance decrease takes place. This reinforces the hypothesis that the current may play a role in the supposed dopant activation. It is also interesting to note that the resistance decrease described above is in contrast with the increase noticed during the calibration of the high-temperature probes taking place at temperatures higher than 750 °C. This reinforces the explanation proposed in section 6.3.3.1 for this phenomenon, i.e. that the increase was due to modifications taking place at the metal-semiconductor interface. In fact, contrarily to the vacuum characterization case, during the calibration of the

probes the whole device is submitted to high temperature.

The resistance change has a negative impact on the operation and control of the microheater. For a given  $I_D$  the smaller the microheater resistance, the smaller the delivered power. This results in a lower temperature and consequently in a smaller relative decrease of the initial resistance. For example the temperature reached with the second sweep for  $I_{Df} = 7.0$  mA is already 15 °C lower compared to the one obtained for the first sweep. The impact of the resistance decrease is also visible in the plot of Fig. 6.20 where the  $P_H$  and  $P_T$  obtained for the sweeps made with an  $I_{Df}$  of 5.0 and 10 mA are compared. In Fig. 6.21 the normalized  $R_H$  corresponding to these current sweeps is plotted. For this graph the  $R_H(20^{\circ}\text{C})$  measured before the corresponding sweep was employed for the normalization. As explained, the smaller the resistance, the smaller its relative decrease.

Finally, in the last column of Table 6.9 we report the  $P_H$ ,  $P_T$  and their difference. The power consumption increases with the  $I_{Df}$  as also does their difference. This last is due to the fact that the microheater resistance decrease due to the temperature, causes more power to be dissipated by the contact arms of the microheater.



Figure 6.20: Power dissipated by the complete microhotplate and by the microheater as a function of the driving current for the current sweeps performed with the lowest and highest final current. The data are intentionally displayed up to an  $I_D$  of only 8.0 mA.

$I_{Df}$ (mA)	$egin{array}{c} R_H(20^\circ C) \ (\Omega) \end{array}$	$\begin{array}{c} \Delta R_H(20^\circ C) \\ (\%) \end{array}$	$\begin{array}{c} R_H(I_{Df}) \\ (\Omega) \end{array}$	$\frac{R_H(I_{Df})}{R_H(20^\circ C)}$	$\begin{array}{c} T(I_{Df}) \\ (^{\circ}\mathrm{C}) \end{array}$	$P_H$ (mW)	$P_T$ (mW)	$\Delta P$ (mW)
0.1	1379.5	-	-	-	-	-	-	
5.0	1377.8	-0.123	1056.7	0.766	500	26.42	46.02	19.60
6.0	1372.6	-0.500	984.5	0.715	642	35.44	62.29	26.84
7.0	1364.7	-1.073	922.4	0.672	790	45.20	80.09	34.90
$7.0~(2^{nd})$	1359.0	-1.486	921.9	0.676	775	45.18	80.07	34.89
8.0	1340.0	-2.863	863.1	0.635	955	55.24	98.99	43.75
9.0	1278.4	-7.329	791.1	0.590	>1000	64.08	117.34	53.26
10	1215.1	-11.917	711.9	0.557	>1000	71.19	134.11	62.92

Table 6.9: Selected resistance, temperature and power data obtained for each of the current sweeps.



Figure 6.21: Variation of the normalized microheater resistance as a function of the driving current for the current sweeps performed with the lowest and highest final current. The data are intentionally displayed up to an  $I_D$  of only 8.0 mA.

#### 6.3.3.3 Annealed microhotplates

The resistance variation induced by the suggested dopant activation and or redistribution, limits the maximum operative temperature to values below 650 °C or maybe lower. To expand the possibilities of the nanoreactor, a higher temperature is desired. Also the resistance of the microheaters has to be as stable as possible to allow accurate control of the temperature during operation. To solve these problems a high temperature annealing was performed on some devices. The annealing was done in a furnace at a temperature of 1000 °C, in a N<sub>2</sub> atmosphere, and for a time of 1 hour. Work performed by our group on the same poly-SiC:N layer has shown that at this temperature oxidation does not occur even in an O<sub>2</sub> atmosphere [146]. In addition, a work performed and published by our group after the findings described here, reports on the decrease of the resistivity of similar poly-SiC:N layers upon annealing at 1000 °C [147].

The resistance values measured at room temperature before and after annealing for test structures and microhotplates fabricated on the same chip are reported in Table 6.10. In all cases the annealing causes a decrease of the resistance with a magnitude ranging from 2.6 to 9.5 %. For example, the microheater of device M-14 has a resistance of 1504.3  $\Omega$  which drops to 1402.6  $\Omega$  after the annealing, i.e. a decrease of about 7 %. For the test structure present on the same chip the resistance drops from 1541.4 to

Dev-ID	М	icrohotplate	9	Test structure			
	$R_H$ ( $\Omega$ )	$R_{H-ann.}$ ( $\Omega$ )	Δ (%)	$\begin{array}{c} R_{H}^{TS} \\ (\Omega) \end{array}$	$\begin{array}{c} R_{H-ann}^{TS} \\ (\Omega) \end{array}$	Δ (%)	
M-9	1500.7	1386.3	7.62	1556.6	1386.3	9.54	
M-10	1536.2	1402.4	8.71	1569.3	1402.4	9.35	
M-14	1504.3	1402.6	6.76	1541.4	1401.0	9.11	
M-15	1467.6	1387.9	5.43	1541.9	1387.9	8.99	
M-16	1429.9	1392.0	2.65	1394.0	1513.4	7.90	

Table 6.10: Resistance values measured before and after annealing for microhotplates and corresponding test structures. The calculated relative variation between the resistance before and after annealing is reported as well.

Table 6.11: Resistance values measured before and after annealing for microhotplates and corresponding test structures. Here the reported relative variations refer to the difference between the microhotplate resistance and that of the corresponding test structure before and after annealing.

Dev-ID	Not annealed			Annealed			
	$R_H$ ( $\Omega$ )	$R_{H}^{TS}$ $(\Omega)$	$ \Delta $ (%)	$R_{H-ann.}$ ( $\Omega$ )	$egin{array}{c} R_{H-ann.}^{TS} \ (\Omega) \end{array}$	$ \Delta $ (%)	
М-9	1500.7	1556.6	3.72	1386.3	1408.1	1.57	
M-10	1536.2	1569.3	2.15	1402.4	1422.5	1.43	
M-14	1504.3	1541.4	2.46	1402.6	1401.0	0.11	
M-15	1467.6	1541.9	5.06	1387.9	1403.2	1.10	
M-16	1429.9	1513.4	5.83	1392.0	1394.0	0.14	

1401.0  $\Omega$ , i.e. a decrease of about 9 %. As reported in Table 6.11 before the annealing, the relative difference between the resistance of the microhotplate device and that of the corresponding test structure ranges between 2.2 and 5.65 %. Considering the size of the chip, such a large difference cannot only be the result of thickness variation of the poly-SiC:N layer. Therefore, it should be due to a non-uniform distribution of active dopants. This hypothesis is supported by the lowering of the relative difference to values below 1.6 % upon annealing. Such a value is reasonably justified by the thickness variation of the poly-SiC:N layer the chips fabricated close to the edge of the wafer where the deposition is less uniform. Here thickness differences larger than 20 nm across the chip are possible.

After the annealing the resistance-temperature characteristic of some

devices was verified by using an Agilent 4165C Semiconductor Parameter Analyzer and a Cascade probe station equipped with a heating chuck. Measurement data were acquired between 50 °C and only 200 °C the maximum temperature obtainable with this system. The measurement was performed only on the test structures. For these a good thermal transfer between the chuck and the microheater was ensured by the Si substrate under the microheater. The normalized calibration points obtained for one of the measured devices (M-14) are plotted in Fig 6.22 and compared to the normalized calibration curve obtained for the high-temperature probes. The calibration points obtained for the annealed test microheater, lay above the calibration curve of the high-temperature probes. The smaller decrease of the resistance with the temperature is shown also by the smaller coefficients of the second order polynomial fit. The resistance-temperature calibration of the non-patterned poly-SiC:N layers indicated a similar behavior, with lower resistivity layers showing a smaller resistance decrease with the temperature.



Figure 6.22: Normalized calibration data acquired for the test structure of an annealed device compared to that of a not-annealed device obtained through the characterization of the high-temperature probes.

#### Characterization in vacuum

The operation of the corresponding microhotplate was tested in vacuum in the same way as for the non-annealed devices described in section 6.3.3.2. However, in this case the current sweep steps were set to 0.5 mA and once reached a certain maximum value  $I_{Dmax}$  the current sweep was performed backward by decreasing  $I_D$  down to 1.0 mA again in steps of 0.5 mA. The value of  $I_{Dmax}$  was set to 6.0 mA for the first cycle and then increased from 7.0 mA to 9.0 mA in steps of 0.5 mA after each cycle.

In Fig. 6.23 the  $R_H$  measured at each current step and for each current sweep is plotted as a function of  $I_D$ . In Table 6.12 the values of the room temperature resistance  $R_H(20^{\circ}C)$  measured after each scan together with its variation relative to the  $R_H(20^{\circ}C)$  measured right after the annealing, are reported. The lowest resistance reached in each current sweep together with its normalized value is also reported. Due to the unavailability of calibration data at high-temperature for the annealed poly-SiC:N layer, it was not possible to calculate the exact temperatures reached by the microheater. In Table 6.12 the temperature values estimated using the  $C_{R-T}(T)$ obtained for the high temperature probes up to 700 °C and extrapolating up to 1000 °C (section 6.3.3.1), are given.

Considering the effect of the annealing on the resistance-temperature characteristic, shown by the calibration performed up to 200°C, the temperature was underestimated with an error which should increase with the temperature. The measurement points recorded for the forward and backward sweeps overlap perfectly up to an  $I_{Dmax}$  of 8.0 mA. For this current the estimated highest temperature is 886 °C, corresponding to a peak temperature of about 943 °C obtained by finite element analysis (see Chapter 7). This value is close to the annealing temperature. Already at  $I_{Dmax}$ of 8.5 mA the estimated highest temperature is 975 °C, corresponding to a peak temperature in the center of the membrane of about 1040 °C. For this sweep a small difference between the forward and backward curve was noticed. Also, up to  $I_{Dmax}$  of 8.0 mA the  $R_H(20^\circ C)$  slightly increases after each current sweep, while a decrease is recorded after the microheater is submitted to a current of 8.5 mA. By Increasing  $I_{Dmax}$  to 9.0 mA the difference between the forward and backward data is clearly visible, with smaller values recorded in the backward sweep. Also a decrease of about 0.7 % of the  $R_H(20^\circ C)$  is recorded. This indicates that the temperature reached by the microheater for  $I_{Dmax}$  of 9 mA is definitely higher than 1000 °C in at least part of the poly-SiC:N microheater.

