Barium disilicide: Development of a novel, low cost and earth abundant absorber material for thin film solar cell applications

**Fechnische Universiteit Delft** 

S. van Doorene



Challenge the future

## Barium disilicide: Development of a novel, low cost and earth abundant absorber material for thin film solar cell applications

by

## S. van Doorene

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Supervisor: Dr. O. Isabella Thesis committee: Prof. dr. M. Zeman, TU Delft Dr. A. J. Böttger, TU Delft MSc. R. Vismara, TU Delft MSc. Y. Tian, TU Delft

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## Abstract

Thin film photovoltaic (PV) technology has the advantage of absorbing light and producing electricity by using less material with respect to the crystalline silicon (c-Si) counterpart. Therefore, thin film technologies could potentially be able to generate electricity at a lower price. This line of reasoning has led to an ongoing search for (new) high efficient and cheap photovolatic material(s). From the alkaline-erath metal di-silicide, orthorhombic barium disilicide has sparked recent interest. Studies have shown that this material exhibits good electrical properties, a high absorption coefficient and a bandgap of 1.3 eV, which is tunable up to 1.4 eV by Sr doping, thereby matching the solar spectrum. However, these studies have mainly been performed on molecular beam epitaxially grown material. Since this is a very slow production technology, it is not suitable for (low cost) large scale production. Therefore, this thesis aims to contribute to the development of low cost high quality barium disilicide thin films, resulting in the following research quations:

How to develop high quality barium disilicide suitable for thin film solar cell applications, using radio frequency magnetron sputtering as a low cost deposition technique?

In the first part of this report, the material properties, demonstrated in published work, are reviewed in more detail. Furthermore, previous studies in which barium disilicide has been deposited by RF magnetron sputtering, are discussed. Also, the equipment used for material deposition and characterization, are reviewed.

In the first experimental chapter, the thickness uniformity of deposited barium disilicide is treated. The theory predicts higher deposition rates and less uniform material thicknesses for shorter target to substrate distances (TSD). The optimal TSD is determined to be 135 mm, resulting in a deposition rate of 6.63 nm/s.

In the following chapters of the report, the properties of room temperature and high substrate temperature deposited material are discussed. The room temperature deposited material is determined to be amorphous and degenerate. Consequently, the material exhibits high absorbance at low photon energies, a high charge carrier concentration in the order region of  $10^{21}$  cm<sup>-3</sup> and low carrier mobility in the range of 0.28 - 0.65 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The material deposited at a target to substrate distance of 135 mm has a Ba to Si ratio of 1:2, which matches the ideal ratio of barium disilicide.

Depositing the material at high substrate temperatures, improves the material quality. The best material is obtained at the maximum achievable substrate temperature of 450 °C, while it is expected that higher substrate temperatures result in even better material quality. The obtained material is amorphous directly on top of the substrate, while it is (partially) crystalline at the surface. Consequently, the absorbance is still high for low photon energies, thus there is no indication of an optical bandgap. On the other hand, the charge carrier concentration is already several orders of magnitude lower compared to the room temperature material, with a charge carrier concentration in the region of  $10^{17}-10^{18}$  cm-3. This is accompanied by an increase in the charge carrier mobility to 7.69 - 12.6 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. However, the activation energy indicates a degenerate material, which is contradictory to the results of the Hall setup. Nevertheless, the existence of semiconducting material is demonstrated by an illuminated over dark conductivity ratio larger than 1.

Post-growth annealing of the material has been investigated as a tool to further enhance the material quality. The results indicate an increase in crystallinity upon post-growth annealing with temperatures over 550 °C. The optimal annealing strategy is proven to be a combination of both temperature and time. In this work, post-growth annealing at 700 °C resulted in the best material properties. This result is however affected by 2 important phenomena that occur during the annealing process. Firstly, the high temperature crystallizes the material, improving its quality. On the other hand, the high temperature results in surface oxidation. In this process barium is preferentially oxidized over silicon, resulting in a barium and oxygen rich surface material and a silicon rich bottom material. This oxidation is detrimental for the overall material quality. The oxidation results in the formation of pc-Si and thereby in a reduced fraction of orthorhombic barium disilicide in the sample. Nevertheless, post-growth annealing has improved the quality of both room temperature deposited and high temperature deposited material.

The best RT annealed samples exhibit an indirect optical bandgap of 0.99 eV, with a corresponding direct bandgap of 1.87 eV. The best HT annealed one indicates an indirect bandgap of 1.10 eV and a direct bandgap of 1.42 eV. This is close to the in literature reported indirect and direct bandgap of 1.25 and 1.37 eV, respectively. On the other hand, the electrical properties of the RT annealed material are better than the HT annealed material, with a charge carrier concentration in the region of  $10^{16}$  and  $10^{18}$  cm<sup>-3</sup>, respectively and a charge carrier mobility in the region of 7 - 47 and 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. Furthermore, the illuminated over dark conductivity increased after annealing, suggesting an improvement of the semiconducting behaviour.

This leads to the conclusion that the best strategy for obtaining high quality orthorhombic barium disilicide is by post-growth annealing the material. However, the main challenge is to investigate surface oxide preventive measures, due to its detrimental effect on the material. On the other hand, deposition of the material at even higher substrate temperatures than was researched in this work, could possibly result in high quality thin film material without the need for post-growth annealing.

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## Preface

This master thesis report is the final aptitude test of the Sustainable Energy Technology master's degree program at Delft University of Technology. The work was conducted at the Photovoltaic Materials and Devices group, which is a research group at the Delft University of Technology. In this section of my report, I would like to thank all the people that helped me during this 9 month period of hard work.

In particular I would like to thank my daily supervisor's Robin Vismara and Yilei Tian. Both of you were always there in case I needed some advice. Also, the fruit-full discussions with respect to the interpretation of the results and helping me decide which direction to go to, were of great help during this project. This work greatly benefited from the enthusiasm of my supervisor Dr. O. Isabella. and his determination to make this project a success. You were able to motivate me in times where I needed an extra boost. Thank you for your guidance and supervision. Furthermore, I would like to thank Martijn Tijssen and Stefaan Heirman for instructions, guidance and keeping all equipment up and running of the clean rooms and measurement rooms, respectively. I am also thankful for the measurements performed by Dr. P. Sutta at the new technologies research centre of the university of West Bohemia in Pilsen, Czech Republic and the measurements performed by this colleagues at the university of Bratislava in Slovakia. Further, I would like to thank my fellow student Aditya Chaudhary, who was my sparring partner throughout the project. Besides, I would like to thank Prof. Dr. M. Zeman and Dr. A.J. Böttger for complementing my graduation committee and also for their time and effort in judging my work.

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*S. van Doorene Delft, May 2017* 

# 1

## Introduction

In this era it is widely accepted that humanity faces a major problem: 'Global warming.' Relative to the pre industrial age, the atmosphere temperature has already increased by 0.6 °C at the beginning of the 21st century [13]. Predictions for temperature change at the end of the 21st century show a total increase between 1.7 up to 3.5 °C depending on the scenario [13]. According to the fifth assessment report (AR5) of the IPCC [13] the main cause of global warming is the anthropogenic greenhouse gas (GHG) emissions and in particular the emission of  $CO_2$  gas. Also in this report it is emphasised that the resulting climate change due to global warming will create new risks and increase existing ones for mankind. This could manifest in increased human mortality and economic losses.

Industrial processes and the combustion of fossil fuels for energy, electricity and heat are the largest contributors to the total GHG emissions [13]. Lowering GHG emissions for these sectors could make a significant contribution to the mitigation of global warming. Sustainable energy technologies (SETs) have a huge potential to lower GHG emissions. There are various SETs available such as solar energy, wind, geothermal and biomass. Solar energy has the largest energy harvesting potential of all the SETs, with a total of 120,000 TW of solar energy reaching the earth's surface [14]. Comparing this to the the global primary energy demand of 2012, which was approximately 16-18 TW (525 EJ/year) [15], it is evident that solar energy has the potential to become one of the biggest energy sources in the global energy mix.

One of the major challenges is to generate electricity from photovoltaics at a price comparable to electricity generated by fossil fuels. Topics in the photovoltaic (PV) field to accomplish this objective are: increasing the efficiency of PV technologies and lowering production costs. The costs of silicon wafers still make up a large portion of the cell's price for crystalline silicon technologies [1]. One possibility for reducing these costs is reducing material usage. This line of reasoning has actually led to the development of thin film silicon technology [3]. Economics tells us that prices go up if the demand is high and the supply is scarce. Consequently it is desired to use materials in PV technology which are abundant in order to scale up to the required energy scale. Since thin film technologies like CIGS and Cadmium telluride (CdTe) require rare elements indium (In) and tellurium (Te) respectively, make these technologies less favourable for terawatt scale usage [6]. This argumentation has triggered the search for new semiconducting materials to be exploited in the thin film photovoltaic industry. One example is the study of alkaline-earth-metals di-silicides and di-germanides [2]. One particular semiconducting material that seems to have the potential to fulfil these requirements is barium disilicide (BaSi<sub>2</sub>). Recent studies have shown that orthorhombic BaSi<sub>2</sub> has a high absorption coefficient [16],[3], good electrical properties for thin film solar cell applications [16], [17] and a bandgap of approximately 1.3 eV [16], [18]. With these properties BaSi<sub>2</sub> has a good basis for high efficient thin film solar cell applications.

Most of these studies are based on molecular beam epitaxy (MBE) grown BaSi<sub>2</sub> absorber material [11]. While MBE is a great tool for experimental work due to the precise control of the composition of the grown material [19], it is a relatively slow growth process [6]. For future potentially large scale applications of BaSi<sub>2</sub>, other deposition techniques are of interest. Currently the photovoltaic materials and devices (PVMD) group at TU Delft University focuses on the development of thin film BaSi<sub>2</sub> layers deposited by radio frequency (RF) magnetron sputtering. Magnetron sputtering (MS) is currently a popular deposition technique for thin film growth. The technique is efficient and stable, while it is

also scalable to industrial levels [20]. However there are only few studies regarding RF magnetron sputtered  $BaSi_2$  thin films [11]. Furthermore, not many solar cells containing a  $BaSi_2$  absorber layer have been fabricated. At the time of writing the highest efficiency reported is 9.9% for a heterojunction (HTJ) device consisting of c-Si wafer with a thin  $BaSi_2$  absorber layer on top [21]. Theoretically, the efficiency of a  $BaSi_2$  homojunction device should be able to reach higher values of up to 25% for a 2 µm thick  $BaSi_2$  homojunction device [16]. It is evident that further research is needed to bridge the gap between the theoretically possible and the practically achieved efficiency. This thesis therefore aims to contribute to the development of high quality  $BaSi_2$  thin films for photovoltaic applications.

The goal of this thesis results in the following research question, which is treated in this report:

How to develop high quality barium disilicide suitable for thin film solar cell applications, using radio frequency magnetron sputtering as a low cost deposition technique?

The following five sub-questions are researched in order to answer the research question:

- What are the properties of orthorhombic barium disilicide suitable for thin film solar cell applications and what is the state of the art in this field?
- 2. How to deposit the most uniform barium disilicide films by means of radio frequency magnetron sputtering?
- 3. How does this most uniform room temperature sputtered material perform optically and electrically?
- 4. How does high temperature deposition change the quality of the barium disilicide?
- 5. How does post-growth annealing change the material quality?

The first sub-question is researched by means of a literature review. The other four sub-questions are researched through experiments. The experiments are conducted at the Else Kooi Laboratory (EKL), which is located at the TU Delft. A RF magnetron sputtering machine (Kurt J. Lesker) is used to deposit barium disilicide thin films. The Kurt J. Lesker is equipped with a 3 inch barium disilicide target manufactured by Tosoh Corporation, Tokyo Japan. The target to substrate distance can be varied between 65 mm and 160 mm. The substrate temperature can be controlled from 25 °C up to approximately 450 °C during deposition. Furthermore, for annealing purposes a Carbolite AAF 11/7 furnace is available, which is equipped with nitrogen backing gas flow and is able to reach temperatures up to 1100 °C.

In order to answer the research question, the report is structured as follows. The first chapter is the introduction chapter, which introduces the topic and justifies the relevance of this research. Since the topic concerns a novel absorber material, the second chapter consists of an extensive literature review on the material properties and the state of the art. Chapter 3 discusses the equipment which is used for material deposition and characterization during this research. This is followed by chapter 4, which treats the thickness uniformity (or uniformity in short) of the deposited thin films and the deposition rate. The uniformity is an important aspect of the films for further experiments because it shows which area of the film is within certain thickness ranges. The thickness of the film obviously affects the results of the (characterization) measurements. This effect is also important with the view of future research on barium disilicide based solar cells. In chapter 5 the optical and electrical properties of room temperature deposited barium disilicide are discussed. Since the most uniform target to substrate distance doesn't result in the highest temperature, chapter 5 also discusses the properties of RT deposited films with a smaller target to substrate distance (T-S). Thereafter in chapter 6 the results of high temperature depositions are treated. Depositing at elevated temperatures is a method to obtain (more) crystallized material. Another method for obtaining (more) crystallized material is post-growth annealing of the material, which is therefore discussed in chapter 7. Finally, in chapter 8 the conclusions of this work and the outlook for further research are set forth.

# 2

# Properties of barium disilicide suitable for thin film photovoltaic applications

Although research studies on  $BaSi_2$  go back to at least 40 years, there is nowadays an increased interest in this compound for possible integration in thin film photovoltaics. Only recently, published work presented theoretical data regarding the band structure, which is in good agreement with experimental data of  $BaSi_2$  [2], while this has been attempted previously with less accurate results [22, 23]. In this chapter of the report the characteristics of  $BaSi_2$  are presented, based on the most recent theoretical and experimental results, obtained from literature. This sections first treats the material properties in terms of crystal structure, band diagram and resulting optical and electrical characteristics of the material. After these fundamental properties, the production of barium disilicide by RF magnetron sputtering is reviewed.

### 2.1. Material properties

In this section the material properties of orthorhombic barium disilicide are discussed. First the crystal structure and band structure are treated. Thereafter, the optical and electrical properties are analyzed. This is followed by a section elaborating on the influence of the grain boundaries on the material properties. Furthermore, the recombination mechanism and the various dopants are discussed. Lastly, the abundance of the elements is reviewed.

#### 2.1.1. Crystal structure

Barium disilicide is a compound that contains barium and silicon atoms and the material is part of the alkaline-earth-metal silicides [2]. There are five intermediate barium silicide phases that can be formed at room temperature:  $Ba_2Si$ ,  $Ba_5Si_3$ , BaSi,  $Ba_3Si_4$ ,  $BaSi_2$  [24, 25]. The heat of formation of  $BaSi_2$  is the third highest of these phases. The heat of formation is higher for both  $Ba_3Si_4$  and BaSi, while it is lower for  $Ba_2Si$ ,  $Ba_5Si_3$  [24].

There are three main crystal structures known for  $BaSi_2$ : cubic, trigonal and orthorhombic [2, 26]. The crystal structure of the cubic and trigonal phases are depicted in published work of Imai et al. [27]. The properties of  $BaSi_2$  depend on its crystal structure. The orthorhombic crystal structure is the most suited for utilization in photovoltaics because of its bandgap of 1.1-1.3 eV and due to its stability at room temperature and ambient pressure [2]. The trigonal and cubic  $BaSi_2$  phases are only formed at higher pressures and temperatures and are metastable at ambient conditions [26, 28].

The unit cell of orthorhombic  $BaSi_2$  is depicted in figure 2.1 and contains 24 atoms. The  $BaSi_2$  crystal has 2 crystallographically-inequivalent sites for barium:  $Ba^{(1)}$  and  $Ba^{(2)}$ , while is has 3 crystallographically-inequivalent sites for silicon:  $Si^{(3)}$ ,  $Si^{(4)}$  and  $Si^{(5)}$  [1]. In this material the silicon is bound in isolated tetrahedrons and is considered to be a Zintl anion. Orthorhombic  $BaSi_2$  is thus a Zintl phase [4]. A Zintl phase is described as the transition between metallic and ionic bonding of an alkali or alkaline



Figure 2.1: Unit cell of orthorhombic barium dislicide, source: [1]

earth metal with a metal, semimetal or semiconductor [29, 30]. In other words, a Zintl phase is an intermetallic phase with an ionic bonding component [29]. A more elaborated definition of a Zintl phase compound can be found in [30]. In this material the barium atoms are positively charged ( $Ba^{2+}$ ), while the Si<sub>4</sub> tetrahedra are negatively charged ( $[Si_4]^{4-}$ ) [31].

The orthorhombic  $BaSi_2$  unit cell has the following dimensions: a = 0.89 nm, b = 0.68 nm and c = 1.16 nm [2, 32]. From the unit cell it is calculated that  $BaSi_2$  contains approximately  $3.4 \cdot 10^{22}$  atoms/cm<sup>-3</sup>, in which there are approximately  $1.1 \cdot 10^{22}$  atoms/cm<sup>-3</sup> barium and approximately  $2.3 \cdot 10^{22}$  atoms/cm<sup>-3</sup> silicon. Finally, it is reported that the density of the material is 5.14 g/cm<sup>3</sup> [16].

#### 2.1.2. Band structure

Theoretical and experimental studies have shown that the upper valence band (VB) mainly consist out of Si-3p states, while Ba s,p,d and Si-3s states are present to a lesser extend [2, 16, 33]. The conduction band consist out of mainly Ba-d states and to a lesser extend Si-s and p states [2, 16, 33]. The density of states (DOS) derived by Kumar et al. [2], is presented in figure 2.2. The reported effective density of states at the valence band is  $N_V = 2.0 \cdot 10^{19} \text{ cm}^{-3}$  and is  $N_C = 2.6 \cdot 10^{19} \text{ cm}^{-3}$  at the conduction band [16].



Figure 2.2: Density of states of orthorhombic BaSi<sub>2</sub>, source: [2]



Figure 2.3: Band diagram of orthorhombic BaSi<sub>2</sub>, source: [2]

In figure 2.3 the band diagram deduced by kumar et al. [2] is presented. From the band diagram it is observed that orthorhombic  $BaSi_2$  has an indirect bandgap of  $E_g^{indirect} = 1.25$  eV. Due to the relatively flat conduction and valence band, the direct bandgap is only 0.12 eV larger than the indirect bandgap:  $E_g^{direct} = 1.37$  eV [2]. This theoretically derived bandgap agrees with various other experimentally determined bandgaps of 1.1 up to 1.3 eV [2, 16, 18, 34]. The large discrepancy in the experimentally determined optical bandgaps are attributed to measurement errors due to the relatively flat conduction band and by possible strain effects on the bandgap [2].

Furthermore, the material has an electron affinity of  $\chi = 3.3 \text{ eV}$  [18, 35, 36]. The Fermi level is positioned 0.22 eV below the conduction band for unintentionally doped (intrinsic) BaSi<sub>2</sub>:  $\phi_s \approx 3.5 \text{ eV}$  [4], resulting in an (intrinsic) n-type material. This (intrinsic) n-type conductivity of BaSi<sub>2</sub> is attributed to silicon vacancies in the lattice [1].

#### **2.1.3.** Optical properties

Numerous studies have shown that  $BaSi_2$  has a high absorption coefficient, with reported values of  $3 \cdot 10^4$  cm<sup>-1</sup> [16] up to  $10^5$  cm<sup>-1</sup> [16, 35] at a photon energy of 1.5 eV. Multiple absorption coefficient diagrams of the material can be found in published work: [2, 3, 11, 16, 18, 37, 38]. The absorption coefficient ( $\alpha$ ) and the complex refractive index published by Vismara et al. [3] are adopted and presented in figure 2.4. In figure 2.4a the absorption coefficient of  $BaSi_2$  is compared with other thin film technologies.

It is observed that  $BaSi_2$  outperforms almost all other thin film technologies between the spectral range of 350 - 1200 nm. At most wavelengths the absorption coefficient is 1 to 2 orders of magnitude larger than that of c-Si. Consequently, a  $BaSi_2$  based absorber layer can be much thinner than a c-Si absorber layer in order to absorb an equal amount of light. Only CIGS has a higher absorption coefficient for low photon energies, corresponding to wavelengths of 650 nm and higher.

The complex refractive index, consisting of the refractive index (n) and extinction coefficient ( $\kappa$ ), is depicted in figure 2.4b for a wavelength range of 300 - 1200 nm. It is observed that the refractive index reaches its maximum value of approximately 4.5 between 450 and 600 nm, while for the longer wavelengths the refractive index decreases to roughly 3.5.



Figure 2.4: Absorption coefficient of  $BaSi_2$  compared with other commonly used thin film technologies (left) and the complex refractive index of  $BaSi_2$  (right), source: [3]

#### Photoresponsivity

Photoresponsivity is an important parameter to compare efficacy of photovoltaic cells. Photoresponsivity measures the capability of a device to convert photons into charge carriers, which are thereafter collected, as function of the wavelength. In literature, external quantum efficiency (EQE) values of 60% [39] and 75% [40] have been reported for  $BaSi_2$  based solar cells for bias voltages of 2.0 and -1.0 V, respectively. In these setups, the  $BaSi_2$  absorber layer was 400 nm and 600 nm thick, respectively. Du et al. mention that the internal quantum efficiency (IQE) can be improved up to 90% by increasing the absorber layer thickness to 3 µm [39] andthat the EQE can be increased by improving the surface passivation of  $BaSi_2$  [40].

#### **2.1.4.** Electrical properties

As previously mentioned, unintentionally doped (intrinsic) barium disilicide is a n-type material and thus the electrons and holes are the majority and minority charge carriers, respectively. The lowest reported electron densities of the intrinsic material is:  $5 \cdot 10^{15} - 1 \cdot 10^{16}$  cm<sup>-3</sup> [16, 18]. The squared intrinsic carrier concentration  $(n_i^2)$  at room temperature is calculated to be  $n_i^2 = 8 \cdot 10^{16}$  cm<sup>-3</sup> [16]. By using the effective density of states at the conduction band given in section 2.1.2, assuming an electron concentration at thermal equilibrium of  $1 \cdot 10^{16}$  cm<sup>-3</sup> and using equation 3.21, it is possible to obtain a calculated Fermi level that is positioned 0.20 eV below the conduction band. This agrees with the value reported by Baba et al. [4].

Undoped BaSi<sub>2</sub> has a relatively large diffusion length and long lifetime of the minority charge carriers. The diffusion length is reportedly  $L_h \approx 8 - 10 \mu m$  [16, 41] for 300 - 500 nm thick epitaxially grown films. The lifetime is  $\tau_h \approx 8 - 10 \mu s$  [16] for a 500 nm thick epitaxially grown film, with a 3 nm thick Ba or Si capped surface layer for surface passivation. These diffusion lengths and lifetimes are effective values, meaning that it is affected by the surface and interface recombination of the tested sample [31]. Hara et al. [31] have estimated that the bulk minority carrier diffusion length, in which there is no contribution of surface and interface recombination, is approximately  $L_b \approx 60 \mu m$  and the bulk minority carrier lifetime is  $\tau_b \approx 14 \mu s$ , both under the assumption that the mobility of the minority charge carriers is  $\mu_h = 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .

Furthermore, the sum of the surface recombination ( $S_0$ ) and interface recombination ( $S_w$ ) is estimated to be:  $S_0 + S_w = 8.3$  cm/s, which is of the same order of magnitude as passivated Si surface [31]. In the same study, it is reasoned that the relatively low surface recombination can be attributed to the ionic bonding mechanism in BaSi<sub>2</sub>. In contrast to Si, there are no dangling bonds, which act as recombination centres, on the surface of a perfect ionic crystal. Instead, the surface recombination is attributed to the Ba<sup>2+</sup> cations and [Si<sub>4</sub>]<sup>4-</sup> anions on the surface, which act as trap states for the minority charge carriers. Due to the low surface recombination, the surface trap levels are expected to be close to the band edges [31]. Although the surface recombination can be low, it depends on the quality of the surface. Suemasu [16] reported a large variety in the minority carrier lifetime and related

this to the quality of the surface. Passivating the surface of the material with a 3 nm Ba or Si capping layer, results in a constantly large carrier lifetime due to the reduced surface recombination [16].

Furthermore, it is reported that the mobility of electrons of intrinsic ( $n_0 = 5 \cdot 10^{15}$ ) BaSi<sub>2</sub> at room temperature is  $\mu_e = 820 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  [18]. The hole mobility is assumed to be in the order of  $\mu_h = 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  [31, 42] for p-type ( $p_0 = 1 \cdot 10^{16} - 1 \cdot 10^{17}$ ) doped material. By using the Einstein relationship:  $D_n/\mu_n = D_p/\mu_p = k_B T/e$  [43], the corresponding diffusion coefficients are  $D_e = D_n \approx 21 \text{ cm}^2/\text{s}$  and  $D_h = D_p \approx 2.6 \text{ cm}^2/\text{s}$ , respectively. However, these values are only true for the aforementioned carrier concentrations and temperatures, since the diffusion coefficient is affected by both these parameters.

#### **2.1.5.** Grain boundaries

The effect of grain boundary (GB) size and orientation was investigated for  $BaSi_2$  films grown on Si(111) substrates [4, 41, 44–47] and on Si(001) substrates [17, 48]. In all studies  $BaSi_2$  was a-axis oriented epitaxially grown.

BaSi<sub>2</sub> on Si(111) has 3 epitaxial variants that are rotated by 120° about the surface normal [41, 44]. The grain boundaries mostly consists of BaSi<sub>2</sub> {011} planes [41]. In the study of Baba et al. [41], the grain sizes were relatively small, with an approximate length of 0.1 - 0.3  $\mu$ m. Nevertheless, the diffusion length of minority charge carriers in the BaSi<sub>2</sub> layer was much larger: approximately 10  $\mu$ m [41]. It was presumed that the grain boundaries act as recombination centres, which is typically the case for semiconductors, and therefore multiple studies aimed to increase the grain size. Larger grain sizes, in excess of 4.0  $\mu$ m, were achieved by changing the MBE parameters [46] and by post-growth annealing [45].

Another study presumed that the GBs do not act as recombination centres, since the diffusion length is 2 orders of magnitude larger than the length of the grain boundaries [4]. In this study the potential variations around the GBs were investigated for BaSi<sub>2</sub> layers on Si(111) and on Si(001). The grain boundaries of the BaSi<sub>2</sub> layer on Si(111) shows downward bending in the band diagram, while the BaSi<sub>2</sub> layer on Si(001) indicates upward bending in the band diagram, as is depicted in figure 2.5 [4]. As mentioned before, in the case of BaSi<sub>2</sub> on Si(111) the grain boundaries mostly consist out of (011) and (0-11) planes [4]. The downward bending is explained by the observation that the (011)/(0-11) planes consist only of Ba atoms [4]. These Ba atoms are positively charged in the crystal, as is described in section 2.1.1. Therefore Baba et al. [4] speculate that this is the reason for the higher potential barrier for the holes, which are thus repelled towards the grain interior. Consequently, this reduces the recombination at the GB and thereby also explains the large diffusion length and lifetime [4]. The average barrier height is measured to be approximately 30 meV [4].