Three additional forward current sweeps with an  $I_{Df}$  of 9.0 mA were performed to confirm the resistance change. The obtained data are plotted in Fig. 6.24 and the  $R_H(20^{\circ}C)$  measured after each sweep reported in Table 6.12. A final value of 1385.7  $\Omega$ , corresponding to a decrease of 1.2 % was found after the 4<sup>th</sup> sweep. The resistance decrease was further investigated by submitting the microheater to a constant current of 9.0 mA and by continuously monitoring its resistance. The decrease-rate of the resistance value was large in the first four minutes then it became much smaller. The

Table 6.12: Selected resistance, temperature and power data obtained for each of the current sweeps preformed on the annealed device.

I <sub>Dmax</sub> (mA)	$egin{array}{c} R_H(20^\circ C)\ (\Omega) \end{array}$	$\Delta R_H(20^\circ C) \ (\%)$	$R_H(I_{Dmax}) \ (\Omega)$	$\frac{R_H(I_{Dmax})}{R_H(20^\circ C)}$	$T(I_{Dmax})$ (°C)	$P_H$ (mW)	$P_T$ (mW)	$\Delta P$ (mW)
0.1	1402.6	-	-	-	-	-	-	-
6.0	1402.3	-0.2	1018.8	0.726	610	36.68	62.43	25.75
7.0	1403.7	0.078	961.3	0.686	737	47.11	80.77	33.66
7.5	1404.6	0.143	936.2	0.667	797	52.65	90.60	37.95
8.0	1404.7	0.150	911.7	0.649	886	58.35	100.82	42.48
8.5	1401.6	-0.071	886.0	0.631	975	64.01	111.22	47.21
9.0 (1st)*	1392.4	-0.727	856.5	0.611	> 1000	69.38	121.51	52.13
9.0 (2nd)*	1389.2	-0.955	853.9	0.613	> 1000	69.17	121.26	52.10
9.0 (3rd)*	1387.1	-1.105	852.4	0.610	> 1000	69.05	121.13	52.08
9.0 (4th)*	1385.7	-1.205	851.6	0.614	> 1000	68.98	121.05	52.07
9.0 (1h in vac.) **	1370.2	-2.310	-	-	Ξ.	-	-	-

\* scan performed only forward therefore  $I_{Dmax} \equiv I_{Df}$ . \*\* Measurement performed at constant current.



Figure 6.23: Variation of the resistance of the annealed microheater M-14 as a function of the driving current for different current sweeps performed forward and backward with an increasing maximum current. The data measured for the forward and backward sweeps overlap perfectly up to an  $I_{Dmax}$  of 8.0 mA.



Figure 6.24: Consecutive forward current sweeps performed all with a final current of 9 mA. The data measured slightly deviates at each sweep.

measurement was stopped after 1 hour when the standard variation of the resistance value in the last 60 seconds of measurement was smaller than a 0.02  $\Omega$ . After this test a value of 1370.2  $\Omega$  was measured for  $R_H(20^\circ C)$ ,

corresponding to a variation of -2.3 %. This change is small but enough to reduce the accuracy of the temperature measurement of the TEM microhotplate. In addition, the resistance-temperature characteristic might again be modified, thus affecting the microhotplate operation.

Considering these results we can say that this specific microhotplate can operate in a stable way at least up to 8.0 mA where the peak temperature should be below 1000 °C, that is the annealing temperature. For this device the normalized resistance and the corresponding estimated temperature for the sweep performed with an  $I_{Dmax}$  of 8.0 mA are plotted in Fig. 6.25. The power dissipated by the heater  $P_H$ , and that dissipated by the complete device  $P_T$  are plotted in Fig. 6.26. Also, their values for currents higher than 6.0 mA are reported in Table 6.12. The increase in the difference between  $P_T$  and  $P_H$  as  $I_D$  increases, can be explained in the same way as for the case of the not annealed devices. When flowing a current of 8.0 mA,  $P_T$ and  $P_H$  are about 58 and 100 mW, respectively. As the dissipated power is a measure of the temperature, annealed devices having the same geometry should not exceed these values to prevent the permanent drift of their resistance characteristic. The maximum current that can be flown instead depends on the value of the resistance that can be different from device to device due to variations in the thickness of the poly-SiC:N layer. Finally, the voltage drop across the heater  $V_H$  and that on the power terminals of the microhotplate  $V_T$ , are also plotted in Fig. 6.26. The maximum value for  $V_T$  is about 13 V thus exceeding the maximum voltage that can be provided by the electronic control box of the nanoreactor which is 6.5 V. Therefore, using the control box this microhotplate cannot reach temperatures above 350 °C.

The results above demonstrate the effectiveness of the annealing which allows extending the operative temperature of the SiC microhotplate above those of the not annealed ones. Taking a safety margin, we can say that the annealed devices can operate in a stable way up to a temperature of 900 °C (peak). At this temperature the total dissipated power is lower than 100 mW, thus making the device suitable for our application. However, a redesign to lower the total resistance of the microhotplate and thus the voltage drop is required to be able to use the available electronic control box.

#### Characterization in ambient air

The operation of the annealed microhotplates was also tested in ambient air. An Agilent 4165C Semiconductor Parameter Analyzer and a Cascade probe station were employed. The microscope of the probe station was



Figure 6.25: Normalized resistance of the annealed device M-14 measured as function of a stepwise increasing current with a maximum value of 8.0 mA. The corresponding temperature calculated using the  $C_{R-T}(T)$  function is also plotted.



Figure 6.26: Power dissipated by the microheater and by the complete microhotplate of the annealed device M-14 measured as function of a stepwise increasing current with a maximum value of 8.0 mA. The corresponding voltage drops are also plotted.

equipped with a video camera to observe the microheater during operation. The microheater was powered by sending a current increasing stepwise from



Figure 6.27: Optical microscope images of an annealed microhotplate powered with a stepwise increasing current in ambient air. The images were acquired with and without illumination to highlight either the buckling of the membrane or the glowing of the microheater caused by the temperature rise. Both buckling and glowing increase with the temperature. The temperatures indicated in the images were determined by using the recorded microheater resistance and the  $C_{R-T}(T)$  conversion function.

0 to 12.0 mA in steps of 0.5 mA. In the meanwhile, the voltage drop across the microheater was monitored. Pictures of the glowing microheater were acquired with and without illumination. A selection of the acquired picture is shown in Fig 6.27. These show the glowing of the microheater and the deformation (buckling) of the membrane due to the heat. The temperature of the microheater was calculated by using the calibration function  $C_{R-T}(T)$ obtained for the high temperature probes. For the reasons already indicated in the previous sections, this temperature it is just an estimation which is less accurate at high temperatures. The buckling of the membrane was visible in the images as a darkening of a portion of the membrane. The higher the temperature the larger the deformation of the membrane and thus the darker the membrane. A small deformation of the membrane was first noticed at a temperature of 542 °C (not shown). The microheater glowing started in the center of the membrane at a temperature of about 620 °C. The glowing expanded to the rest of the microheater as the temperature increased. The glowing gives an idea of the heat distribution on the microheater. Slightly tilted elliptically shaped isothermal regions seemed to be present. This observation was exploited for refining the finite element analysis presented in the next chapter. At the highest temperature the elevated intensity of the light emitted by the warmest portion of the microheater resulted in the saturation of the CCD sensor of the camera and in a white area in the images. This area enlarged with the temperature indicating that all that portion of the microheater had reached at least a temperature above the saturation point.

#### 6.3.3.4 Operation of the microhotplates in a TEM

The performance of the SiC TEM microhotplates was verified by conducting a heating experiment in a TEM. For this experiment the temperature control system developed for the nanoreactor was employed. The electronic control box was adapted to be able to control microheaters with a NTC. However, the limitation on the voltage was not addressed. Consequently, to deliver all the required power to reach elevated temperatures a microhotplate having a total resistance smaller than 1 k $\Omega$  at high temperatures was required (see section 6.3.1). Such a low resistance was achieved with an alternative design of the poly-SiC:N wire. An optical picture of this device is shown in Fig. 6.28. The poly-SiC:N wire has a width of 50  $\mu$ m and a length of about 875  $\mu$ m between the points A and D indicated in the figure. Compared to the devices characterized above, this has a microheater wire with less windings, less windows, larger power contacts, and thinner sense contacts. This device was fabricated together with the devices char-



Figure 6.28: Optical microscope image showing the design of the microhotplate employed for the heating experiment in TEM. The devices has an asymmetric design of the contact poly-SiC:N wires and a short and wide microheater. acterized above to verify the feasibility and the mechanical stability at high temperature of a less symmetric design that should allow for a lower power loss. The fabrication proved to be feasible with no cracked membranes or heaters. Moreover, these were strong enough to sustain the buckling caused by the temperature. However, as for this design a less uniform heat distribution and smaller heated area were expected, a thorough characterization was not performed.

The heating experiment consisted in the melting and evaporation of gold nanoparticles using the aforementioned microhotplate. A drop of ethanol with in suspension gold nanoparticles of 10 nm in diameter (BBInternational) was dispensed on the microhotplate membrane. The evaporation of the ethanol resulted in gold nanoparticles dispersed on the membrane, on the heater and on the electron transparent windows. The device then was mounted in a heating holder and placed in a TEM. The holder had similar features to those of the one described in section 2.2.1 but was devoid of gas lines and inlet/outlet openings. The TEM microscope was a FEI Titan equipped with a field emission gun operated with an accelerating voltage of 300 kV. The parameters of the temperature-resistance curve calculated for this device as  $R_H(20^\circ C) \times C_{R-T}(T)$  were inserted in the LabVIEW script controlling the electronic box (see section 2.2.3). The microheater employed was not annealed because the benefits of this step were not known at the moment of the experiment. Therefore, the temperature set and measured during the experiments was accurate, at best, up to 750 °C.