Figure 2.5: Band banding at the GBs for the (011) planes consisting of  $Ba^{2+}$  ions left and for the (001) planes consisting of  $[Si_4]^{4-}$  tetrahedra right, source: [4]

Moreover, in the study of Takabe et al. [47], they show that the minority carrier lifetime does not depend on the size of the grains, but highly depends on the surface condition [47]. Mirror like surfaces result in a low minority carrier lifetime of approximately 0.4  $\mu$ s, while cloudy surfaces result in much higher minority carrier lifetimes of roughly 8  $\mu$ s [47]. They were unable to control the surface quality and thus they were not able to control the minority carrier lifetime by in situ capping of the surface by a 3 nm Ba or Si layer [47], which is also mentioned in section 2.1.4.

Another study attempted to increase the grain size by growing  $BaSi_2$  on Si(001) substrates [48]. BaSi<sub>2</sub> on Si(001) substrates only has 2 epitaxial variants, which are rotated 90° with respect to each other about the surface normal [48]. Their reasoning was that the reduction of the amount of epitaxial variant would lead to larger grain sizes. In this study they were able to obtain grain sizes of  $1 - 6 \mu m$ , which are larger than the grain sizes of  $0.1 - 0.3 \mu m$  reported for BaSi<sub>2</sub> on Si(111), confirming their hypothesis. However, a difference this large was not expected, thus it is mentioned that further study is required to understand this mechanism. Furthermore, it is noteworthy to mention that the lattice mismatch between BaSi<sub>2</sub> and Si(001) is much larger than for BaSi<sub>2</sub> and Si(111). In the case of the Si (001) substrate the lattice mismatch is 0.1% for BaSi<sub>2</sub>[001] and 12.5% for BaSi<sub>2</sub>[010], while it is 0.1%for BaSi<sub>2</sub>[001] and 1.0% for BaSi<sub>2</sub>[010] on the Si(111) substrate. Nevertheless, the BaSi<sub>2</sub> film grown on the Si(001) substrate was found to be almost strain-free.

For  $BaSi_2$  on Si(001) substrates the grain boundary potentials were also investigated by Baba et al. [4]. In this study it was found that the GBs mostly consist out of  $BaSi_2(001)$  planes. In the  $BaSi_2(001)$  plane only Si atoms are present. These Si atoms are bounded in negatively charged tetrahedra, as explained in section 2.1.1. Baba et al. [4] speculate that this is the reason for the higher electrostatic potential at the GB with respect to the interior of the grain, repelling electrons. The average barrier height is found to be 50 meV for Si[110] and 30 meV for Si[1-10] [4]. The upward band bending at the GBs is shown on the right side of figure 2.5.

In the study of Baba et al. [17] they investigated the effect of these differences in GBs, on the minority carrier diffusion length. The study shows that the minority carrier diffusion length in BaSi<sub>2</sub> on Si(111) is much larger compared to BaSi<sub>2</sub> on Si(001), with a minority carrier diffusion length of 8.6  $\mu$ m and 1.5  $\mu$ m, respectively. These results confirm that the GBs in BaSi<sub>2</sub> on Si(001) act as recombination centres, while the GBs in BaSi<sub>2</sub> on Si(111) do not act as recombination centres.

In summary, it is shown that the crystal plane of the GBs in n-type BaSi<sub>2</sub>, determine whether the GBs act as recombination centre, or that the GBs repel the minority holes. Thus increasing the grain size in BaSi<sub>2</sub> is more important if the GB act as recombination centres, compared to the case where the GBs repel the minority carriers. On the other hand, it is demonstrated that the surface quality has a very large influence of the minority carrier diffusion length. A low surface recombination can be established by passivating the BaSi<sub>2</sub> surface with a capping layer. Furthermore, the substrate material determines the epitaxial variants of the BaSi<sub>2</sub>. Regarding future use in photovoltaic devices, it is concluded that it is very beneficial to be able to control the crystal planes of the GBs in BaSi<sub>2</sub>, in order to repel the minority charge carriers.

#### 2.1.6. Recombination mechanism

Hara et al. [5] studied the recombination mechanism of excess-carriers in undoped BaSi<sub>2</sub> films. In their study they found that the excess-carrier decay can be divided into 3 parts with increasing lifetime: Auger recombination, Shockley-Read-Hall (SRH) recombination and SRH recombination due to the carrier trapping effect. As a result of the indirect bandgap of BaSi<sub>2</sub>, Auger and SRH recombination are more likely to occur than radiative recombination [5]. The photoconductivity decay curves of different laser intensities, indicating the three different recombination mechanism, are depicted in figure 2.6.

The initial rapid decay of charge carriers, is attributed to Auger recombination as a result of the high charge carrier concentration. However, Auger recombination is not likely to occur when illuminating the material with the AM 1.5 spectrum. Therefore, the second decay mode, which is SRH, determines the minority-carrier lifetime and is thus considered to be the one of interest. It is observed in figure 2.6 that by lowering the intensity of the light source, the SRH recombination resulting in constant decay reduces, while the SRH with carrier trapping effect becomes predominant. The SRH with carrier trapping, is a slower recombination process and therefore the minority carrier lifetime increases for decreasing light intensity. Hara et al. [5] explain this behaviour as follows. At lower carrier concentrations there are less un-trapped carriers that are able to move towards recombination centres, resulting in



Figure 2.6: Photoconductivity decay curves for 4 different laser intensities, revealing the recombination mechanism in BaSi<sub>2</sub>, source: [5]

longer lifetimes. Furthermore, the study correlates the recombination probability with the dislocation density and therefore they suggest that dislocations act as recombination centres. The study presents equations for calculating the recombination velocity and the effective lifetime of the excess charge carriers of the material.

#### **2.1.7.** Doping

In this section of the report, various dopant elements are discussed. Most of these dopants alter the majority charge carrier concentration of the material, while there are also atoms that modify the bandgap of BaSi<sub>2</sub>. The following dopant atoms are elaborated on: Al, Sb, As, B, Cu, Ga, In, P, Ag and Sr, while Li, K, Na and Cs are also briefly reviewed. These dopants atoms are mostly group III and group V elements, while some are transition metals.

In a study of Imai and Watanabe [49] it is stated that the substitution of Si is energetically more favourable than the substitution of Ba in the  $BaSi_2$  lattice [16]. Therefore it is expected that group III dopants are predominantly p-type dopants, while group V dopants act as n-type dopants. Although this applies to most of the dopant elements, there are exceptions. One of these exeptions is Ga, which results in n-type doping instead of p-type.

Multiple factors are important for achieving high majority charge carrier concentrations. First of all, the maximum concentration of dopant atoms that can be incorporated in the BaSi<sub>2</sub> lattice, determines the potential of the maximum amount of charge carriers that can be donated or accepted. The diffusion coefficient of the dopants within the BaSi<sub>2</sub> lattice and along the GBs, are important parameters when inserting the dopant elements into the BaSi<sub>2</sub> lattice by thermal diffusion. Furthermore, the donor and acceptor energy levels with respect to the conduction and valence band, determines the fraction of ionization of the doping atoms. A smaller energy difference results in a larger fraction of ionization and consequently a higher (majority) charge carrier concentration. The donor and acceptor energy levels of the dopants, with respect to the nearest band, presented in this section are derived in literature by equation 2.1 [50, 51]:

n-type: 
$$n(T) \propto \exp(-\frac{E_{\mathsf{D}}}{2k_{\mathsf{B}}T})$$
 p-type:  $p(T) \propto \exp(-\frac{E_{\mathsf{A}}}{2k_{\mathsf{B}}T})$  (2.1)

Where n(T) and p(T) are the majority charge carrier concentrations for n-type (electrons) and p-type (holes) material, respectively.  $k_{\rm B}$  is the Boltzmann constant, T is the absolute temperature and  $E_{\rm D}$  and  $E_{\rm A}$  are the energy levels with respect to the conduction and valence band of the donor and acceptor atoms, respectively.

#### Materials for controlling the charge carrier concentration

In this section of the chapter the dopant atoms that alter the majority charge carrier concentration of the material are reviewed. The following atoms are discussed: Al, Sb, As, B, Cu, Ga, In, P, Ag and alkali metals.

**Aluminum** Doping the material with aluminum, which is a group III material, results in a p-type material, thus it is concluded that aluminum is a p-type dopant [42, 52]. Furthermore, aluminum doping shows a relative uniform dissemination throughout the depth of the layer. However, an inexplicable strong segregation of aluminum atoms towards the undoped  $BaSi_2$  - Si interface and towards the surface after annealing was observed [42, 52]. The diffusion coefficient as function of temperature is derived by [53]. They report an activation energy of 0.63 eV and 0.58 eV for lattice and GB diffusion. Furthermore, the acceptor energy level is in the range of 50 - 140 meV [54]. The same paper reported a maximum obtained hole doping concentration of  $10^{17}$  [54], while varying the Al vapour pressure 2 orders of mangnitude. Therefore it is concluded that the control of the hole concentration by Al dopoing is difficult [42, 52] and thus Al is not considered to be suitable for high p-type doping concentrations.

**Antimony** Antimony, a group V element, is identified as a n-type doping material for  $BaSi_2$  [42, 55, 56]. The electron concentration in the material can be controlled between  $10^{16}$  cm<sup>-3</sup> and  $10^{20}$  cm<sup>-1</sup> [55]. However, doping the material with antimony deteriorates the crystallinity of the material, resulting in a decrease in the mobility for increased electron doping concentrations. The activation energy of GB and lattice diffusion are 0.65 eV 0.77 eV respectively, which is comparable to aluminum, while it is large compared to boron [56]. A plot of the diffusion coefficient as function of temperature can be found in [56]. According to Zhang et al. [56] a low diffusion coefficient is crucial for realizing a steep pn junction with high carrier concentration and therefore they conclude that Sb doping is not favourable to use for a (steep) BaSi<sub>2</sub> pn junction. Nevertheless, Suemasu does identify Sb as a suitable dopant for a BaSi<sub>2</sub> pn junction configuration, probably due to its ability to reach high carrier concentrations [16].

**Arsenic** Arsenic is a group V element and a n-type dopant [57]. The activation energy for GB and lattice diffusion are 0.88 eV and 0.91 eV, respectively [56]. In the same paper a graph of the diffusion coefficient as function of temperature can be found. Furthermore, the maximum electron concentration obtained by As doping, is limited to  $2 \cdot 10^{17}$  cm<sup>-3</sup> [57]. A higher arsenic dose in combination with annealing, results in an altered material layer on the surface which contains high concentrations of oxygen atoms [57]. Therefore it is assumed that arsenic as dopant, is not suitable for obtaining high electron concentrations in BaSi<sub>2</sub>.

**Boron** Group III element boron is a p-type dopant for  $BaSi_2$  [51, 58]. It is reported that the concentration of holes can be controlled from  $10^{17}$  cm<sup>-3</sup> up to  $2 \cdot 10^{20}$  cm<sup>-3</sup> [58]. The highest activation rate, which is the amount of ionized boron atoms in the material, achieved without post annealing, is more than 20%, resulting in a hole concentration of  $6.8 \cdot 10^{19}$  cm<sup>-3</sup> [51]. The acceptor level activation energy ( $E_A$ ) is 23 meV, which is small compared to Al [51, 58]. It is suggested that the low activation energy of boron in BaSi<sub>2</sub> is the reason for the high carrier concentration [58]. On the other hand, the lattice and GB diffusion activation energies are relatively high compared to other dopants, with values of 4.6 eV and 4.4 eV, respectively [59]. However, the diffusion coefficients are relatively low for boron. The diffusion coefficient as function of temperature can be found in [53, 56]. It is concluded that boron is suitable as p-type dopant for BaSi<sub>2</sub>.

**Copper** Experiments have shown that copper, which is a transition metal, is a n-type dopant [42, 52]. In these studies, it is reported that high copper doping concentrations in  $BaSi_2$  result in a reduced crystallinity of the material. However, no segregation effects as with aluminum doping have occurred [52]. In contrast to aluminum, copper doping varied the electron concentration of the material significantly, with charge carrier concentrations ranging from  $10^{16}$  cm<sup>-3</sup> up to  $10^{20}$  cm<sup>-3</sup> [42]. Although results also indicate that the electron concentration jumps from  $10^{16}$  cm<sup>-3</sup> to  $10^{18} - 10^{20}$  cm<sup>-3</sup> without a gradual transition. Therefore, they conclude that it is difficult to control the electron concentration with Cu doping [42].

**Gallium** Experimentally it is found that gallium, a group III element, is a n-type dopant [42, 60]. Kobayashi et al. [60] ascribe this to the substitution of Ba atom by a Ga atom in the lattice. However, Imai et al. [49] calculated that the substitution of Si is energetically favorable over the substitution of Ba, therefore stating that the n-type behavior of Ga doping cannot be ascribed to the substitution of Ba by Ga. Nevertheless, it is observed that increased Ga doping deteriorates the crystalline quality of

BaSi<sub>2</sub> [60]. Furthermore, the donor level activation energy ( $E_D$ ) is approximately 0.12 eV [60]. The electron density varied abruptly from  $10^{15}$  cm<sup>-3</sup> to  $10^{20}$  cm<sup>-3</sup>, thus the electron density could not be controlled in between these values [42, 60]. Therefore Kobayashi et al. [60] conclude that Ga is not a suitable n-type dopant for BaSi<sub>2</sub>.

**Indium** Group III element indium is a p-type dopant for  $BaSi_2$  [55, 60], which agrees with the theory that it is energetically most favourable to substitute Si in the lattice [49]. In the case of indium doping, degradation of the crystal lattice is also observed [55]. Furthermore, the hole concentration can be controlled between  $10^{16}$  cm<sup>-3</sup> and  $10^{17}$  cm<sup>-3</sup> [42, 55, 60]. Kobayashi et al. [60] suggest that the majority of the In atoms were not activated, resulting in the relatively moderate charge carrier concentration. Therefore, In doping is only suitable for moderate doping levels, while it is not suitable for heavy doping.

**Phosphorous** Phosphorus is a group V element and acts as an electron donor in BaSi<sub>2</sub>, making it a n-type dopant [50, 61]. Phosphorus has the potential to induce less strain in the BaSi<sub>2</sub> material than other n-type dopants due to the similar atomic radius as the substituted Si [61, 62]. The maximum achieved electron density is  $10^{18}$  cm<sup>-3</sup> [61]. However, at these high doping levels the crystal structure of BaSi<sub>2</sub> is destroyed. Most of the damage can be undone by rapid thermal annealing (RTA) at temperatures between 500 - 800 °C for annealing times of 1 - 30 seconds [61, 62]. Although, RTA at temperatures of 800 °C results in the formation of the undesirable metastable trigonal phase, which can act as recombination centre [62]. Also, segregation of P to interface and surface areas is observed when performing RTA [61, 62]. Suppression of the segregation can be achieved at temperatures over 800 °C. However, at these high temperatures decomposition of BaSi<sub>2</sub> becomes an issue [62]. Instead, Hara et al. [62] suggest to lower the RTA time or temperature to reduce segregation. Furthermore, the activation energy is derived to be 80 meV [50]. In conclusion, it can be said that currently phosphorus doping is only suitable for low and medium doping concentrations.

**Silver** The transition metal Ag acts as a p-type dopant in  $BaSi_2[42]$ . In the same study, it is found that Ag doping reduces the crystallinity of the material. Furthermore, the hole concentration varies only little:  $1 \cdot 10^{16} - 3 \cdot 10^{16}$  cm<sup>-3</sup>, while the vapour pressure ratio of Ag to Ba was varied by several orders of magnitude. Therefore Khan et al. [42] conclude that there is little control over the hole concentration in  $BaSi_2$  for Ag doping.

**Alkali metal fluorides** Hara et al. [63] doped  $BaSi_2$  by using alkali metal fluorides. In this study LiF, NaF and KF were investigated as possible dopants. The mechanism of electron donation, is attribute to the interstitial dissociated Li metal that thereby donates an electron, which is similar to the mechanism of Cu atoms [63]. All 3 alkali metals act as electron donors from which the LiF treatment resulted in the highest electron concentration:  $3 \cdot 10^{20}$  cm<sup>-3</sup> by RTA at 500 °C [63]. The demerit of this doping technique is the formation of barium fluoride, oxidation of the material and the formation of silicon in the material [63]. The NaF and KF treatment resulted in electron concentrations of less than  $10^{18}$  cm<sup>-3</sup> [63].

#### Dopants for bandgap modification

Strontium (Sr) can be used to modify the bandgap of  $BaSi_2$  [64–67]. Strontium is a group II element just like barium, therefore they are isoelectronic [64]. It is calculated that  $Ba^1$  sites are preferentially replaced compared to  $Ba^2$  sites [64]. Furthermore, the replacement of the a  $Ba^1$  atom with a Sr atom, decreases the lattice parameters for increasing Sr content up to the composition:  $Ba_{0.24}Sr_{0.76}Si_2$ [65, 66]. Usually with semiconducting silicides, a decrease in lattice constant results in a decrease in the bandgap. However, this is not the case in  $Ba_{1-x}Sr_xSi_2$  [64]. The increase of Sr content results in an increase of the bandgap, which reaches approximately 1.4 eV at  $Ba_{0.48}Sr_{0.52}Si_2$  [66, 67]. It is worth mentioning that the bandgap of  $SrSi_2$  itself is smaller than the bandgap of  $BaSi_2$  [2, 66].

Besides strontium, other elements were considered for bandgap tuning. Imai et al. [68] calculated the influence on the bandgap by incorporating alkali metals Na, K and Cs. Substitution of barium by sodium, potassium or caesium is energetically unfavorable, therefore the solubility will be limited [68]. Nevertheless, for all 3 elements it is calculated that the bandgap of BaSi<sub>2</sub> widens [68]. Furthermore, it is expected that the substitution of Ba by K or Cs leads to p-type material [68].

Another study investigated the effect of carbon incorporation on the bandgap of  $BaSi_2$  [69]. It is energetically more favourable to substitute the  $Si^{(5)}$  site in the lattice by carbon than other Si sites [69]. However, the incorporation of carbon is not likely to happen at all, since incorporation in the  $BaSi_2$  lattice is in all cases not energetically favourable. Nevertheless, a widening of the bandgap is predicted, in the case that more than 10% of the silicon atoms are substituted by carbon atoms [69].

In summary, the dopants In, Ag, Al, K, Cs and B are p-type dopant, while Sb, As, Cu, Ga, Li, K and P are n-type dopants. From these n-type dopants, Cu, Ga, Li and Sb are able to reach high carrier concentration, while only the dopants: Sb and Li have good controllability with respect to the doping concentration. However, the drawback of Li is the formation of barium fluoride. Furthermore, phosphorous doping is suitable for medium doping concentrations up to 10<sup>18</sup> cm<sup>-3</sup>. Boron is the only p-type dopant that is able to achieve high (controllable) doping concentrations.

#### 2.1.8. Abundance of materials

One of the reasons why  $BaSi_2$  is interesting as an absorber material, is due to the abundance of barium and silicon in the earths upper crust. It is preferred to have abundant materials for large (GigaWatt) scale production and adoption of this technology [6]. In figure 2.7 the abundance of elements is presented. The amount of atoms in the earths upper crust are given with respect to  $10^6$  atoms of silicon. The figure indicates that silicon is the second most abundant material in the earth's upper crust, while only oxygen is slightly more abundant. Barium is also relatively abundant with  $10^2$  atoms per  $10^6$  silicon atoms. However, the difference is already 4 orders of magnitude.

In the case of doping, it is also preferable to have dopant atoms that are not scarce and preferably are not elements used in major industry. If the material is scarce or heavily used, basic economics predict that the price of the material goes up. Also, when the material is heavily used in other industries, the availability of this dopant for the photovoltaic industry reduces. Therefore, it is also interesting to evaluate the abundance of the dopants suitable for high concentration doping.

Antimony is identified as a high concentration n-type dopant in the previous section. In figure 2.7 it can be seen that the abundance of antimony is  $10^{-1}$  atoms per  $10^{6}$  silicon atoms, which is comparable to the abundance of silver. This indicates that antimony is a relatively scarce material, which is not favourable for large (GigaWatt) scale production. However, the doping concentration of heavy doping is in the region of  $10^{19} - 10^{20}$  atoms per cm<sup>-3</sup>, which is 2 - 3 orders of magnitude less than the  $10^{22}$  atoms of Si and Ba in BaSi<sub>2</sub>. This (partially) reduces the scarcity problem. Nevertheless, it could be worthwhile to investigate the usage of other n-type doping materials that are more abundant, particularly when the technology reaches large scale production.



Figure 2.7: Abundance of atoms found in the upper earths crust, source: [6]

On the other hand, boron is identified as a suitable p-type dopant for high hole concentration. In the abundance chart, it is observed that the abundance of boron is  $10^2$  atoms per  $10^6$  Si atoms. The abundance of boron is thus in the same order of region as the abundance of barium. Therefore boron is in terms of abundance, with respect to large scale production, a suitable p-type doping material.

Regarding strontium doping for tuning the bandgap of  $BaSi_2$ , it is observed that this element is relatively abundant with  $10^2$  atoms per  $10^6$  Si atoms. This is also comparable to the abundance of barium. Thus also Sr is a suitable dopant for large scale production.

#### **2.2.** RF magnetron deposition of barium disilicide

Most of the literature reported in this section, is based on molecular beam epitaxially (MBE) grown  $BaSi_2$  [11]. However,  $BaSi_2$  was also deposited by vacuum evaporation [70–72], vertical Bridgman method [34] and RF sputtering [11, 73, 74]. This study focuses on the deposition of  $BaSi_2$  by RF magnetron sputtering, as is explained in the introduction chapter. In this section, the previous work on RF magnetron sputtered  $BaSi_2$  is reviewed. This is followed by a section elaborating on the implications for the material of thermal treatment in combination with the used substrate. The lats part elaborates on surface oxidation of the material.

#### **2.2.1.** RF magnetron sputtered barium disilicide

In literature 2 approaches were found for sputtering deposition of  $BaSi_2$ . The first approach is by depositing the  $BaSi_2$  layer at room temperature (RT), which is followed by post-growth thermal annealing in order to crystallize the material [73, 74]. The other approach is by depositing at high (substrate) temperatures ranging from 390 - 600 °C [11]. In these studies, the  $BaSi_2$  layers were successfully deposited on Si(111), Si<sub>3</sub>N<sub>4</sub> and glass substrates [11, 73, 74]. Furthermore, alkali-free glass results in reduced crack formation in the absorber layer compared to quartz substrates [11]. This is attributed to a better matching of the thermal expansion coefficient of alkali-free glass with  $BaSi_2$ , compared to quartz substrates in combination with  $BaSi_2$  [11].

In order to determine a starting recipe of the RF magnetron sputtering deposition in this work, the process parameters of the various studies are reviewed. It is observed that all studies deposit at an RF power of 100 W. The target material is either barium [73] or barium disilicide [11, 74]. The target diameter is only given by Yang et al. [73], resulting in a power density of 3.5 W/cm<sup>2</sup>. In the study of Latiff et al. [11], the target to substrate distance is 70 mm. Furthermore, the argon flow varies from 10 - 20 SCCM, while an argon pressure of 0.5 - 1.5 Pa was used. The deposition times ranges from 10 minutes up to 30 minutes, which results in a material thickness of 600 nm up to 1  $\mu$ m.

Sputtering deposition at room temperature results in amorphous BaSi material [74]. The amorphous material is post-growth annealed in order to crystallize it. Yang et al. [73] concluded that the optimum annealing temperature is 800 °C for RT deposited barium on silicon substrates. However, Yoneyama et al. [74] concluded that the optimum annealing temperature is slightly lower at approximately 650 °C, in which they used a barium disilicide target. They reported the formation of poly-crystalline silicon at higher temperatures [74]. The formation of poly-crystalline silicon occurs when BaSi<sub>2</sub> decomposes in barium gas and solid silicon at elevated temperatures [24].

In the study of Latiff et al. [11], there was no post-growth annealing step performed. In this study the tendency is that higher substrate temperatures during deposition result in better material quality, in which less metallic barium silicide phases, such as  $Ba_2Si$  and  $Ba_5Si_3$ , are formed. The optimal substrate temperature is determined to be 600 °C. Therefore, in this work, it would be interesting to research the material properties of  $BaSi_2$  deposited at a substrate temperature in the range of 400 - 700 °C.

Interestingly, in the study of Yoneyama et al. [74], they investigated what the effect of the substrate is on the material quality of solid phase crystallized (SPC)  $BaSi_2$ . The result of SPC  $BaSi_2$  on a Si(111) substrate is compared to the result of an amorphous  $Si_3N_4$  substrate. The XRD pattern for these samples are almost identical and therefore they conclude that there is (almost) no effect of the substrate surface on the crystal orientation for SPC  $BaSi_2$  films [74].

#### **2.2.2.** Implications of thermal treatment

Annealing is also used for strain relaxation in the thin  $BaSi_2$  films by Hara et al. [31]. In this study, they post-growth annealed MBE grown films at 800 °C for 30 seconds in an argon environment. The result is an enhancement of the lifetime of up to 60 times for films with a thickness over 850 nm. They relate this enhancement of lifetime to relaxation of the lattice strain in the  $BaSi_2$  film. Thus for obtaining  $BaSi_2$  thin films with a long carrier lifetime, it is important to have low lattice strain in the material.

The lattice strain is affected by the difference in thermal expansion coefficient of the substrate and the deposited material. A large mismatch in thermal expansion coefficient, increases the chance on strain accumulation, cracking and exfoliation of the film upon post-growth thermal treatment [75]. In the study of Imai [76], the linear thermal expansion coefficient of  $BaSi_2$  is determined to be  $17.4 \cdot 10^{-6}$  K<sup>-1</sup>,  $14.9 \cdot 10^{-6}$  K<sup>-1</sup> and  $14.8 \cdot 10^{-6}$  K<sup>-1</sup> for respectively the a ( $\alpha_a$ ), b ( $\alpha_b$ ) and c ( $\alpha_c$ ) direction of the crystal. This is roughly 6 times larger than the linear thermal expansion coefficient of Si, which is  $2.6 \cdot 10^{-6}$  K<sup>-1</sup> at 298K [76].