Before starting the heating experiment, the transparency of the a-SiC<sub>r</sub> windows was tested by acquiring high resolution TEM images of the gold nanoparticles. The images were analyzed by fast Fourier transform (FFT) using ImageJ software. This allowed us to determine the smallest visible lattice spacing, which is a measure of the achievable resolution and thus of the transparency. An atomic-resolved TEM image of a gold nanoparticle is shown in Fig 6.26. The image shows the lattice fringes of the nanoparticle superimposed to the amorphous pattern of the  $a-SiC_x$  window. The 2D FFT transform of this image (inset in Fig. 6.29) indicates that the smallest resolved lattice fringes have a spacing of 0.13 nm. This confirmed the results obtained for the a-SiC  $_x$  windows discussed in section 4.3.2.2 . Also, it proved the possibility of integrating the  $a-SiC_x$  windows in the SiC microhotplate. During the transparency test we noticed that the size of the nanoparticles deviated from the nominal size. Circularly-shaped nanoparticles with a diameter up to about 40 nm, and elongated-shape nanoparticles with lengths up to about 90 nm were present. This was due to agglomeration phenomena that took place in the suspension used to load the particles on the microhotplate.



Figure 6.29: High resolution TEM image of a gold nanoparticle on one of the a-SiC<sub>x</sub> windows of the microhotplate. The 2D fast Fourier transform is shown in the inset. The outer bright points in the FFT correspond to the smallest resolved lattice fringes, which have a spacing of 0.13 nm.

For the heating experiment the temperature of the microheater was progressively increased while observing the gold nanoparticles on the windows. A selection of TEM images acquired during the experiment are shown in Fig. 6.30. The temperature was first set to 600 °C for 13 minutes and then to 800 °C for 3 more minutes. At these temperatures no changes in the nanoparticles were detected. The temperature was then increased to an estimated value of about 1000 °C, where it was kept for about 3 minutes. During this time the sudden disappearing of the smallest nanoparticles as well as the progressive size reduction of the larger ones was observed. This demonstrated the melting and consequent evaporation in the high vacuum of the microscope of the nanoparticles. The melting temperature of nanoparticles usually differs from that of their bulk counterpart. As shown in Fig. 6.31, the melting temperature of gold nanoparticles decreases with the diameter of the nanoparticles. At 20 nm the melting temperature is below 1000 °C that is smaller than the bulk melting temperature (1064 °C) thus justifying the observed evaporation. However, the rate of the observed evaporation process decreased as the time passed. This was due to the fact that the resistance of the microheater decreased progressively due the temperature-induced changes in the poly-SiC:N layer. This mislead the temperature control system causing this to aim to a resistance value corresponding to a lower temperature. Considering the graph of Fig. 6.31, the temperature dropped to values below 920 °C. To restart the evaporation process the temperature should rise to a value of about 1200 °C. The actual temperature corresponding to this value is unknown but is most probably above 1064 °C as the fast evaporation of the gold nanoparticles having a diameter larger than 20nm, was observed. After this experiment a decrease in the room temperature resistance of the microheater was recorded. This dropped from a 393.5 to 344.7  $\Omega$ , corresponding to a decrease of about 14 %. As the highest resistance decrease measured for the devices annealed at 1000 °C devices was about 9.5 %, we conclude that temperatures higher than 1000 °C were achieved during the heating experiment thus supporting the observations above.



Figure 6.30: TEM images of gold nanoparticles on an electron transparent window. The sequence shows the progressive shrinkage and disappearing of the nanoparticles as the microheater temperature is set to 1000 °C. For this temperature three different images acquired at three different times are shown.



Figure 6.31: Melting point of gold nanoparticles as a function of their diameter. For values smaller than 20 nm the melting point lower than 1000  $^{\circ}$ C. Adapted from [148], source [149].

#### 6.4 Conclusions

Low resistivity poly-SiC:N thin films were obtained by in-situ doping with nitrogen of LPCVD poly-SiC layers. The poly-SiC:N layers were characterized and found suitable as heating material for the fabrication of microheaters. The temperature-resistance characteristic of the as-deposited layers was determined up to temperatures of 700 °C. SiC based microhotplates integrating a low resistivity poly-SiC:N layer were successfully fabricated and the temperature-resistance characteristic verified.

Two different microheater designs were shown capable of operating at high temperature without mechanical failure. The instability of the microheater resistance observed at high temperature was caused by dopant thermo-electrical induced dopant activation. A high temperature annealing step was employed to stabilize the resistance of the poly-SiC:N layer integrated in the TEM microhotplates. These microhotplates resulted much more stable and capable of operating at temperatures of at least to 900 °C. The heating experiment performed in the TEM demonstrated the capabilities of the devices and the suitability of low resistivity poly-SiC:N layers as heating material. In addition, the SiC-based TEM microhotplate represents the first successful attempt of integrating all the developed SiC layers together, thus it can be considered as the first step toward the realization of the SiC-based nanoreactor described in the next chapter. 188

# CHAPTER 7

# The SiC-based nanoreactor

## 7.1 Introduction

In this chapter we present a new version of the MEMS nanoreactor realized by employing the different SiC layers discussed in the previous chapters. These layers are integrated in the fabrication flow of the surface micromachined nanoreactor reported in Chapter 2 to illustrate the advantages of their use in MEMS nanoreactors. In addition, some modification of the nanoreactor design, motivated by the desire to overcome some critical fabrication steps and/or to improve analysis capabilities, are implemented.

## 7.2 Fabrication improvements

The use of SiC as fabrication material proved to be very advantageous as it helped to address some important issues related to the fabrication of the surface micromachined nanoreactor, previously presented in Chapter 2 and in [80]. A schematic cross-section of a SiN<sub>x</sub>-based surface micromachined nanoreactor is shown in Fig. 7.1. The device has a channel height of 4.5  $\mu$ m for easier loading of the samples inside the reaction chamber and integrates a molybdenum (Mo) heater as this shows better performance and easier patterning compared to the Pt heater.

In the following sub section we describe some of the critical steps for the fabrication of this nanoreactor version and point out the specific aspects

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that could benefit from the use of SiC layers.

Figure 7.1: Schematic cross-section showing the fabrication layers and topography of the surface micromachined nanoreactor fabricated with a channel height of 4.5  $\mu$ m and integrating a molybdenum microheater. Layer thickness and sizes of windows, plug, and pillar are approximately to scale.

#### 7.2.1 Windows release

The last step in the fabrication of the nanoreactor is the release of the top and bottom electron transparent windows by wet etching of the LPCVD TEOS oxide layer protecting them. This step is very critical as the thickness this oxide layer is different for the top and bottom windows and it can have a relatively large variance across the wafer. For the windows on the top side of the chamber the oxide works as landing layer during their definition performed by dry etching of a stack of  $SiN_x$  and oxide layers (Fig. 7.1). For the windows on the top side of the chamber the LPCVD TEOS oxide works as protection layer during the substrate removal for the release of the nanoreactor reaction chamber. The etching time required to open the windows has to be properly tuned to remove both oxides within the same step. In fact, any oxide residues on the windows caused by an etch step that is too short would drastically reduce the transparency of the windows, making them unusable. An example of a not properly released window is shown in Fig. 7.2. On the other hand, as the etchant is an HF-based solution, an unnecessarily long etch would reduce the thickness of the  $SiN_x$ windows, thus making them mechanically less strong and less resistant to beam radiation. For a remaining thickness of less than 10 nm the windows will break, making the device unusable. A way to address this point is to make the windows thicker than the desired nominal thickness (e.g. 20 nm

instead of 15 nm). This allows some over-etch and ensure the transparency. As already pointed out in Chapter 4, the use of  $\operatorname{a-SiC}_x$  instead of  $\operatorname{SiN}_x$  is advantageous in this respect. Due to its chemical inertness, the  $\operatorname{a-SiC}_x$  windows can withstand etching times that are long enough to guarantee the opening of the windows without affecting their thickness. This is extremely beneficial as it eases the fabrication process and drastically improves reproducibility and yield.



Figure 7.2: (a) SEM images of a window with a uniform layer of LPCVD TEOS oxide left after the window release step. (b) Correctly released window for comparison.

#### 7.2.2 Sacrificial etch

Another critical step in the fabrication of the surface micromachined nanoreactor is the etching of the sacrificial layer leading to the formation of the microchannel. As explained in Chapter 5, small access holes present in the top  $SiN_x$  layer of the microchannel allow the etch of the sacrificial layer by means of an HF-based solution. Also in this case the etching time has to be properly tuned so to completely remove the sacrificial layer without causing an excessive thinning of the structural top and bottom  $SiN_x$ layers. Excessive thinning can make the whole structure less strong, thus affecting the maximum achievable pressure and the overall robustness of the microchannel. In addition, due to the different etch rate inside and outside the microchannel, the final thickness of the structural layer is not exactly know. As will be discussed in 7.3.1 this can affect the definition of the windows. Moreover, any small variation in channel height will lead to deviations in the designed flow conductance of the microchannel, as this scales with the third power of the height. On the other hand, an etching shorter than the required one may result in pyramid-shaped residues right in correspondence of the windows. These are difficult to spot during the fabrication and can lead to devices which are not usable. As for the windows, by using poly-SiC as construction material for the microchannel walls, the etching time can be safely increased to ensure the complete removal of the sacrificial layer without affecting the subsequent fabrication steps or the nanoreactor performances. Therefore, also in this case, the use of SiC eases the fabrication process and improves reproducibility and yield.



Figure 7.3: (a) TEM image of a window with a pyramid-shaped residue of the sacrificial layer. The residue is located in the middle of the bottom window as visible in the SEM cross-section (b) where a large pyramid is shown.

### 7.2.3 Microheater integration

The integration of the microheater on top of the reaction chamber of the nanoreactor poses also some problems. The microheater and the wiring are currently made of Mo, as this material provides very good performance [76]. However, Mo suffers from oxidation when exposed to temperatures above 250 °C in ambient air. Encapsulation of the whole Mo layer is therefore required, not only to ensure the electrical isolation of the microheater contacts but also to be able to subject the nanoreactor at high temperatures in ambient air. This is the case when device characterization and testing are performed (e.g. resistance-temperature calibration). Also, exposure of the nanoreactor to high temperature in an oxidizing environment is required for the preparation and treatment of samples for the TEM experiments and for cleaning possible hydrocarbon contaminants. An LPCVD SiN<sub>x</sub> layer of 300 nm is employed to ensure effective protection of the Mo. In addition, an intermediate layer of PECVD TEOS having a similar thickness is needed to prevent the Mo oxidation during the loading of the wafers in the LPCVD

furnace for the  $\operatorname{SiN}_x$  deposition. The presence of these additional layers on the reaction chamber of the nanoreactor makes the correct definition of the windows critical and time consuming. As shown in Fig. 7.1 a stack of  $\operatorname{SiN}_x$  and oxide layers has to be etched to define the windows. Due to non-uniformities in the thickness of these layers across the wafer and to non-uniformities in the etching step, incomplete etching of the stack may take place. This may lead to the non-correct definition and release of the windows as shown in Fig. 7.4. Extending the etching time may result in excessive thinning of the landing layer with consequences in the release of the windows as explained in section 7.2.1. It may also result in the damaging and perforation of the windows in some areas of the wafer, thus reducing the yield.