Hara et al. [75] researched the limit at which the  $BaSi_2$  film starts to crack as a result of post-growth annealing. The trend is that thinner  $BaSi_2$  films, deposited on Si(111), are able to withstand a higher annealing temperature cycle before the films start to crack. According to this study, a 100 nm thick  $BaSi_2$  film on silicon substrate should be able to withstand an annealing temperature of 800 °C without cracking, while a 1 µm thick film should remain below 700 °C [75].

The substrates that are used in this experimental study, are Corning EAGLE XG<sup>®</sup> and Heraeus spectrosil 2000<sup>®</sup> fused silica. The corning glass has a linear thermal expansion coefficient of  $3.17 \cdot 10^{-6}$  K<sup>-1</sup> in a temperature range of 0 - 300 °C. It has a glass transition point (Tg) at around 500 - 600 °C [77]. The Tg of 500 - 600 °C implies that this glass substrate is not suitable for post-growth annealing of BaSi<sub>2</sub> films. The linear thermal expansion coefficient of the fused silica glass, is in the region of  $0.5 \cdot 10^{-6} - 0.6 \cdot 10^{-6}$  K<sup>-1</sup> for temperatures between 0 - 900 °C [78, 79]. The material can be used up to a temperature of more than a 1000 °C. Hence, the temperatures required for thermal treatments of BaSi<sub>2</sub> are well within the limit of the silica glass. However, the linear thermal expansion coefficient is approximately 5 times lower than that of silicon. Therefore, there is even a higher risk of cracking and exfoliation of the BaSi<sub>2</sub> thin film upon post-growth annealing when using quartz instead of silicon substrates.

#### 2.2.3. Surface oxidation

Surface oxidation occurs when the  $BaSi_2$  films are exposed to air after deposition. In the study of Takabe et al. [47], it is reasoned that a high oxygen ratio in the surface layer of the film, is responsible for a long minority carrier lifetime. The proposed reason is that the oxide layer passivates the surface, which results in a low surface recombination speed. In the same study they were able to passivate the surface by capping it with a 3 nm thick Ba or Si layer. On the other hand, Hara et al. [80] report that the presence of oxygen in the BaSi<sub>2</sub> bulk material affects the crystal structure. In the same study they also state that Ba atoms are preferentially oxidized with respect to Si atoms, thus possibly resulting in a Ba-rich surface oxide layer.

# 3

## Equipment for material deposition and characterization

In this chapter the equipment used for both material deposition and characterization is discussed. It is important to know how the various machines operate, what purpose they were used for and what physical relations are used for deriving the quantities of interest, in order to correctly interpret the results. The structure of this chapter is as follows. First the equipment used for material deposition is treated, consisting of the RF magnetron sputtering machine and the thermal evaporator. Thereafter the equipment used for material characterization is reviewed, in which the optical and electrical measurement methods are discussed respectively.

### **3.1.** Equipment for material deposition

This section deals with the two machines used for physical vapor deposition. First the RF magnetron sputtering machine is reviewed, which was extensively used to deposit thin films of  $BaSi_2$  on substrates. Secondly, the thermal evaporator machine is treated. This machine was used for depositing silver contacts on the  $BaSi_2$  samples, which are needed for electrical measurements.

#### **3.1.1.** Radio frequency magnetron sputtering

A Kurt J. Lesker RF magnetron sputtering machine, in short: LESKER, was used for depositing BaSi<sub>2</sub> thin films on glass substrates. The working principle of this device is explained as follows. The working gas in the chamber, argon is used in this experimental work, is partially ionized due to the an oscillating electromagnetic field [6]. Due to the electric field these positively charged argon ions are bombarded onto the target material. As a result, target material is sputtered (removed) from the target. These atoms have high energies and collide with the working gas until there energy reduces to the thermal energy [10]. The sputtered target material then diffuses through the deposition chamber and deposits onto the substrate and deposition chamber walls. Furthermore, in this process secondary electrons are emitted, which support in maintaining the plasma [81]. The magnetic field of the magnetron influences the pathway of electrons, enabling a higher ionisation efficiency in the plasma and thereby increasing non-conducting materials, due to charge buildup at the surface of the target [82]. Therefore a radio frequency oscillating electric field is applied, to be able to sputter non-conducting targets. A schematic overview of the RF magnetron sputtering process is presented in figure 3.1.

The parameters, that can be adjusted in order to tune the deposited material properties, of the LESKER are: temperature with a range of 25 °C up to approximately 450 °C substrate temperature, target to substrate distance with a range of 65 to 160 mm, gas flow species, gas volume flow, gas pressure, and target material composition.



Figure 3.1: Schematic overview of the RF magnetron sputtering operating principle, figure from [7]

#### **3.1.2.** Thermal evaporation

Silver contacts were deposited via thermal evaporation by a Provac PRO500S metal evaporator. This machine is able to deposit metals via electron beam evaporation and via thermal evaporation, depending on the required metal. In this case, silver is deposited by thermal evaporation. The working principle of both these methods is: evaporation of metal and subsequently condensation of the metal vapour on the substrate. In the case of the electron beam method, the energy is delivered through an intense electron beam, which is directed by magnetics fields and emitted by a tungsten filament [6]. In the case of thermal evaporation, the energy is provided by resistively heating a tungsten boat via a high current. The process is performed under a high vacuum ranging from  $10^{-3}$  to  $10^{-6}$  Pa, to minimize oxidation of the evaporated metal [6].

In order to obtain the exact dimensions of the contacts, the samples are mounted onto a holder with an incorporated mask. Thereafter the substrate holder is placed on a rotating stage inside the evaporation chamber, where the evaporation process takes place. A deposition rate of 1 nm/s and a thickness of 300 nm was used for all silver contacts.

### **3.2.** Equipment for material characterization

In this section the equipment for material characterization is discussed. First, the optical methods for characterization are treated. The optical methods used in this work are: Spectroscopic Ellipsometry (SE), Spectrophotometry, Raman spectroscopy, X-ray diffraction and Auger electron spectroscopy. The second part deals with the electrical measurement methods, consisting of: Hall setup, Four-point probe, Dark and Illuminated conductivity and the activation energy.

#### **3.2.1.** Spectroscopic Ellipsometry

The spectroscopic ellipsometer used in this work, is the ESM-300 by J.A. Woolam Co. The machine was used to determine the thickness and roughness of the material.

The working principle of the ESM-300 spectroscopic ellipsometer is the following. The light source emits light, with a wavelength range of 191.3 nm up to 1688 nm, onto a sample with different angles of incidence. This light is polarized before it reaches the surface of the sample, where it interacts with

the material of the sample. The light is reflected from the sample towards a polarization analyser. The interaction with the sample changes the polarization of the light. More specifically, the change in polarization between incident and reflected light ca be quantified by the following parameters: ( $\Psi$ ) and Delta ( $\Delta$ ). The fundamental equation relating these properties with each other is given by equation 3.1 [83]:

$$\rho = \tan(\Psi) \cdot \exp(i\Delta) = \frac{r_{\rm p}}{r_{\rm s}}$$
(3.1)

In which  $r_p$  and  $r_s$  are the reflectivity for p-polarized light and s-polarized light, respectively and  $\rho$  is the ratio of reflectivity for p-polarized over reflectivity for s-polarized light, all defined as complex numbers.  $\Psi$  is defined as the ratio of the magnitude of  $r_p$  over the magnitude of  $r_s$ :  $\Psi = \frac{|r_p|}{|r_s|}$  and  $\Delta$  is the phase difference before and after reflection:  $\Delta = \delta_1 - \delta_2$  [83].

After the measurements, data needs to be fitted with a model in order to extract the desired material properties. The correctness of the fit is given by the root mean squared error (RMSE), called simply mean squared error (MSE) for historical reasons. The inputs of the MSE are the Psi and Delta of the fitted model and the experimental values for each measured wavelength. For more information regarding the MSE, it is referred to the manual: [83].

Besides thickness and roughness, with this setup it is also possible to derive other material properties, such as the complex refractive index of a material. However, such analysis goes beyond the scope of this work, and it is thus not treated here.

#### **3.2.2.** Spectrophotometry

A spectrophotometer of the type Lambda 950 made by PerkinElmer was used for measuring reflectance (R) and transmittance (T) as a function of wavelength. The apparatus uses a monochromator which is able to transmit light of a specific wavelength from the light source. The device can transmit monochromatic light towards the sample in a wavelength range of 250 nm up to 3300 nm [84]. The light is either transmitted or reflected from the sample, depending on where the sample is mounted. The transmitted or reflected light is thereafter captured in a so called Integrating Sphere, in which a sensor is able to measure the intensity of the light. This intensity is compared to a reference light beam, which enables the device to determine the reflectance and transmittance in percentages.

The absorbance (A) of the samples can be determined from the reflectance and transmittance measurements by using equation 3.2:

$$A = 100 - R - T \tag{3.2}$$

Where A, R and T are in %. Dividing A, R and T by 100 %, yields the relative values which are dimensionless.



Figure 3.2: Schematic overview of the measured reflectance and transmittance with respect to the irradiance of the source

In order to obtain an indication of the absorption coefficient and the optical bandgap of the material, the R-T-A data is processes via the following method. The absorption coefficient can be determined by using Lambert-Beer law:  $I(x) = I_0 \exp(-\alpha x)$ . Applying this to the situation present in the spectrophotometer, as is schematically shown in figure 3.2, and assuming that the (quartz) substrate does not absorb any light, yields equation 3.3 for the absorption coefficient ( $\alpha$ ):

$$\exp(-\alpha t) = \frac{I(x=t)}{I_0} = \frac{T_{\rm m}}{I_0} \frac{1}{I_0} = \frac{T_{\rm m}}{(1-R_{\rm m})} \frac{1}{(1-R_{\rm m})} = \frac{T_{\rm m}}{(1-R_{\rm m})^2} \to \alpha = -\frac{1}{t} \ln(\frac{T_{\rm m}}{(1-R_{\rm m})^2}) \quad (3.3)$$

Where t is the thickness of the material,  $T_m$  and  $R_m$  are the measured transmittance and absorbance relative to the source,  $I_0$  is the intensity of the light between the substrate and the material on top of it and I(x = t) is the intensity of the light with respect to  $I_0$ .

The absorbance can subsequently be used to determine the optical bandgap by a Tauc plot. The formula that is the basis for this method is given in equation 3.4 [85]:

$$(\alpha h v)^{\frac{1}{n}} = C(h v - E_{\mathfrak{q}}) \tag{3.4}$$

In which *h* is Plack's constant:  $6.626 \cdot 10^{-34}$  Js, *v* is the frequency of light, *C* is a proportionality constant,  $E_g$  is the bandgap and *n* is the exponent that indicates the kind of electronic transition. The exponents that are of interest in this work are:  $n = \frac{1}{2}$ , which denotes a direct allowed transition and n = 2, designating an indirect allowed transition [85]. The Tauc plot is obtained by plotting  $(\alpha hv)^{\frac{1}{n}}$  versus the photon energy (hv). The optical bandgap is then obtained by extrapolating a linear fit from the linear region of the graph to intersect with the x-axis. The photon energy at this intersection is the optical bandgap of the material.

#### **3.2.3.** Raman spectroscopy

The apparatus used for Raman spectroscopy is a Renishaw model type: inVia. The device is equipped with 2 different lasers: An argon laser and a helium neon laser which emit light at a wavelength of 514 nm (green laser) and 633 nm (red laser), respectively. The red laser measures a Raman shift range of 209 up to 813 nm<sup>-1</sup>, while the green laser measures from 19 up to 991 nm<sup>-1</sup>. The absorption coefficient of a material depends on the wavelength of incident light, it is higher for high photon energies (i.e. short wavelengths) and decreases with decreasing energy. Consequently, the red laser is able to penetrate deeper into the material than the green laser, enabling to see how crystallinity varies through depth.

The operating principle of the machine is based on the Raman effect. A small fraction of the incident photons interact with the lattice by inelastic scattering, meaning that the photon and lattice lose or gain energy by this interaction. The other fraction of the incident photons are elastically scattered, thus without an energy transfer. In Raman spectroscopy the inelastic scattering is of interest. Obviously, due to the first law of thermodynamics, if one 'particle' loses energy the other 'particle' has to gain energy. As a result of the change in photon energy, the frequency of scattered photons is slightly increased or decreased in the case of energy gain and loss, respectively. On the other hand, the material lattice also gains or loses energy in terms of phonons [86]. The energy change is highly dependent on the atoms and bonds involved in the lattice, which is the reason why this technique is suitable for structural characterisation. In Raman spectroscopy the change in energy is measured in terms of a Raman shift in cm<sup>-1</sup>.

In orthorhombic  $BaSi_2$  there are 5 fundamental frequencies in terms of Raman shift, which is the result of the hetero structure of the tetrahedra anions in the  $BaSi_2$  crystal structure:  $[Si_4]^{4-}$  [12], as discussed in section 2.1.1. The Raman shift frequencies, given in cm<sup>-1</sup>, matching the anions in  $BaSi_2$  with their relative intensities are presented in table 3.1.

The Raman shift at 276 and 293 cm<sup>-1</sup> are designated as  $v_2(E)$ , 355 and 376 cm<sup>-1</sup> are indicated as  $v_3(F_2)$  and the shift at 486 cm<sup>-1</sup> is denoted as  $v_1(A_1)$  [12]. It is noteworthy to mention that the Raman shift for orthorhombic BaSi<sub>2</sub> at 486 cm<sup>-1</sup> is very close to the Raman shifts for silicon and in particular a-Si. The Raman shifts for a-Si, nc-Si and c-Si appear at: 480, 510 and 520.5 cm<sup>-1</sup>. However, the peak of a-Si should be much broader than the peak of  $v_1(A_1)$ , which makes it possible to distinguish the two.

Fundamental	Relative
Frequency	intensity
$(cm^{-1})$	(-)
276	medium - strong
293	medium
355	medium
376	medium
486	very strong

Table 3.1: Fundamental frequencies of the tetrahedra anion in the orthorhombic BaSi<sub>2</sub> lattice, source: [12]

With the results of Raman spectroscopy, it is also possible to compare the crystallinity of a material. This can be done by determining and comparing the full width at half maximum (FWHM) of the peaks in the Raman plot of different samples. The material which is the most crystallised, has the smallest FWHM value and thus has the sharpest appearing peaks.

#### **3.2.4.** X-ray diffraction

X-ray diffraction (XRD) analysis was performed by the new technologies research centre of the university of West Bohemia in Pilsen, Czech Republic. The setup consists of an automatic powder X-ray diffractometer by X'Pert Pro for carrying out the XRD patterns with a wavelength of 0.154 nm. The measurements were taken by an ultra fast linear semiconductor detector by PIXcel. In this work an asymmetric Seemann-Bohlin setup was used, as is shown in figure 3.3. In this setup the penetration dept of the x-ray's is relatively shallow compared to other setups, which is beneficial for the thin samples used in this work, because less diffraction lines of the substrate material are observed. The angle of incidence of the x-rays is denoted as ( $\omega$ ) and was fixed at 0.5 °in this work. The angle of the detector is given as 2 $\theta$ . The detector measures the intensity of the scattered x-rays as function of angle (2 $\theta$ ).

XRD is a technique used for structural characterisation. In this work the XRD analysis was used to determine whether the material was crystalline or amorphous, the orientation of the crystal lattice, the material phase and the crystal sizes.

The basic principles in XRD are the following. X-rays are emitted by the source and irradiate the sample. These X-rays interact mostly with the electrons of the material, by which the X-rays are scattered. This scattering of X-rays results in constructive and destructive interference. The detector measures the interference pattern of the scattered x-rays and is thereby able to derive the distance between the atoms by using Bragg's law [87].



Figure 3.3: Schematic overview of the XRD setup



Figure 3.4: Schematic overview showing the condition for Bragg's law, source: [8]

Bragg's law defines at which angle ( $\theta$ ) the constructive interference pattern is the strongest for a certain crystal lattice and is given by equation 3.5:

$$2d\sin(\theta) = n\lambda \tag{3.5}$$

Where *d* is the distance between atoms,  $\theta$  is the angle of incident and scattered photon as shown in figure 3.4, *n* is an integer that multiplies the wavelength  $\lambda$  of the x-ray.

Bragg's law can be explained by the following reasoning. The scattered x-rays result in constructive interference when the path-length difference  $(2 \cdot (d \sin(\theta)))$  is equal to an integer times the wavelength. The reason for this is that waves are then in phase with each other, resulting in constructive interference.

#### **3.2.5.** Auger electron spectroscopy

Auger electron spectroscopy (AES) was used to obtain the composition of the material as a function of depth. The depth analysis was obtained by sputtering away a certain amount of the material in between measurements, since AES is only able to collect data from the top 5 atomic layer depending on the ionization energy of the material [88]. The measurements were carried out at the university of Bratislava in Slovakia.

The working mechanism of this device is based on the Auger effect, which is explained as follows [89]. The surface of the material is bombarded with an electron beam. When an electron collides with an electron from the inner shell of an atom, it is possible to remove this electron. The remaining atom is thereby ionized and this leaves a hole in the inner shell (denoted as K). Since this atom configuration is not stable, an electron from a more shallow level, indicated as  $L_1$ , will relax and fill up the hole. As a result of this process, energy is released with an amount of:  $K - L_1$ . This excess energy can be emitted as a photon, or it can excite another electron from a shallow level (designated as  $L_{2,3}$ ) into the vacuum. The emitted secondary electron is referred to as the Auger electron. The kinetic energy ( $E_{\text{kinetic}}$ ) that this electron has obtained in the process, which is measured in an AES setup, is given by equation 3.6 [89]:

$$E_{\text{kinetic}} = K - L_1 - L_{2,3} \tag{3.6}$$

Equation 3.6 is an approximation of the actual energy which is released, since it doesn't take the shift in atomic energy levels into account, which in turn is induced by the re-distribution of the Coulomb field [89]. By comparing the measured energy with the expected energy calculated by using equation 3.6, it is possible to determine the atom from which the Auger electron originated. Performing this method for a spectrum of energies makes it possible to derive the composition of the material.



Figure 3.5: Schematic representation of the Auger effect, source: [9]

#### **3.2.6.** Hall setup

The Hall setup is an apparatus mainly used for determining the following fundamental material properties: carrier density and mobility. The device used in this research was the HMS-5000 from Ecopia. The working principle of the device is based upon the Hall effect, which is explained as follows. There are four contact points with the material of interest. A current is set, which runs between two opposite contacts. Thereafter, a magnetic field is applied perpendicular to the surface area of the sample. Due to the magnetic field, the positive charges are pushed to one side of the sample, while the negative charges are pushed to wards the opposite side, due to the Lorentz Force. Due to this charge separation, a voltage can be measured by the other 2 contacts. This measurement enables to calculate the bulk charge carrier concentration by using equation 3.7 [90]:

$$(n+p) = \frac{IB}{q|V_{\rm H}|t} \tag{3.7}$$

Where *I* is the current in A, *B* is the magnetic field strength in T, *q* is the elementary charge of  $1.602 \cdot 10^{-19}$  C,  $|V_{\rm H}|$  is the absolute value of the measured Hall voltage in V and *t* is the thickness of the sample in m. The sign of the Hall voltage determines if the material is n-type or p-type. Thus *n* is the bulk charge carrier concentration for n-type material (electrons), while *p* is the bulk charge carrier concentration for p-type material (holes), both in cm<sup>-3</sup> [90].

Combining the Hall measurement with the van der Pauw resistivity measurement, from which the sheet resistance  $R_s$  can be obtained, enables to determine the Hall mobility by using equation 3.8 [90]:

$$\mu = \frac{|V_{\rm H}|}{R_{\rm S}IB} \tag{3.8}$$

Where  $\mu$  is the mobility in cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>,  $\mu_n$  is the mobility for electrons,  $\mu_n$  is the mobility for holes and  $R_s$  is the sheet resistance in  $\Omega$ /sq.

The resistivity is a property determined from the fundamental properties: mobility and bulk charge carrier concentration. The results of equations 3.7 and 3.8 can be used to determine the resistivity via equation 3.9 [43]:

$$\rho = \frac{1}{\sigma} = \frac{1}{q(\mu_{\rm n}n + \mu_{\rm n}p)} \tag{3.9}$$

In which  $\rho$  is the resistivity with units  $\Omega$  m and  $\sigma$  is the conductivity in S/m.

Under the assumptions that the mobility for electrons and holes are of the same order of magnitude and that one carrier concentration is much greater than the other carrier concentration, equation 3.9 can be reduced to  $\rho \approx \frac{1}{q(\mu_n n)}$  for n-type material and  $\rho \approx \frac{1}{q(\mu_n p)}$  for p-type material.

The van der Pauw measurement for resistivity measures 8 voltages and 8 currents for various contact combinations. The resistance between the contacts is calculated from these voltages and currents. The

sheet resistance is thereafter calculated by numerically solving the van der Pauw equation by iteration. The van der Pauw equation is given by equation 3.10 [90]:

$$\exp(-\pi \frac{R_{\rm A}}{R_{\rm s}}) + \exp(-\pi \frac{R_{\rm B}}{R_{\rm s}}) = 1$$
 (3.10)

Where  $R_A$  and  $R_B$  are two characteristic resistances with units  $\Omega$ , as explained in [90].

It is important to note that there is a current limit to ensure that the power dissipation in the sample does not exceed a certain maximum value. The limit for the maximum allowed current is given by equation 3.11 [90]:

$$I < (200R)^{-0.5} \tag{3.11}$$

In which *R* is the resistance in  $\Omega$  measured between two opposite contacts.

The requirements for the sample dimensions for both these measurements are fortunately not very stringent. An arbitrarily shaped sample suffices as long as it is simply connected, has 4 small contacts, preferable placed in the corners, and the sample thickness is thin, both relative to the sample size [90]. Thus squared or rectangular shaped samples can easily fulfill this requirement. However, if the resistance in one of the contacts is much higher than in the other, if the sample material is damaged in terms of cracks or holes, or if the material is not very uniform, it could induce errors in the measurements [90]. More sources of error are given by [90].

The preparation of the samples for this measurement is the following. After deposition the samples are cut into smaller pieces of approximately 10 x 10 mm. Thereafter the silver contacts are made by applying some silver paste on the edges. The last step is to anneal the silver contacts inside a Heratherm OMS60 oven by Thermo scientific set to 150 °C for 30 minutes. After the samples are cooled to room temperature, they can be used for measurements in the Hall setup. The samples are measured multiple times, without shifting them, to obtain a statistical average and standard deviation of the quantities of interest.

#### **3.2.7.** Four-point probe

A CMT-SR2000NW four-point probe system from from Advanced Instrument Technology was used in this research for determining the sheet resistance  $R_s$  of the material. This method makes use of 4 contacts placed in line with each other. The two outer contacts supply a current through the sample, while the inner two contacts measure the voltage drop between the inner contacts [91]. This separation of source and measurement contacts is exactly what makes the 4 point probe more reliable than a twopoint contact technique. One of the problems in a two-point measurement device is that the measured resistance also includes the contact resistance between the wires and the sample, possibly resulting in too high values of the sheet resistance. Besides this difference, there are some additional advantages of using the four-point technique over the two-point technique, which are discussed in [91].

The derivation of the sheet resistance from current and voltage measurements is as follows. Considering a semiconductor material bar as a resistor, then the resistivity  $\rho$  is determined as: [43, 91]:

$$V = IR = I(\frac{\rho L}{A}) = I(\frac{\rho L}{Wt}) \rightarrow \rho = \frac{VWt}{IL}$$
(3.12)

In which *R* is the resistance in  $\Omega$ , *A* is the cross sectional area in m<sup>2</sup>,  $\rho$  is the resistivity in  $\Omega$ m, *W* is the width of the sample in m, *L* is the length of the sample in m, *t* is the thickness of the sample in m, *V* is the voltage drop between the contacts in V and *I* is the current through the material in A.

The sheet resistance  $R_s$  is defined as:

$$R_{\rm s} = \frac{\rho}{t} \tag{3.13}$$

 $R_{\rm s}$  has the unit  $\Omega$ , however it is conventional to use the unit  $\Omega$ /sq. Combining equation 3.13 with equation 3.12 and applying Ohms law yields:

$$R = \frac{V}{I} = R_{\rm s} \frac{L}{W} \tag{3.14}$$
For a square sample, equation 3.14 reduces to:

$$\frac{V}{I} = R_{\rm s} \tag{3.15}$$

From equation 3.15 it is clear how the current and voltage measurements of the four-point probe result in the sheet resistance of the sample. However, in equation 3.15 it is assumed that the sample is squared. In order to use samples of arbitrary shape, there is a correction factor introduced of 4.532 [91], resulting in equation 3.16:

$$R_{\rm s} = 4.532 \frac{V}{I} \tag{3.16}$$

The only constraint for using this correction factor is that the sample dimensions should be much greater than the spacing of the contacts in the measurement device [91].

#### **3.2.8.** Dark and Illuminated conductivity

The apparatus used for measuring the current voltage (IV) relation under illumination and in the dark was a model WXS-90S-L2,AM1.5GMM super solar simulator from Wacom. The IV measurements can be used to determine the conductivity, similar to the principles and equations explained in 3.2.7, however this machine uses two probes for the measurements. The geometry of the samples with the contacts is shown in figure 3.6. This metal grid is obtained by placing the sample in the Provac, which deposits the silver metal by thermal evaporation as explained in section 3.1.2. This is followed by a thermal annealing step in a Heratherm OMS60 oven by Thermo scientific at 150 °C for 30 minutes.

The conductivity ( $\sigma$ ) can be calculated by rearranging equation 3.12:

$$\sigma = \frac{1}{\rho} = \frac{IL}{VWt} \tag{3.17}$$

The ratio  $\frac{L}{W}$  for this metal grid is specified as:  $\frac{1}{40}$ . Rewriting equation 3.17 yields:

$$\sigma = \frac{L}{RWt} = \frac{1}{40Rt} \tag{3.18}$$

Where the resistance R in equation 3.18 is determined form the current voltage measurements as follows. The current is plotted (y-axis) as a function of voltage (x-axis), where-after a linear fit is applied to the graph. The gradient of the fitted line is the conductance, thus the reciprocal of this gradient results in the resistance.

The conductivity is determined both in the dark and under AM 1.5 illumination. The samples are not shifted in between dark and illuminated measurements, so that the contact resistance is the same for both measurements. This enables a comparison between the dark and illuminated conductivity, where the difference should solely be a result of the difference is illumination.