Figure 7.4: (a) SEM image of a window where residues of the last  $SiN_x$  layers are found after the definition step. (b) TEM images showing the effects of a non-properly defined window: residues of both  $SiN_x$  and oxide layers are visible.

Another problem is related to the patterning of the Mo layer. After a dry etching, typically an oxygen plasma is required to remove the photoresist. However, because this would oxidize the Mo, the patterning is typically performed by means of wet etching. For this step, PES solutions, a mixture of phosphoric, nitric and acetic acid, which quickly etch the Mo, are employed. This causes some undercut of the Mo lines, introducing a spread in the resistance value of the microheater. In addition, after the etching the photoresist needs to be removed by means of acetone or N-Methyl-2-Pyrrolidone (NMP). This method produces a less clean surface, leading to adhesion problems between the Mo and the encapsulation layer, as shown in Fig. 7.5. Fuming nitric acid, which would allow a more effective cleaning, cannot be employed as it would completely etch the Mo.



Figure 7.5: Optical microscope image of a molybdenum microheater showing delamination of the embedding oxide and  $SiN_x$  layer stack.

The fabrication of a microheater made of poly-SiC:N solves the integration problems discussed above. This layer can be patterned by photolithography and plasma etching, thus allowing accurate control of the microheater dimensions and thus ensuring its reproducibility. The metallization required to reduce the resistance of the contact wires can be made of Al which can be easily patterned. Moreover, only this layer requires encapsulation to ensure its electrical isolation. The poly-SiC:N microheater can stay uncovered as it does not suffer from oxidation at lest up to 900 °C also in a wet environment [147]. This means that no additional layers are present on the reaction chamber of the nanoreactor, thus making easier the definition of the windows and also contributing to lowering power consumption.

# 7.3 Design improvements

The schematic cross section of the SiC nanoreactor is shown in Fig. 7.6. Compared to the standard surface micromachined nanoreactor, in this SiC-based version some design modifications were implemented. The modifications were meant to improve either the fabrication or the functionality of the nanoreactor. These improvements do not necessarily require the use of SiC-based construction material, so can be implemented in a SiN version as well. More in general, they can be integrated in the fabrication flow of nanoreactors independently of the construction materials employed. The three most important improvements are described in the following subsections.



Figure 7.6: Schematic cross-section showing the fabrication layers and the topography of the SiC-based surface micromachined nanoreactor. The microchannel of this nanoreactor is designed to have double height. The metallization of the wiring of the poly-SiC:N microheater is made of Al. Layer thickness and sizes of windows, plug, and pillar are approximately to scale.

#### 7.3.1 Flat windows

As previously mentioned, a thick TEOS oxide layer deposited by PECVD is employed to define the microchannel height and then removed during the sacrificial etch. The surface topography of this sacrificial oxide layer essentially copies the topography of the surface on which it is deposited. For this reason in correspondence of the bottom window this layer shows a depression. The width of this depression shrinks with the thickness of the TEOS oxide deposited. The top structural layer of the microchannel and the window layer deposited on it follow this topography, giving rise to a window that is not flat. This is shown in the schematic of Fig. 7.1 and in the SEM images of Figs. 7.2 and 7.3 and 7.7. This situation is not ideal as it further complicates the accurate definition and release of the windows. In Fig. 7.8 residues of  $SiN_x$  right in correspondence of the steepest regions of the window profile are visible. This is where the layers of the stack are thicker due to the present topography. A possible solution is to increase the thickness of the etch stop layer, that is the TEOS oxide right above the window layer. This however is not ideal as it might have some drawbacks. The TEOS oxide working as etch stop layer is in fact obtained by internally coating the microchannel through the access holes. A thicker layer would require the resizing of these holes. Also, the thickness of the layer deposited inside the microchannel is about half of that deposited on the outside. Therefore, a

thicker layer would add considerable thickness on top of the microchannel which is not ideal.



Figure 7.7: SEM images showing the non-flat profile of the  $SiN_x$  windows of the surface micromachined nanoreactor fabricated with a thick sacrificial TEOS oxide layer for a channel of about 4.5  $\mu$ m.



Figure 7.8: TEM images showing residues of  $SiN_x$  and oxide layers due to a non-correct etching of these layers prior to the release of the windows. The residues are localized in correspondence of the steepest part of the window profile. In the right image only a  $SiN_x$  ring is left, this is shifted from the center as it floats during the release of the windows due to the etching of the underlying oxide.

A more elegant solution was implemented in the SiC-based nanoreactor. A planarization of the sacrificial TEOS oxide was performed prior the deposition of the structural top layer of the microchannel. The planarization procedure consisted in consecutive depositions and etching of the sacrificial TEOS oxide. The result is shown in Fig. 7.9, where the layer on top of the window is practically flat and do not resemble the bottom topography.



Figure 7.9: (a-b) SEM cross-sections showing the nearly flat profile of top structural layer fabricated in correspondence of the bottom window. (c) Released flat a-SiC<sub>x</sub> window. (d) For comparison, a window opening where the a-SiC<sub>x</sub> layer is missing is shown. The absence of the a-SiC<sub>x</sub> layer makes the bottom window visible.

#### 7.3.2 Flat support membrane

Another problem of the standard nanoreactor design is that the released membrane integrating the microchannel and the reaction chamber of the nanoreactor buckles. This situation is not ideal from the mechanical point of view, especially when high temperatures need to be reached. The temperature increase may in fact result in further deformation of the membrane, causing failure or undesired shift of the image during TEM operations. The cause of the buckling is again the thick sacrificial TOES oxide. This, due to its compressive stress and large thickness, leads to the bending of the otherwise flat  $SiN_x$  structural layers. As a solution to this problem, in the SiC-based nanoreactor the sacrificial oxide TEOS oxide was removed from the support membrane area prior to the deposition of the top structural layer of the microchannel (Fig. 7.6). This approach has the additional benefit of eliminating the heat loss through this layer. In Fig. 7.10 the flat membrane obtained with the proposed solution is shown and compared to the buckled one of the standard nanoreactor design. However, this solution comes with a drawback that is the increased topography. High

topography strongly affects the conformality and uniformity of the photoresist layers. For this reason, in the SiC-based device, the channel height was designed to be lower as compared to that of the  $SiN_x$ -based nanoreactor design described here. The fabrication of a microchannel using the selfsealing technique proposed in Chapter 5 would help to flatten the surface topography by the elimination of the plugs. This would allow to increase the microchannel height.

#### 7.3.3 Flow restriction

A reduction in the amount of gas flowing into the microchannel of the nanoreactor is desired to better exploit the sensing capabilities of the mass spectrometer connected at the outlet of the microchannel during TEM experiments. In order to preserve the specimen loading capabilities ensured by the relatively large height of the microchannel, a flow restriction was implemented by thinning down the microchannel only at the exit of the reaction chamber. This resulted in a microchannel with a double height as illustrated in Fig. 7.6. This design also comes with the important advantage of drastically reducing the velocity of the gasses flowing through the reaction chamber. This increases the gas residence time, and minimizes the temperature and pressure gradients induced by the gas flowing at high velocity. These experimental conditions are beneficial for the study of catalytic reactions [42].

From the inlet to the reaction chamber, the microchannel was designed to have an effective height of 1.9  $\mu$ m. The actual height of the microchannel 2.5  $\mu$ m is in fact reduced by the internal coating of TEOS oxide needed to form the etch stop layer for the definition of the windows. The remaining part of the microchannel was instead designed to a have an effective height of only 300 nm. The flow conductance of the microchannels scales approximately with the third power of the height, so the conductance of the lower part of the microchannel is about 250 times lower compared to that of the high microchannel. Therefore, the flow is established by the lower part of the microchannel. Compared to a standard surface micromachined nanoreactor with an effective microchannel height of about 4.5  $\mu$ m, the proposed design should scale down the flow considerably.

In Fig. 7.11 a detail of the transition between the thick and thin channels is shown. Interference fringes are visible in the thin channel right after the transition. The origin of these fringes is not completely understood. The detachment of the pillars or the presence of residues of not properly rinsed etchants were investigated and excluded. Therefore, we suspect that the fringes are the result of the deformation of the top structural layer caused



Figure 7.10: (top) Optical microscope image of the SiC-based surface micromachined nanoreactor with a flat support membrane. (bottom) The buckled membrane of the standard surface micromachined nanoreactor for comparison.



Figure 7.11: (a) Optical microscope image showing the transition between thick and thin channel of the SiC-based nanoreactor. Interference fringes are visible at the top structural layer of the low microchannel after the transition. (b) SEM image of the transition region showing that the top structural layer is flat. This image also shows the topography of the microchannel as well as the plugs and the pillars.

by the different strain between the top structural layer of the thick and thin channels. These layers are in fact deposited on a sacrificial TEOS oxide that has a different thickness, which leads to a difference in the strain level. This difference is accommodated by the deformation of the top structural layer of the thin channel. In the SEM image shown in Fig 7.11 no deformation is visible, indicating that the top microchannel is probably under tension rather than compression.

# 7.4 Design and optimization of the poly-SiC:N microheater

The design of the poly-SiC:N microheater integrated in the SiC-based nanoreactor was optimized to achieve a uniform temperature distribution in the reaction chamber. This reduces the difference between the temperature set during a TEM experiment and the actual temperature in the microheater chamber. Also during experiments it is desirable to have all the windows at the same temperature.

The design was optimized by means of finite element analysis performed using COMSOL Multiphysics. The unknown material parameters were first estimated by modelling the TEM microhotplate design characterized in Chapter 6. In particular, the thermal conductivity of the poly-SiC and poly-SiC:N layer were estimated starting from values found in literature and by fitting the simulated data to the real measurements. Then the asymmetric microheater design employed in the TEM experiment described in section 6.3.3.3 was used as starting point for the optimization. Its reduced resistance and size were in fact very close to those required for the integration in the SiC-based nanoreactor. The dimensions and positioning of the microheater windings and contact wires were then modified to obtain a uniform heat distribution on most of the windows. In this process, the constraints on the maximum resistance discussed in Chapter 6 were also taken into account.