The reason for comparing both these conductivities is the following. When the illuminated conductivity is higher than the dark conductivity, it indicates an increase in the total charge carrier concentration (*n*) as result of the added light induced charge carriers ( $\delta n$ ):  $n = n_0 + \delta n$  [43]. In equation



Figure 3.6: Overview of the metal grid used for the activation energy and the illuminated and dark conductivity measurements

**3.9** it can be seen that when the charge carrier concentration increases, the conductivity increases and the resistivity decreases. Finally, demonstrating that there are light induced charge carriers upon illumination, proves that the obtained material exhibits semiconducting behaviour.

#### **3.2.9.** Activation energy

The activation energy was determined by an apparatus from Simac Masic bv. for which the control software is developed in-house. The operating principle of the machine is as follows. The apparatus measures the dark conductivity for a temperature range of 130 - 60 °C. The conductivity is a function of temperature, described by the Arrhenius equation (3.19):

$$\sigma(T) = \sigma_0 \exp(-\frac{E_a}{k_B T})$$
(3.19)

In which  $\sigma(T)$  is the temperature dependent conductivity in S/m,  $\sigma_0$  is the pre-exponential factor of the Arrhenius equation, also given in S/m,  $E_a$  is the activation energy in eV,  $k_B$  is the Boltzmann constant:  $1.38 \cdot 10^{-23}$  J/K and T is the temperature in K.

The conductivity is determined by measuring the current and voltage, in a similar manner as explained in section 3.2.8. The sample used, is the same previously employed for the dark and illuminated conductivity. Therefore the metallic grid is the same as shown in figure 3.6 and equation 3.17 can be used once again to calculate the conductivity.

The activation energy ( $E_a$ ) provides information regarding the position of the Fermi level ( $E_F$ ) with respect to either the conduction ( $E_C$ ) or the valence band ( $E_V$ ). The position of the Fermi level is given by equation 3.20 for p-type and n-type material respectively:

p-type: 
$$E_a = E_F - E_V$$
 and n-type:  $E_a = E_C - E_F$  (3.20)

Finally, the position of the Fermi level can be used to calculate the charge carrier concentration according to equation 3.21 and 3.22 for n-type and p-type material respectively [43]:

$$n_0 = N_{\rm C} \exp(\frac{-(E_{\rm C} - E_{\rm F})}{k_{\rm B}T})$$
 (3.21)

$$p_0 = N_V \exp(\frac{-(E_F - E_V)}{k_B T})$$
 (3.22)

In which  $n_0$  and  $p_0$  are the electron and hole concentration at thermal equilibrium, respectively in cm<sup>-3</sup>,  $N_{\rm C}$  and  $N_{\rm V}$  are the temperature dependent effective density of states in the conduction and the valence band, respectively in cm<sup>-3</sup>,  $E_{\rm C}$ ,  $E_{\rm V}$  and  $E_{\rm F}$  are the positions of the conduction band, valence band and Fermi level, respectively in eV.

## 4

## Thickness uniformity of RF magnetron sputtered barium disilicide

This chapter deals with the second sub-question presented in the introduction: 'How to deposit the most uniform barium disilicide films by means of radio frequency magnetron sputtering?' As already mentioned in the introduction it is important to know the material uniformity (in short: uniformity) for measurements and future research. Better uniformity of the material enables to use a larger area of the substrate for experiments and measurements. However it is also important to know the deposition rate at the most uniform target to substrate distance (TSD). This enables to predict the thickness of the material for a given deposition time. Both these subjects are treated in this chapter of the report.

The chapter is structured as follows. First the theoretical framework is discussed, in which the influence of the TSD on the uniformity and deposition rate is described. Thereafter, the methodology is introduced. The results are discussed in the following section, including uniformity and deposition rate. The last part of the chapter deals with the conclusions.

## **4.1.** Theoretical framework

In this experimental section the influence of the TSD on the material uniformity and the deposition rate at the most uniform TSD is researched. Literature was consulted in order to gain understanding of the transport phenomena of the particles in the deposition chamber.

In literature there are 2 regions identified between the target and the substrate [10, 92], which is schematically presented in figure 4.1. The first region, which is called the cooling region, is directly above the target, where the sputtered atoms have an energy larger than the thermal energy. In this region the sputtered neutrals collide with the plasma and thereby lose part of their energy. At a certain distance from the target, the sputtered atoms/molecules lost all energy in excess of the thermal energy. This point is the so called virtual source and the distance from the target to the virtual source is the thermalisation distance [10, 92]. The second domain is called the diffusion region, which is the area between the virtual source and the substrate. In this region the transport of atoms/molecules is governed by diffusion [10, 92]. The distance from the virtual source to the substrate is the virtual source distance (VSD). The TSD is therefore the sum of the VSD and the thermalisation distance. Furthermore, in the cooling region the deposition rate is not a function of the TSD and remains constant, while in the diffusion region the deposition rate decreases for increasing TSD [10].

The thermalisation distance as function of RF power and sputtering pressure is presented in the paper of Vasant Kumar et al. [10]. The thermalisation distance is is determined to be approximately 2 cm for a pressure of 10 µbar ( $\approx$  7.5 µmHg) argon and a RF power of 100 W [10]. The thermalisation distance increases for increasing RF power, thus the actual thermalisation distance decreases in the case of 50 W used in this work. However this thermalisation distance has been determined for an indium tin oxide (ITO) (90% In<sub>2</sub>O<sub>3</sub> + 10% SnO<sub>2</sub>) target, while in this work a BaSi<sub>2</sub> target is used.



Figure 4.1: Schematic representation of the cooling and diffusion region in the sputtering process, figure adapted from [10]

Upon comparison of the atomic mass (ma), it is observed that Ba  $(ma \approx 137 \text{ amu})$  is:  $\frac{137}{115} \approx 1.19$  as heavy as indium (In)  $(ma \approx 115 \text{ amu})$  and  $\frac{137}{119} \approx 1.15$  as heavy as tin (Sn)  $(ma \approx 119 \text{ amu})$ . Furthermore, silicon  $(ma \approx 28 \text{ amu})$  is:  $\frac{28}{16} \approx 1.75$  as heavy as Oxygen (O)  $(ma \approx 16 \text{ amu})$ . This comparison shows that the atomic mass of the heaviest atoms Ba and In/Sn are of the same order of magnitude, while there is a more substantial difference (1.75) between the two lightest atoms Si and O. It is therefore expected that the virtual source distance of the ITO target and the BaSi<sub>2</sub> target are also of the same order of magnitude. However, the effect of the atomic mass of the sputtered atom are related by equation 4.1 [92]:

$$h = \frac{n\lambda}{P}\cos(\alpha) \tag{4.1}$$

In which *h* is the thermalisation distance, *n* is the number of collisions of the sputtered material with the gas atoms, *P* is the gas pressure and  $\alpha$  is the maximum angle of scattering of the sputtered atom, given by equation 4.2 [92]:

$$\alpha = \arctan(\frac{M_{\rm G}}{M_{\rm S}}) \tag{4.2}$$

Where  $M_{\rm G}$  and  $M_{\rm S}$  is the mass of the gas atoms and sputtered atoms, respectively. In this work argon was used, which has an atomic mass of approximately 40 amu. The scattering angle and the cosine of the scattering angle of the two heaviest atoms (Sn and Ba) are:  $\alpha_{\rm Sn} = \arctan(\frac{40}{119}) \approx 0.324$  rad,  $\alpha_{\rm Ba} = \arctan(\frac{40}{137}) \approx 0.284$  rad,  $\cos(\alpha_{\rm Sn}) \approx 0.948$ ,  $\cos(\alpha_{\rm Ba}) \approx 0.960$ . The same analysis for the two lightest atoms gives:  $\alpha_{\rm O} = \arctan(\frac{40}{16}) \approx 1.19$  rad,  $\alpha_{\rm Si} = \arctan(\frac{40}{28}) \approx 0.96$  rad,  $\cos(\alpha_{\rm O}) \approx 0.371$ ,  $\cos(\alpha_{\rm Si}) \approx 0.573$ . Under the assumption that the mean free path, amount of collisions and pressure is the same, the following conclusions can be drawn. The heavier atoms have a longer thermalisation distance than the lighter atoms. This conclusion has the following two important implications. Firstly, the thermalisation distance of the barium is longer than that of the silicon. Thus the ratio of barium to silicon is expected to vary as function of TSD. Secondly, the thermalisation distance of barium is approximately  $(\frac{\cos(\alpha_{\rm Ba})}{\cos(\alpha_{\rm Sn})})$  1.3% longer than that of tin and therefore also slightly longer than of indium. Considering this small difference and taking the lower RF power in this work into account, it is reasoned that the actual thermalisation distance of the sputtered barium and silicon in this work are shorter than the minimum TSD (65 mm) of the LESKER machine. Ultimately, this analysis justifies a diffusive mass transfer modeling approach with respect to the effect of the TSD on the material uniformity and deposition rate.

In order to gain further understanding of the effect of TSD on the uniformity and the deposition rate, an analysis of the idealized diffusive mass transfer was conducted. The detailed analysis and derivation can be found in appendix A.

The influence of the TSD on the deposition rate in this analysis agrees with the literature described above: The deposition rate decreases for increasing TSD. Furthermore, the analysis predicts that uniformity increases (more uniform) for increasing TSD.

It should be noted that the aforementioned theoretical prediction is an idealized situation. Thus other effects on the mass transport such as the argon gas flow inside the chamber, the dimensions of the deposition chamber and horizontal diffusion over the surface of the deposited film, are not taken into account. The actual deposition rate and uniformity are therefore experimentally determined. The methodology of these experiments is discussed in section 4.2.

## 4.2. Methodology

Corning EAGLE XG<sup>®</sup> glass was used as substrate. The glass was thoroughly cleaned in an ultrasonic bath for at least 10 minutes per fluid, containing first acetone and thereafter isopropanol. The glass was mounted on the substrate holder and placed in the deposition chamber of the RF magnetron sputtering machine. The standard recipe, as described in appendix B, was used for deposition with the following adjustments for the uniformity experiments: the deposition time was 20 minutes, the film thickness was therefore also less than 500 nm and the substrate was Corning EAGLE XG<sup>®</sup>. The TSD was varied for 4 different samples: 85 mm, 110 mm, 135 mm and 160 mm. For the deposition rate experiment, the same recipe was used as described above with the following changes: the TSD was constant at 135 mm, while the deposition time was varied for 5 different samples: 2 min, 5 min, 10 min, 15 min and 20 min. After deposition the samples were measured by spectroscopic ellipsometry (SE), according to the measurement pattern of figure 4.2. It is assumed that the material is deposited circular symmetric on the substrates. According to this assumption, it suffices to measure only the 5 positions indicated in figure 4.2. The glass substrates have dimensions of 10 x 10 cm and the distance between the measurement points is  $\sqrt{2}$  cm. The SE data is fitted with a model to obtain the thickness of the layer. The model is based on a Cody-Lorentz oscillator, which is tailored to each individual sample. However, for all 5 measurements per sample, the same model is used to derive the thickness of the BaSi<sub>2</sub> film.



Figure 4.2: Schematic of the SE measurement points

## **4.3.** Uniformity as function of target to substrate distance

The uniformity of the before-mentioned 4 target to substrate distances is plotted in figure 4.3. The y-axis represents the thickness relative to the centre for each sample, while on the x-axis the radius of the measurement spot from the centre of the substrate is displayed. In the graph it can be seen that for a TSD of 85 mm the material is the least uniform. The relative thickness, within the first 25 mm from the centre, reduces the most for a TSD of 85 mm compared to other TSDs. Interesting is the increase of the relative thickness at a radius of 40-45 mm, while thereafter the relative thickness decreases again. There seems to be a trend breach for this TSD compared to the other TSDs. This trend breach also doesn't correspond to the trend expected by the theory as described in section 4.1 and appendix A. A reason for this behaviour could be the relatively large (root) means squared error (MSE) of over 37 for the fit of the model with the measurements, as can be seen in table C.1 in appendix C. Unfortunately, there was no standard model available for this material at the time of the measurements. Therefore the models were self-made with little previous experience, which could explain the relatively large MSE. Another reason could be that the mass transfer doesn't occur according to the expected spherical diffusive mass transfer. However no further efforts were made to research this behaviour since it falls outside the scope of this research.

The relative thickness of the TSDs of 110 to 160 mm does show a clear trend, that also corresponds



Figure 4.3: Uniformity plotted for various target to substrate distances

to the trend expected by the theory in section 4.1 and appendix A: the relative thickness decreases for increasing radius. Furthermore, in the 15 mm radius closest to the centre, the TSD of 110 mm results in the most uniform layer. However, this difference in relative thickness is minor, also considering the relatively high MSE of high twenties and thirties, which can be seen in appendix C, the differences could be within the error margin. For a radius larger than 15 mm it is observed that the TSD: 135 mm has the best uniformity. According to the theory it is expected that the largest TSD results in the most uniform material. This trend holds for the TSD range of 85 mm up to 135 mm. However for a TSD of 160 mm the uniformity is slightly worse than for a TSD of 135 mm. Therefore it was chosen to perform the follow-up experiments with a TSD of 135 mm.