The results of the finite element analysis performed on the three designs indicated above, are shown in Figs. 7.12, 7.13 and 7.14. These figures show the heat distribution on the whole support membrane for the same peak temperature in all three designs. The temperature profile corresponding to the central part of the membrane, that is where the windows are located, is also shown. This was obtained by means of cutting lines extending from the center in the x and y directions for a length of 150  $\mu$ m. The microheater with the highest resistance characterized in Chapter 6 has an average temperature of 563 °C for a peak temperature of 602 °C, a difference

of about 6.9 % (Fig. 7.12). The temperature profile in the central part of the membrane shows the non-uniform heat distribution of this design. The temperature differences between the center and the edges of the cut line is about 60 °C, corresponding to a variation of 12 %. The asymmetric design (Fig. 7.13) with the lower resistance has an average temperature of 578 °C for a peak temperature of 603 °C, a difference of about 4.3 %. The temperature profile in the central part of the membrane shows the non-uniform and non-symmetric heat distribution of this design. For the x direction, a temperature differences of about 140 °C between the center and the edges of the cut line is found, corresponding to a variation of 30.8 %. The temperature variation across the y direction is less with a temperature difference of about 70 °C, corresponding to a variation of about 13.6 %. The optimized design (Fig. 7.14) shows a smaller difference between the peak temperature and the average one and a much more uniform heat distribution. The average temperature obtained for a peak temperature of 603 °C is 587 °C, which corresponds to a variation of only 2.6 %. The temperature profile in the y-direction is almost constant with temperatures comprised between 595 and 607 °C. In the y direction the difference between the center and the edges of the cut line is about 40 °C, that is a difference of about 7.1 %. The poly-SiC:N microheater fabricated according to the optimized design and integrated on top of the microchannel of the SiC-based nanoreactor is shown in Fig. 7.15. Compared to a metal layer the poly-SiC:N microheater was patterned in a relatively easy way and maintained the nominal dimensions (section 7.3).





Figure 7.12: (left)Temperature distribution across the whole membrane of the microheater design characterized in Chapter 6, obtained by finite element analysis. (right) Temperature profile along cut lines extending for a length of 150  $\mu$ m from the center of the membrane in the x and y directions; the cut lines are indicated in the left-side graph by dashed lines.



Figure 7.13: (left)Temperature distribution, obtained by finite element analysis, across the whole membrane of the microheater employed for the TEM experiment described in section 6.3.3.3. (right) Temperature profile along cut lines extending for a length of 150  $\mu$ m from the center of the membrane in the x and y directions; the cut lines are indicated in the left-side graph by dashed lines.





Figure 7.14: (left)Temperature distribution across the whole membrane of the optimized microheater obtained by finite element analysis. (right) Temperature profile along cut lines extending for a length of 150  $\mu$ m from the center of the membrane in the x and y directions. The temperature temperature distribution in the microheater area is very uniform; the cut lines are indicated in the left-side graph by dashed lines.


Figure 7.15: (a) Optical and (b) SEM images of the poly-SiC:N microheater designed for obtaining an uniform temperature profile and integrated on top of the microheater windings. (c) SEM image showing the well defined edge of the microheater very close to a window. The plugs and pillars covered and uncovered by the poly-SiC:N layer are also visible.

## 7.5 SiC nanoreactor testing

The fabricated SiC nanoreactors were tested to verify the basic functionality of the single elements, that is: the windows, the microchannel and the microheater.

The windows of the SiC nanoreactor were tested in TEM using the same procedures and instrumentation described in section 4.3.2.2 and section 6.3.3.4. This resulted in TEM images of gold nanoparticles with a resolution down to 0.12 nm. They demonstrate again that the transparency is very good, well beyond the limit of 0.20 nm that is required by catalysis applications. This is the more important because the images were made this time through a pair of  $a-SiC_x$  windows, of a thickness of 15 nm each. As mentioned the high resolution is a result achieved thanks to the small controlled thickness of the  $a-SiC_x$  windows that could be achieved thanks to the properties of this material as explained in section 7.2. The integrity and functionality of the microchannel were tested by using the same instrumentation and procedures described in section 5.3.3.3. All the devices that passed an integrity inspection at the optical microscope proved to be also leak tight, with leak rates below the detection limit of the setup of  $4.0 \times 10^{-9}$ Pa·m<sup>3</sup>/s. This test was performed up to a maximum pressure of 300 kPa. At this pressure flow rates of about  $5.5 \times 10^{-6}$  Pa·m<sup>3</sup>/s were recorded. This can be compared to the flow of the surface micromachined nanoreactor at the same pressure which is about  $6.9 \times 10^{-4}$  Pa·m<sup>3</sup>/s. Therefore, the proposed flow restriction allows for a 125-fold reduction in the flow.



Figure 7.16: High resolution TEM image of a gold nanoparticle loaded inside the SiC-based nanoreactor and imaged through the top and bottom  $a-SiC_x$ windows of 15 nm. The FFT shown in the inset demonstrates that lattice fringes with a spacing of 0.12 nm are visible.

### 7.6 Conclusions

A SiC-based nanoreactor was successfully fabricated by surface micromachining. The basic functionality of its  $a-SiC_x$  windows, ploy-SiC microchannel, and poly-SiC:N micorheater were verified. This demonstrated the possibility of integrating the developed SiC layers in one common process flow, and to achieve a nanoreactor with the performance advantages deriving from the SiC layers. In addition, the advantages of the use of SiC as fabrication material compared to the currently employed material have been presented and discussed. Moreover, modifications to the standard nanoreactor design have been introduced and implemented in the SiCbased nanoreactor. The proposed modifications, advantageous in terms of fabrication and performance, can also be applied to surface micromachined nanoreactors fabricated using conventional construction material. The SiC-based nanoreactor

## CHAPTER 8

## **Conclusions and Future work**

### 8.1 Conclusions

The MEMS nanoreactor is a miniaturized reaction chamber specifically designed to work in combination with TEM microscopes. Such a device is an extremely powerful tool as it enables to perform the otherwise impossible task of studying in-situ interactions between solid nanoparticles and gasses at high temperature and high pressure in TEM. This opens new possibilities for the characterization and development of nanocatalysts, which nowadays play an increasingly important role in the efficient production of synthetic materials and chemicals.

In this thesis the development of alternative construction materials and modified fabrication techniques to improve manufacturing and performance of the MEMS nanoreactor, was reported.

A modular approach has been followed by developing a specific LPCVD SiC layer for each of the three main elements of the nanoreactor. An amorphous SiC (a-SiC) layer was developed for the electron transparent windows, a polycrystalline SiC (poly-SiC) layer for the microchannel, and a nitrogendoped polycrystalline SiC (poly-SiC:N) layer for the microheater. Each of these three layers was integrated in a simplified fabrication flow to verify its suitability and to test its properties. Also, solutions exploiting the properties of the SiC layers, aiming to improve the nanoreactors fabrication process, were successfully implemented. Finally, the possibility to integrate the three newly developed SiC layers into one process was demonstrated

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by fabricating a SiC-based nanoreactor. Here design solutions intended to improve the fabrication and performance of this device were proposed. The main conclusions of this thesis are here summarized.

#### a-SiC<sub>x</sub> for electron transparent windows

- LPCVD a-SiC layers with different stoichiometry and properties can be obtained by varying the flow ratio of the gas precursors (GFR), at a fixed deposition temperature of 760 °C and pressure of 80 Pa.
- The best a-SiC layer for electron transparent windows is deposited by setting the *GFR* to 2.0 (gas flows: SiH<sub>2</sub>Cl<sub>2</sub>= 46 sccm and C<sub>2</sub>H<sub>2</sub> (5% in H<sub>2</sub>)= 454 sccm). These settings result in a carbon-rich layer (a-SiC<sub>x</sub>; x ≈ 1.49) also containing oxygen in a small amount (4.4-5.9%). The oxygen is included due to impurities present in the precursor gasses. The additional oxygen present at the surface is due to the oxidation that takes place during the unloading of the wafers from the LPCVD furnace. The deposition across the wafer is very uniform and the layers are continuous down to a thickness of about 15 nm. The growth rate determined for this layer is almost linear and low enough (about 0.2 nm/min) to perform the accurate deposition of very thin layers as those required for the windows. This layer is extremely smooth with an RMS surface (S<sub>Q</sub>) of about 0.24 nm, it shows excellent chemical inertness and is hydrophilic. The residual stress, is tensile with a value of about 0.7 GPa (for a layer of 40 nm).
- The selected a-SiC<sub>x</sub> layer can be integrated in a process for the fabrication of electron transparent windows embedded on a freestanding SiN<sub>x</sub> membrane. The high chemical inertness of the a-SiC<sub>x</sub> layer permits to control the thickness of the windows, thus resulting in a very high manufacturing yield. This is a great advantage compared to SiN<sub>x</sub> windows that, due to their thinning down during the release in HF-based solutions, suffer from poor control in the final thickness and in possible consequent breakage. The use of a-SiC<sub>x</sub> therefore eases the fabrication process while increasing the reproducibility. During the acquisition of images of nanoparticles in the TEM, the a-SiC<sub>x</sub> windows demonstrates very good transparency allowing resolutions of 0.12 nm, which is close to the limit of the TEM microscope employed. This high transparency is due to the low density of the material (2.7 g/cm<sup>3</sup>) and to the low atomic number of the constituent elements. Moreover, during the imaging no motion of the nanoparticle related

to charging effects is observed. The  $a-\operatorname{SiC}_x$  windows show survival times that are 3 to 9 times longer compared to those of the standard  $\operatorname{SiN}_x$  windows. The high resistance to the TEM electron beam is an advantage as it allows for safer operation, reducing the risk of damage and consequently of gas leak from the nanoreactor to the TEM vacuum. In addition, it extends the operation range of the nanoreactor by allowing experiments with more intense beam. Finally, in some cases the lack of nitrogen (N) compared to  $\operatorname{SiN}_x$  can be advantageous when the nanoreactor is employed in experiments involving N. The proposed  $a-\operatorname{SiC}_x$  layer can thus be advantageously employed for the fabrication of electron-transparent windows.

#### Poly-SiC for nanoreactor microchannels

- LPCVD poly-SiC layers can be deposited at a fixed temperature of 860 °C, and pressure of 80 Pa. By varying the flow ratio of the gas precursors (GFR), layers with different stoichiometry, grain structure, surface, roughness, electrical conductivity and residual stress are obtained. A clear correlation between grain structure and other properties, such as residual stress and electrical conductivity, is present. The mechanical properties are instead only slightly influenced by the GFR.
- The LPCVD poly-SiC layer most suited as construction material for the microchannel of the nanoreactor is deposited by setting the GFRto 5.0 (gas flows: SiH<sub>2</sub>Cl<sub>2</sub>= 100 sccm and C<sub>2</sub>H<sub>2</sub> (5% in H<sub>2</sub>)= 400 sccm). These settings result in a practically stoichiometric layer (Si/C =0.992) that exhibits a low tensile residual stress of about 0.3 GPa. The residual stress is the discriminating property for the selection of this layer, as this is a fundamental requirement for the fabrication of robust and freestanding structures that do not buckle.
- Surface micromachined channels that can self-seal after the sacrificial etch can be realized by using the selected poly-SiC layer. The self-sealing microchannel design was specifically developed to solve the sealing problems typical of the nanoreactor fabrication. The newly developed sealing method is feasible thanks to the elevated chemical inertness of the poly-SiC. Microchannels fabricated with this method show no damages or fractures and are leak-thigh with leak rates below the detection limit of our experimental setup ( $4.0 \times 10^{-9}$  Pa·m<sup>3</sup>/s).

The microchannels are capable of withstanding a pressures of 600 kPa applied at the inlet, thus demonstrating their strength. For higher pressures, the observed failure is due to the lack of anchoring of the supporting pillars of the microchannel ceiling in that area. Finally, the flow of the microchannels can be measured and the experimental data can be fitted to the proposed analytical model. These results prove the effectiveness of the proposed sealing technique and, more in general, the possibility of designing and fabricating surface micromachined channels made of poly-SiC. The poly-SiC layer can be therefore integrated in the fabrication of the nanoreactor microchannel, either in the conventional process or in conjunction with the developed scaling technique.

#### Poly-SiC:N for nanoreactor microheaters

- The *in-situ* doping of the poly-SiC layers can be achieved by the addition of NH<sub>3</sub> during the deposition. By increasing the flow of the doping gas, an increasing amount of N atoms is included in the layers. This takes place at expenses of the C atoms and, consequently, the poly-SiC:N layers result slightly silicon-rich. These layers have a smother surface compared to the poly-SiC ones. Also, all the poly-SiC:N layers present a similar grain structure which is only slightly influenced by the increase of the amount of N atoms. Nevertheless, their resistivity decreases with the amount N atoms included. At the maximum NH<sub>3</sub> flow employed, the amount of N detected in the layers is about 3.6 % and the recorded resistivity is about  $2.5 \times 10^{-3} \Omega \cdot \text{cm}$ . The resistivity of the poly-SiC:N layers is thickness dependent. Layers with a thickness of about 1  $\mu$ m show lower resistivity compared to layers with a thickness of about 600 nm. The layers have higher residual stress when NH<sub>3</sub> flows higher than 3.0 are employed. The resistivity of the poly-SiC:N layers decreases as the temperature increases (i.e. negative temperature coefficient, NTC). The decrease is dependent on the doping level, with the higher the doping the higher the linearity in the decrease. The temperature-resistance characteristic of the as-deposited layers is stable at least up to 700 °C.
- The most suitable poly-SiC:N layers for the fabrication of microheaters are those with the lowest electrical resistivity. These are those having a thickness of about 1  $\mu$ m and deposited using the highest NH<sub>3</sub> flows. These layers present a medium-high residual stress. However,

as they do not need to be employed for the fabrication of continuous freestanding structures, their level of residual stress level is acceptable. The layer exhibiting the lowest resistivity and lowest residual stress is considered as the best candidate to be employed as conductive layer for the microheaters fabrication.

 SiC-based microhotplates integrating a low resistivity poly-SiC:N layer have been successfully fabricated and the temperature-resistance characteristic verified. Two different microheater designs, capable to operate at high temperature without mechanical failure, have been implemented. The instability of the microheater resistance observed for temperatures above 700 °C is caused by thermo-electrical induced dopant activation. A high temperature annealing step ( @ 1000 °C, in N<sub>2</sub>, for 1 hour) stabilizes the resistance of the poly-SiC:N layer integrated in the TEM microhotplates. These annealed microhotplates results much more stable and are capable of operating up to temperatures of at least to 900 °C. The heating experiment performed in the TEM demonstrates the suitability of low resistivity poly-SiC:N layers as heating and sensing material. In addition, the SiC-based TEM microhotplate demonstrates the possibility of integrating all the developed SiC layers in a common fabrication process, as a first step towards the fabrication of a SiC-based nanoreactor.

#### The SiC-based nanoreactor

- The successful fabrication of a SiC-based nanoreactor demonstrates the possibility of integrating the developed SiC layers in a complex process flow. The use of SiC as construction materials results advantageous as it allows a more controllable and reliable fabrication of windows, microchannel and microheater. Due to its chemical inertness, the a-SiC<sub>x</sub> can be employed for the fabrication of windows of a well determined thickness. For the same reason the poly-SiC can be used for microchannels that are not thinned down during the sacrificial etch. The poly-SiC:N can be advantageously utilized as microheater material, as it can be patterned in a controllable way and does not suffer from oxidation. In general, the developed SiC layers can be integrated independently (or in a modular way) in the fabrication of standard surface micromachined nanoreactors.
- The modifications to the standard nanoreactor design implemented

in the SiC-based nanoreactor are advantageous in terms of fabrication and performance. In fact, they make possible to obtain flat electron transparent windows, a flat support membrane, a microchannel with variable section to achieve flow restriction, and an optimized microheater for better heat uniformity. These design modifications can also be applied to surface micromachined nanoreactors fabricated using conventional construction material.

### 8.2 Future Work

The SiC-based devices presented in this thesis require more extensive testing and further development before they can be employed as standard tools for *in-situ* TEM experiments. A few relevant aspects are here listed:

- An integral test to assess the capabilities and performance of the newly developed SiC-based nanoreactor in TEM needs to be performed. For example, known reactions between gas and nanoparticles could be studied. With these experiments, the effectiveness of the proposed flow restriction and the uniform heating should be assessed. More in general, the whole process of preparation and realization of a real *in-situ* experiment should be performed to definitely prove the validity of the proposed design and construction materials.
- The SiC-based TEM microhotplates presented in Chapter 6 should be further tested to validate their suitability to perform *in-situ* heating experiments also in the presence of gasses. These devices could in fact become standard tools for performing *in-situ* experiments in differentially pumped TEMs.
- The self-sealing method proposed in Chapter 5 was not implemented in the SiC-based nanoreactor due to lack of time, as this would have required an additional redesign. However, the use of this sealing technique can be extremely beneficial. The high topography plugs, in fact, makes the process difficult and slow as it requires the photoresist coating in several lithography steps to be formed by spray-coating instead of the faster and more common spin-coating technique. Therefore, it would be interesting to integrate the self-sealing technique in the next nanoreactor design.

Apart from their use in devices for *in-situ* TEM (window devices, microhotplates and nanoreactors), we expect that the SiC layers described in this thesis and the correlated fabrication techniques, will be useful in microfabrication technology in general. In particular, devices operating in harsh environments, characterized by high temperatures, radiation, and/or aggressive chemicals can benefit from the use of these SiC layers. Additional characterization and optimization of these layer is required to fully exploit their potential, among which the ones listed here:

- The self-sealing techniques can be employed for the fabrication of surface micromachined channels and cavities, where the sealing layer needs to be avoided.
- The developed poly-SiC:N microheaters or full-SiC microhotplates can be employed in multiple applications operating in harsh environment. Examples are: gas sensing devices, IR-emitters, and high temperature sensors for automotive engines and aeronautic/aerospace propulsion systems. For example, the use of poly-SiC is currently under investigation for the realization of microthrusters required for the propulsion of small satellites.
- The a-SiC<sub>x</sub> layer, thanks to its high chemical inertness, high continuity at small thicknesses, and the feasible controllable dry etching, can be employed as protective coating for the fabrication and operation of MEMS structures and devices where prolonged exposures to harsh chemicals is required. In addition, the low growth rate makes it extremely suitable for the homogeneous filling and coating of bundles of carbon nanotubes as reported in [150]. Finally the high refractive index and smoothness make the a-SiC<sub>x</sub> layer suitable for the realization of waveguides. In this respect, characterizations to determine the exact refractive index and absorption coefficient of this material need to be done. In particular, ellipsometric models and the necessary measurements for its validation are required. Finally, the accurate determination of the exact conditions at which the oxidation of this material occurs and solutions to prevent it should be investigated as well.
- The poly-SiC layers can be employed for the fabrication of structural freestanding elements and movable structures in MEMS devices. The stress of these layers is tunable, which is advantageous in the design

of devices. More work should be done to achieve layers with lower roughness and on the mechanical characterization (e.g. determination of the yield strength). For example, deposition parameters could be tuned to achieve a very strong layer with low roughness and low tensile stress. Also the influence of the thickness on properties like: stress, stress gradient, roughness, and grain size could be investigated. Moreover, the development of optical models for an easier and faster determination of the thickness of these layer would be very useful. The accurate determination of the thermal conductivity as a function of the temperature would be extremely relevant for the design of devices where heat transfer is involved.

• The poly-SiC:N can be employed as electrically conductive layer and it is especially suited as heating and sensing material. Further characterization is required to understand the inclusion and/or activation of the doping species. For example, a detailed study of the annealing effect on the resistivity as a function of time and temperature is required. The possibilities for further lowering the resistivity by for example increasing the grain size, could be investigated. In addition, the accurate determination of the resistivity-temperature characteristic at temperatures higher than 700 °C is necessary. Characterization work can be done for the determination of mechanical properties such as: elastic modulus, hardness, and yield strength. These properties are especially relevant when this layer is employed in the fabrication of suspended structures. The influence of the thickness on properties like: stress, stress gradient, roughness, and grain size should be investigated. Also, the development of optical models for an easier and faster determination of the thickness of these layers, would be very useful. The accurate determination of the thermal conductivity as a function of the temperature would be extremely useful for the design of devices where heat transfer is involved. Finally, a characterization of the electric contacts formed between the poly-SiC:N layer and metals is necessary.

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## Summary

Due to their scientific and industrial relevance interactions between solid nanostructured materials and gasses is today a subject of extensive studies in science and industry. These interactions play in fact a fundamental role in the emerging research areas of nanoscience and nanotechnology. Many important fields are predicted to benefit from developments in these areas. Among the others, nanocatalysis can be considered as the one currently taking the greatest advantage. The gas-solid interaction phenomena which are at the base of nanocatalysts functioning are characterized by dynamic events taking place at the nanoscale. An essential condition for their study is therefore the availability of characterization tools which allow to reproduce these events while enabling their direct observation with atomic resolution.

Transmission electron microscopes (TEMs) are currently the instruments of choice for the study of nanocatalysts. This type of microscopes enable the direct observation of nanometric samples with atomic resolution and, at the same time, their chemical characterization by means of spectroscopy analysis techniques. However, TEMs typically operate in high vacuum and at room temperature. Therefore, performing *in-situ* characterizations involving gasses at high pressures and elevated temperatures, as it is the case of catalysis reactions, has always been challenging if not impossible. In recent years, great technological advances have been made for performing in *in-situ* characterizations in TEMs, among others the invention of the MEMS nanoreactor. This instrument is a miniaturized reaction chamber specifically designed to work in combination with TEMs. The nanoreactor is transparent to electrons and allows to recreate the gaseous environment of a typical macroscopic chemical reactor inside the vacuum of a TEM.

The important role of nanocatalysts in catalysis and the need of high resolution in-situ characterization techniques required for their study and development are described in Chapter 1. In the same chapter, the state of the art technological solutions allowing in-situ TEM characterizations

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of interactions between solid nanostructured materials and gasses are discussed. The MEMS nanoreactor is finally presented as the most performing solution. Details on the MEMS nanoreactors, realized by means microfabrication techniques, are reported in **Chapter 2**. Here, its main elements are presented and their stringent requirements enumerated and explained. In addition, a brief description of the instrumentation and tools required for the use and operation of the MEMS nanoreactors is included. Finally, with the aim of improving the functionality and the fabrication of this device, the investigation of silicon carbide (SiC) as alternative construction material is introduced as the main topic of this thesis.

In Chapter 3 the low pressure chemical vapor deposition (LPCVD) system employed for the fabrication of different SiC layers and the techniques, tools and methods employed for their characterization are briefly explained. Then, by following a modular approach, the development and testing of three different types of SiC layers suited for each of the three main elements of the nanoreactor is presented.

In Chapter 4 the deposition and characterization of amorphous silicon carbide (a-SiC) layers is described. The depositions were carried out using  $SiH_2Cl_2$  and  $C_2H_2$  as precursor gases and at a temperature of 760 °C. Three different non-stoichiometric layers were obtained by varying the flow ratio of the precursor gasses (GFR). The layers were thoroughly characterized to verify their suitability as construction material for electron transparent windows. The chemical composition, surface morphology, residual stress. chemical resistance, and layer continuity were determined. The layer with the most suited properties as window material was further characterized to verify its amorphousness and wettability. For this layer the growth rate was also determined and the smallest thickness allowing continuity identified. The thinnest continuous layer was then integrated in a microfabrication process for the realization of electron transparent windows. The fabricated windows were tested for integrity, transparency and resistance to the TEM electron beam. These tests not only demonstrated the suitability of the employed a-SiC layer as alternative material for electron transparent windows but also revealed the higher yield and the higher resistance to the electron beam of this layer compared to standard LPCVD low stress silicon nitride  $(SiN_x)$  layers.

For the microchannel of the nanoreactor, polycrystalline SiC (poly-SiC) layers are considered. The deposition and characterization of these layers is presented in Chapter 5. At a deposition temperature of 860 °C, six poly-SiC layers with different stoichiometry and properties were deposited by varying the *GFR*. These were extensively characterized to identify the most suited layer as alternative construction material for the microchannel

of the nanoreactor. Several properties were determined, among these: the chemical composition, the crystallographic structure, the grain and surface morphology, the residual stress, and the elastic modulus. The relationship between grain structure and other properties such as residual stress and electrical resistivity was identified. In addition, a method for the accurate determination of the thickness of these high roughness layers was proposed. Through this thorough characterization the most suited layer for the fabrication of surface micromachined channels was identified. This layer was employed in the fabrication of surface micromachined channels. The design of the fabricated microchannels was such that these could self-seal after the sacrificial etch. This approach is intended to solve the sealing problems typical of the fabrication of surface micromachined nanoreactors. The microchannels successfully passed the integrity, flow, and strength tests, thus proving the effectiveness of the proposed sealing technique and the feasibility of surface micromachined channels made of poly-SiC.

In Chapter 6 the *in-situ* doping of poly-SiC layers and their characterization is reported. The doping was obtained by the addition of ammonia (NH<sub>3</sub>) in the precursor gas mixture. Six different N-doped poly-SiC (poly-SiC:N) layers were obtained by increasing the flow of the doping gas. The increase of the doping gas flow resulted in a progressive increase in the N dopant inclusion in the layers and in a consequent decrease in their resistivity. These layers were characterized in a similar way as for the poly-SiC layers described in Chapter 5. In addition the change of the electrical resistance with the temperature was determined up to 700 °C. The most suited layer for the fabrication of SiC microheaters was identified. Specifically designed SiC-based TEM microhotplates were then realized and thoroughly characterized using dedicated setups. A high temperature annealing step was performed to stabilize the electrical resistance of the poly-SiC:N layer and achieve a stable operating temperatures of at least 900 °C. Finally, the functionality of the SiC-based microhotplates was demonstrated by the successful evaporation of gold nanoparticles in the TEM.

In Chapter 7 the design and fabrication of a SiC-based nanoreactor is presented. The SiC layers described in the previous chapters were integrated in the fabrication flow of the surface micromachined nanoreactor reported in Chapter 2. First the important fabrication improvements deriving by the use of each of the SiC layers are discussed. Then, the design improvements implemented in the SiC-based nanoreactor are presented, making possible to obtain: flat electron transparent windows, a flat support membrane, a microchannel with variable section to achieve flow restriction, and an optimized microheater for better heat uniformity. These improvements overcome fabrication issues and improve the nanoreactor functionality. Finally in Chapter 8 concluding remarks and recommendations for future work are given.

## Samenvatting

Door hun wetenschappelijke en industriële relevantie zijn interacties tussen nanogestructureerde materialen en gassen tegenwoordig het onderwerp van uitgebreid onderzoek in de wetenschap en de industrie. Deze interacties spelen een fundamentele rol in de opkomende onderzoeksgebieden van de nanowetenschap en nanotechnologie. De verwachting is ook dat vele andere belangrijke velden zullen profiteren van ontwikkelingen in deze gebieden. Een daarvan, nanokatalyse, kan worden beschouwd als het veld dat op het moment het meeste voordeel ondervindt. De gas-vaste stof interacties die aan de basis liggen van het functioneren van nanokatalysatoren worden gekenmerkt door dynamische verschijnselen die plaatsvinden op de nanoschaal. Een essentieel vereiste voor het bestuderen van deze verschijnselen is dan ook de beschikbaarheid voor karakterisatiemiddelen die het mogelijk maken om deze te reproduceren en het tegelijkertijd mogelijk maken om ze direct te observeren met een resolutie op de schaal van atomen.

Transmissie elektronen microscopen (TEMs) zijn op het moment de gebruikelijke instrumenten voor het bestuderen van nanokatalysatoren. Dit soort microscopen maakt het mogelijk om nanometrische monsters direct te observeren met een resolutie op de atoomschaal en hen tegelijkertijd chemisch te analyseren door middel van spectroscopische technieken. TEMs opereren echter bij hoog vacuüm en op kamertemperatuur. Dit maakt het uitdagend, zo niet onmogelijk, om een in-situ karakterisatie uit te voeren in een situatie waarbij gassen bij hoge druk en hoge temperaturen betrokken zijn, zoals in het geval van katalytische reacties. In de laatste jaren is grote vooruitgang geboekt in de technologie om in-situ karakterisaties in TEMs uit te voeren, onder andere de uitvinding van de MEMS nanoreactor. Dit instrument is een geminiaturiseerde reactie kamer die specifiek ontworpen is om samen met een TEM te functioneren. De nanoreactor is transparant voor een elektronenbundel en maakt het mogelijk om de gasomgeving van een typische, macroscopische chemische reactor te reproduceren binnen het

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vacuüm van een TEM.

De belangrijke rol van nanokatalysatoren in katalyse en de behoefte aan in-situ karakterisatietechnieken met een hoge resolutie voor het bestuderen en de ontwikkeling van deze materialen is omschreven in Hoofdstuk 1. In hetzelfde hoofdstuk wordt ook de huidige stand van de techniek besproken wat betreft technologische oplossingen die in-situ karakterisaties van interacties tussen vaste nanogestructureerde materialen en gassen mogelijk maken. De MEMS nanoreactor wordt uiteindelijk gepresenteerd als de best presterende oplossing. Details over MEMS nanoreactoren, verkregen doormiddel van microfabricage technieken, zijn beschreven in Hoofdstuk 2. Hier worden hun belangrijkste elementen gepresenteerd en worden de numerieke eisen, welke aan deze elementen worden gesteld, opgesomd en verklaard. Hiernaast wordt een korte omschrijving gegeven van de instrumenten en gereedschappen die nodig zijn voor het gebruik van de MEMS nanoreactor. Uiteindelijk, met het oog op het verbeteren van functionaliteit en fabriceerbaarheid van het apparaat, wordt het onderzoek van silicium carbide (SiC) als een alternatief constructiemateriaal geïntroduceerd als het hoofdonderwerp van deze dissertatie.

In **Hoofdstuk** 3 worden het lage druk chemische damp depositie (LPCVD) systeem dat gebruikt wordt voor de fabricage voor verscheidene SiC lagen en de technieken, gereedschappen en methoden die gebruikt worden om deze lagen te karakteriseren kort omschreven. Hierna worden volgens een modulaire aanpak de ontwikkeling en beproeving van drie verschillende SiC lagen, geschikt voor ieder van de drie hoofdelementen van de nanoreactor, gepresenteerd.

In Hoofdstuk 4 wordt de depositie en karakterisatie van amorfe silicium carbide (a-SiC) lagen omschreven. De deposities werden uitgevoerd met  $SiH_2Cl_2$  en  $C_2H_2$  als precursor gassen bij een temperatuur van 760 °C. Drie verschillende non-stoichiometrische lagen werden verkregen door de verhouding van de precursor gassen (GFR) te variëren. De lagen zijn grondig gekarakteriseerd om hun geschiktheid als constructie materiaal voor transparante elektronenvensters de verifiëren. De chemische samenstelling, morfologie van het oppervlak, verblijvende spanning, chemische weerstand en continuïteit van de laag zijn vastgesteld. De laag met de meest geschikte eigenschappen voor een venstermateriaal werd verder gekarakteriseerd om de amorfheid en bevochtigbaarheid van de laag te verifiëren. Voor deze laag werd ook de groeisnelheid bepaald, evenals de kleinste dikte die continuïteit van de laag mogelijk maakt. De dunste continue laag werd vervolgens geïntegreerd in een microfabricage proces om de transparante elektronenvensters te maken. Deze vensters werden getest op integriteit, transparantheid en weerstand tegen afbraak door de elektronenbundel van de TEM. Deze tests

demonstreerde niet alleen de geschiktheid van de gebruikte a-SiC laag als een alternatief materiaal voor transparante elektronenvensters, maar toonde ook een hogere opbrengst en betere weerstand tegen de elektronenbundel aan dan de standaard LPCVD lage stress silicium nitride  $(SiN_x)$  lagen.

Voor het microkanaal van de nanoreactor zijn polykristallijne SiC (poly-SiC) lagen beoordeeld. De depositie en karakterisatie van deze lagen is beschreven in Hoofdstuk 5. Bij een depositietemperatuur van 860 °C werden zes poly-SiC lagen verkregen met verschillende stoichiometrie door de GFR te variëren. Deze werden uitgebreid gekarakteriseerd om de meeste geschikte laag voor het gebruik als alternatief constructiemateriaal voor het microkanaal van de nanoreactor te identificeren. Verschillende eigenschappen werden bepaald, onder andere: chemische compositie, kristallografische structuur, korrel- en oppervlaktemorfologie, verblijvende spanning en elastische modulus. De relatie tussen korrelstructuur en andere eigenschappen zoals verblijvende spanning en elektrische resistiviteit werd vastgesteld. Hiernaast werd een methode voor de nauwkeurige bepaling van de dikte van deze lagen met een hoge mate van oneffenheid voorgesteld. Door deze grondige karakterisatie werd de meest geschikte laag vastgesteld voor de fabricage van microkanalen doormiddel van oppervlaktebewerking. Deze laag werd gebruikt voor de fabricage van deze microkanalen. Deze microkanalen werden zo ontworpen dat ze zich na het etsen van een offerlaag zelf kunnen dichten. Deze aanpak is bedoeld om de problemen met het afdichten van de kanalen die gewoonlijk optreden bij de fabricage van nanoreactoren door oppervlaktebewerking te voorkomen. De microkanalen doorstonden tests op integriteit, sterkte en stroming met goed resultaat, waarmee kon worden aangetoond dat de voorgestelde afdichtingstechniek effectief is en dat het maken van poly-SiC microkanalen door oppervlaktebewerking haalbaar is.

In Hoofdstuk 6 wordt de in-situ dotering va poly-SiC lagen en de karakterisering van deze lagen gerapporteerd. De dotering wordt uitgevoerd door het toevoegen van ammonia  $(NH_3)$  aan het mengsel van de precursor gassen. Zes verschillende N-gedoteerde poly-SiC (poly-SiC:N) werden verkregen door de toevoer van het doteringsgas op te voeren. De toename van het doteringsgas resulteerde in een progressieve toename van de inclusie van stikstof in de lagen en in een afname in de resistiviteit als gevolg hiervan. De lagen werden gekarakteriseerd volgens een methode vergelijkbaar als die toegepast op de poly-SiC lagen omschreven in Hoofdstuk 5. Daarnaast werd de verandering in de elektrische weerstand bij toenemende temperatuur bepaald tot 700 °C. Deze metingen werden gebruikt om de meest geschikte laag voor het fabriceren van microverwarmingselementen vast te stellen. Specifiek voor de toepassing ontworpen TEM micro-verwarmingsplaatjes werden vervolgens gefabriceerd en

uitgebreid gekarakeriseerd doormiddel van toepassingsspecifieke opstellingen. Een temperingstap werd vervolgens uitgevoerd bij hoge temperatuur om de elektrische weerstand van de poly-SiC:N laag te stabiliseren en om het mogelijk te maken om stabiele werktemperaturen van minstens 900 °C te bereiken. Uiteindelijk werd de functionaliteit van de SiC-gebaseerde verwarmingsplaatjes aangetoond door het verdampen van gouden nanodeeltjes in de TEM.

Uiteindelijk worden in **Hoofdstuk** 8 concluderende opmerkingen en aanbevelingen voor verder werk gegeven.

# List of Publications

### **Journal Papers**

- G. Fiorentino, B. Morana, S. Forte, and P. M. Sarro, "Role of atomic layer deposited aluminum oxide as oxidation barrier for silicon based materials," Journal of Vacuum Science & Technology A, vol. 33, no. 1, p. 01-142, 2015.
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# About the author

Bruno Morana received both the B.S.c. and M.Sc. degrees in electronic engineering from the Polytechnic of Milan, Milan, Italy, in 2007. During his Master's program he attended the School of Telecommunication Engineering of the Polytechnic University of Madrid, Madrid, Spain. There he joined the Electronic Technology Department to perform his Master's thesis work and successively to work as a Researcher. His Master's thesis and research activities focused on the fabrication and characterization of Si and SiGe nanocrystals embedded in SiO<sub>2</sub> thin films. In 2008, he moved to The Netherlands to work as a Researcher in the Laboratory of Electronic Components Technology and Materials, Technical University of Delft, Delft, The Netherlands. There he focused on the development and optimization of procedures for the ultra-high vacuum-compatible assembly of MEMS nanoreactors. This work was performed in the Delft Institute of Microsystems and Nanoelectronics (DIMES). In 2009 he enrolled in the Ph.D. program of Technical University of Delft to follow his work on MEMS nanoreactors in DIMES laboratories. During the Ph.D. he focused on the development of silicon carbide layers for the fabrication of the new generation of surface micromachined nanoreactors. Since 2014 he has been working for DIMES laboratories now Else Kooi Laboratories (EKL). In EKL he is currently responsible for the small-scale production of MEMS nanoreactors and the design, fabrication, and testing of micromachined devices. His research interests include development of thin films and of microfabrication technologies.

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#### Stellingen

## Behorende bij het proefschrift

Silicon Carbide thin films for MEMS Nanoreactors for in-situ Transmission Electron Microscopy

#### door

#### Bruno Morana

1) De MEMS nanoreactor is een zeer krachtig instrument dat het mogelijk maakt om de interacties tussen gassen en vaste nanogestructureerde materialen *in-situ* te bestuderen bij hoge temperatuur en druk in TEMs (dit proefschrift).

2) Dunne a-SiC<sub>x</sub> lagen kunnen niet alleen goed gebruikt worden als transparante vensters voor transmissie elektronenmicroscopie, maar ook als materiaal voor de fabricage van MEMS apparaten in het algemeen (dit proefschrift).

 Zelf-verzegelende microkanalen verkregen door oppervlaktebewerking zijn een goed alternatief om de negatieve effecten te voorkomen die veroorzaakt worden door de anders noodzakelijke afdichtingslagen (dit proefschrift).

4) De eigenschappen van LPCVD verkregen SiC lagen, kunnen op een gecontroleerde wijze worden geregeld door aanpassing van de depositieparameters. De lagen kunnen worden geoptimaliseerd voor gebruik in de hoofdelementen van een nanoreactor, en kunnen worden geïntegreerd om een SiC versie van de nanoreactor te maken(dit proefschrift).

5) Het gebruik van a-SiC<sub>x</sub> in combinatie met CNTs maakt het mogelijk om structuren te creëren met een grote hoogte-breedteverhouding en regelbare mechanische eigenschappen.

6) Bij het fabriceren van MEMS apparaten kunnen creativiteit en goede handvaardigheid tekortkomingen in een ontwerp goedmaken.

7) In de Dimes cleanroom is de uitspraak "het probleem is je wafer" 99.0% van de tijd onjuist.

8) "Zonder muziek zou het leven een vergissing zijn." (Friedrich Nietzsche)

9) "Ik geloof dat buitenaards leven vrij gewoon is in het universum, maar intelligent leven minder. Sommigen beweren dat het op de planeet Aarde nog niet is ontstaan." (Stephen Hawking)

10) Een geherformuleerd Siciliaans gezegde stelt: "cu nasci quatratu, 'un pò mòriri tunnu". ("Wie vierkant is geboren kan niet als cirkel sterven.")

11) De stellingen van een proefschrift over microfabrikage technology moeten uitgeprint worden op cleanroom papier.

12) "Neem het leven niet te serieus. Je overleeft het toch niet." (Elbert Hubbard)

Deze stellingen worden opponeerbaar en verdedigbaar geacht, en zijn zodaning goedgekeurd door de promotor prof. dr. P.M. Sarro.

### Propositions

#### Accompanying the dissertation

Silicon Carbide thin films for MEMS Nanoreactors for in-situ Transmission Electron Microscopy

by

#### Bruno Morana

1) The MEMS nanoreactor is a very powerful tool enabling *in-situ* studies of interactions between gasses and solid nanostructured materials at elevated temperatures and pressures in TEMs (this thesis).

2) Thin layers of a-SiC<sub>x</sub> can be advantageously employed not only as electron transparent windows for transmission electron microscopy, but also in the fabrication of MEMS devices in general (this thesis).

3) Self-sealing of surface micromachined channels represents a valid fabrication alternative to avoid the negative effects caused by the otherwise necessary sealing layers (this thesis).

4) The properties of the SiC layers deposited by LPCVD can be modified in a controlled way by tuning the deposition parameters. The layers can be optimized for their use as main elements of a nanoreactor and integrated to realize a SiC-based version (this thesis).

5) Using a-SiC<sub>x</sub> in combination with CNTs allows the formation of high aspect ratio structures with tuneable mechanical properties.

6) When fabricating MEMS devices, creativity and good manual skills can counterbalance design shortcomings.

7) In Dimes cleanroom, the statement "the problem is your wafer" is 99.0 % of the times untrue.

8) "Without music, life would be a mistake." (Friedrich Nietzsche)

9) "I believe alien life is quite common in the universe, although intelligent life is less so. Some say it has yet to appear on planet Earth." (Stephen Hawking)

10) A rephrased old Sicilian proverb says: "cu nasci quatratu, 'un pò mòriri tunnu". ("Who is born square cannot die as a circle").

11) Propositions for a thesis on microfabrication technology must be printed on cleanroom paper.

12) "Do not take life too seriously. You will never get out of it alive." (Elbert Hubbard)

These propositions are regarded as opposable and defendable, and as such have been approved by the supervisor prof. dr. P.M. Sarro.