## **4.4.** Deposition rate

The film thickness at a TSD of 135 mm, which induced the most uniform thickness as explained in the previous section, is plotted in figure 4.4. The film thickness is plotted as a function of deposition time for varying radius from the centre of the substrate. This plot shows that the thickness is the largest at the centre of the substrate and decreases towards the edge of the substrate. This corresponds with the theoretical predictions of section 4.1

In order to get a more detailed view on the film thickness as function of time, the thickness at the centre and edge of the substrate are plotted in a separate 2D graph in figure 4.5. In this graph it can be seen that the film thickness at the centre of the substrate seems to increase linearly with the deposition time. On the other hand, this linear trend is not that clearly observed at the edge of the substrate. Therefore a linear fit is applied to the data for the centre. The linear fit is forced to intersect the origin. The result is the black line as shown in figure 4.5. The slope of the line corresponds to a deposition rate of 6.63 nm/min. In the follow-up experiments, the desired film thicknesses are 500 nm and 130 nm, which require deposition times of 75 min and 20 min, respectively.



Figure 4.4: 3D plot of the layer thickness as function of the deposition time for varying radius from the centre



Figure 4.5: Thickness plotted as function of time for the centre and edge of the sample

## **4.5.** Conclusion: uniformity

In conclusion it is observed that the uniformity as function of TSD generally follows the theoretical predictions: higher uniformity for larger TSD. Nevertheless, the most uniform deposited material occurs at a TSD of 135 mm instead of 160 mm, which would be expected by the theory. However the theory presented includes multiple simplifications, which could be the reason for the deviation. On the other hand, the measurements show relatively large MSE's, which can also be a reason for this deviation. Nonetheless, the TSD of 135 mm is used in follow-up experiments. The deposition rate, for the followed recipe, is approximately 6.63 nm/min. This results in a deposition time of 20 min and 75 min for a thickness of 130 nm and 500 nm, respectively.

## 5

## Properties of room-temperature deposited barium-disilicide

In chapter 4 it is concluded that the most uniform material, with respect to thickness, is deposited at a target-to-substrate-distance (TSD) of 135 mm, following the recipe specified in 4.2. In this chapter the material properties, for this deposition recipe, are discussed. Despite these uniformity conclusions regarding the most uniform TSD, experiments were also performed at a TSD of 80 mm for the following reason. For obtaining the highest substrate temperature, which is of interest for the high temperature series described in chapter 6, the TSD had to be reduced to 80 mm. Therefore, the optical and electrical properties of room temperature (RT) sputtered barium disilicide are compared for both these TSDs. Furthermore, the influence of the material thickness on the optical properties is treated, by comparing a 130 and 500 nm thick layer. Reflectance, transmittance and absorbance data for these aforementioned TSDs and thicknesses are plotted together with simulated data for hydrogenated amorphous silicon (a-Si:H) and hydrogenated nano-crystalline silicon (nc-Si:H), for comparison and verification that the resulting material does not simply result in a-Si:H and nc-Si:H. Moreover, the composition and crystallinity of the material, for a TSD of 135 mm, is reviewed by Auger electron spectroscopy (AES) and X-ray diffraction (XRD)/Raman spectroscopy, respectively.

This chapter is structured as follows. The first part deals with the methodology. This is followed by the optical and structural properties. Thereafter, the electrical properties are treated. In the latter part of the chapter, conclusions are discussed.

## 5.1. Methodology

Instead of Corning EAGLE XG® glass, Hereaus Spectrosil® 2000 fused silica was used as substrate for spectrophotometry and Raman spectroscopy measurements. The quartz is more transparent with respect to the Corning glass, making it better suitable for Raman spectroscopy measurements through the substrate. Also, the quartz is able to withstand higher temperatures than the corning glass, which is important when post-growth annealing the material, which is treated in chapter 7. The quartz glass was cleaned prior to deposition in an ultrasonic bath with acetone and isopropanol, for 10 minutes each. On the other hand, AES measurements require a conductive substrate. Therefore, samples were prepared on a c-Si wafer with a 100 nm thermal oxide (SiO<sub>2</sub>) on top, to prevent any influence of the wafer crystal orientation on the growth of BaSi<sub>2</sub>. In some samples, between the SiO<sub>2</sub> and the barium disiliced layers, p- or n-doped pc-Si was deposited, to re-create the conditions in which BaSi<sub>2</sub> will be deposited in photovoltaic devices. For the material deposition, the standard RF magnetron sputtering recipe was used, as described in appendix B. Logically, for the experiments with a TSD of 80 mm, the TSD was changed from 135 mm to 80 mm. The deposition rate for a TSD of 80 mm, at the centre of the substrate, is approximately 8.85 nm/min, which is determined by following the same procedure that was used for determining the deposition rate for a TSD of 135 mm, as described in section 4.2. To obtain the same material thickness at this lower TSD, the deposition time was reduced accordingly. After deposition, the samples were characterized by spectrophotometry, Raman spectroscopy, fourpoint probe, activation energy, dark IV, illuminated IV and by the hall setup. Samples were send to the new technologies research centre of the university of West Bohemia in Pilsen, Czech Republic and to the university of Bratislava in Slovakia, for XRD and AES analysis, respectively.

## **5.2.** Optical and structural properties

In this section of the report, the optical and structural properties of RT deposited  $BaSi_2$  are discussed. First the reflectance, transmittance and absorbance for both TSDs and thicknesses are treated. Thereafter, the crystallinity is reviewed in terms of Raman spectroscopy and XRD. This is followed by the elemental composition, resulting from AES measurements.

### 5.2.1. Reflectance, Transmittance and Absorbance

The reflectance, transmittance and absorbance (R-T-A) of room temperature (RT) sputtered barium disilicide is plotted in figure 5.1. On the left side of figure 5.1 the R-T-A is plotted for a TSD of 135 and 80 mm at a material thickness of 500 nm, while on the right side the the R-T-A is plotted for a material thickness of 130 and 500 nm at a TSD of 135 mm. All R-T-A values are plotted for a wavelength range of 300 - 2500 nm. First the influence of the TSD on the R-T-A is discussed, which is followed by the influence of material thickness on the R-T-A.

In figure 5.1a it is observed that there is no transmittance, except for some noise for wavelengths over 2200 nm, for a TSD of 80 mm. This is different than the transmittance observed for a TSD of 135 mm. At this TSD there is transmittance for wavelengths larger than 1200 nm, in an increasing matter for longer wavelengths (lower photon energies) up to 13.5%. It is speculated that the reason for this difference is due to a difference in composition, resulting in a higher absorption coefficient ( $\alpha(\lambda)$ ) / extinction coefficient ( $\kappa(\lambda)$ ) for the TSD: 80 mm material. As elaborated in section 4.1, barium atoms have a larger thermalisation distance compared to silicon atoms. In the case that the thermalisation distance of Ba is longer than that of Si, it follows that for shorter TSD the Ba to Si ratio is higher (Ba rich) than for longer TSDs, for the same reasoning as the increase in thickness uniformity for longer TSDs, as elaborated in section 4.1 and appendix A. On the other hand, a difference in thickness between the 2 samples also influences the transmittance between the two samples, as is explained in the next paragraph. Therefore it is recommended to verify whether the difference is due to a difference in composition or due to a difference in thickness, or due to a combination of both. This could be researched by means of AES. This technique is able to determine the elemental composition of the material throughout depth and the technique is already used in this work.

Furthermore, it can be seen that the reflectance and absorbance are very comparable for both TSDs, with a value of approximately 26 % and 74 % in the wavelength region of 500 - 1200 nm, respectively. The peaks and valleys appearing in the wavelength range larger than 1200 nm for the TSD of 135 mm, which is the same range as where the material starts transmitting, are the result of constructive and destructive interference. Constructive interference occurs when the reflected waves form the substrate and the reflected wave of the material underneath it are in phase with each other,



Figure 5.1: Reflectance, Transmittance and Absorbance comparison for a TSD of 135 and 80 mm at a thickness of 500 nm (left) and a comparison between a thickness of 130 and 500 nm for a TSD of 135 mm (right).

while at destructive interference the waves are out of phase with each other and thereby canceling out one another. This constructive interference is seen as a peak in reflectance, a valley in absorbance and reduced transmittance, while destructive interference is observed as a peak in absorbance, increased transmittance and a valley in reflectance.

Finally, the absorbance of both TSDs does not show a sudden sharp decay, as can be seen for both the computer simulated absorbances of a-Si:H and nc-Si:H. This sudden strong decrease of absorbance indicates that the material behaves as a semiconductor. More specifically, it indicates the approximate position of the bandgap of the material. The bandgap of orthorhombic BaSi<sub>2</sub> is in the range of 1.1 - 1.35 eV ( $\lambda \approx 1100 - 900$  nm), as discussed in chapter 2. Thus it is concluded that RT sputtered material does not behave as a semiconductor and that the material is not in the orthorhombic BaSi<sub>2</sub> phase. These conclusions are supported by the following XRD and Raman spectroscopy results.

In figure 5.1b the influence of the material thickness on the R-T-A can be seen. It is observed that the thinner material has a transmittance of up to 31.4 %, which is higher than the maximum transmittance of 13.5% for the thicker material. In the case of the computer simulated absorbance for a-Si and nc-Si, it results in a decrease in the absorbance. Furthermore, it can be seen that the thinner sample starts to transmit at smaller wavelengths (higher photon energies), at approximately 500 nm. These results agree with the theory of Lambert-Beer law, as explained in section 3.2.2, subject to the following assumptions. The material properties, thus also the absorption coefficient, is the same for both thicknesses and the absorption coefficient is higher for shorter wavelengths. The effect of constructive and destructive interference is even more pronounced for the thin material than for the thick material, drastically influencing the shape of the R-T-A plot. The reflectance of the thin sample is comparable to the thick sample, approximately 26 %, apart from the interference effects. Under the conditions that: the measured reflectance under normal incidence and the substrate type and thickness is the same for both cases, gives a strong indication that the real part  $(n(\lambda))$  of the complex refractive index  $(n(\lambda) + i\kappa(\lambda))$  is the same for both thicknesses, which is explained as follows. The reflectance (R)for normal incidence ( $\theta_i = 0$ ), which means that the direction of the wave is perpendicular to the plane of the sample, depends only on the real part of the refractive index according to Fresnel equations [6]:

$$R(\theta_{\rm i}=0) = (\frac{n_1 - n_2}{n_1 + n_2})^2 \tag{5.1}$$

Where the subscripts 1 and 2 denote the material corresponding to the incident and transmitted light, respectively. Since both samples have the same substrate material and the same measured total reflectance, it follows from equation 5.1 that the refractive index (n) is the same for the sputtered material.

Regarding the bandgap of the material, results are in line with the ones depicted in figure 5.1a. Thus also the thinner material does not behave as a semiconductor and subsequently is not orthorhombic BaSi<sub>2</sub>. Lastly, all the RT sputtered material presented in this section, behaves optically different than nc-Si or a-Si, as can be seen by the difference in absorbance.

#### **5.2.2.** Structural properties

In figure 5.2 the results of Raman spectroscopy are plotted for the red ( $\lambda = 633$  nm) and green ( $\lambda = 514$  nm) laser on the left and right side of figure 5.2, respectively. In both sub-figures the results are shown for a TSD of 80 and 135 mm, measured from both the front (F) and back (B) side in a stacked line plot. Also, in both sub-figures the Raman shift corresponding to the fundamental frequencies of the tetrahedra anion [Si<sub>4</sub>]<sup>4–</sup>, which are characteristic for orthorhombic BaSi<sub>2</sub>, as explained in section 3.2.3, are plotted for comparison.

In figure 5.2a the Raman spectra of the red laser measurements are plotted. The Raman spectrum is shown up to a Raman shift of 600 cm<sup>-1</sup> since the spectrum remains the same for Raman shifts over that value. Firstly, it is observed that there are no peaks present at the Raman shifts specific for orthorhombic  $BaSi_2$  for both TSDs. The Raman spectrum shown in this figure, is found to be characteristic for amorphous  $BaSi_2$ . Furthermore, there is a clear difference between the Raman spectrum measured at the front side of the sample and the Raman spectrum measured at the back side (through the substrate). This difference is attributed to the influence of the substrate, in this work quartz, when measuring through this layer. However, the differences between the TDSs are minor for both the front and back side measurements.



Figure 5.2: Raman shift of room temperature sputtered samples with a TSD of 80 and 135 mm, for both lasers:  $\lambda = 633$  nm (left) and  $\lambda = 514$  nm (right). Measurements performed on the front of the film (F), as well as on the back (B) of the film (through the quartz substrate).

The Raman spectra of the green laser measurements are presented in figure 5.2b. In this figure the spectrum is shown up to a Raman shift of 1000 cm<sup>-1</sup> for clarity. It is observed that the shape of the front and back side measurements is the same for both green and red lasers. In case of the front side, the intensity drops as the Raman shift increases over 200 cm<sup>-1</sup>. In case of the back side, there is a slight increase up to a Raman shift of 450 cm<sup>-1</sup>, which is followed by a pronounced sharp decrease in intensity. The apparent difference between the red and green laser plots is due to the different Raman shift range in the plots. Also, the red laser measures in a narrower Raman shift range (209 - 813 cm<sup>-1</sup>) then the green laser does (19 - 991 cm<sup>-1</sup>). However, the frequencies that indicate orthorhombic BaSi<sub>2</sub>, are all within the 200 to 600 cm<sup>-1</sup> range, making this the region of interest. Thus also for the green laser measurements there is no orthorhombic BaSi<sub>2</sub> detected and the Raman spectrum shown in figure 5.2b is characteristic for amorphous BaSi<sub>2</sub> measured with a green laser.

Furthermore, the Raman spectra measured by the green laser show a lot more noise than the spectra measured by the red laser. The quality of these measurements depend for a large part on the alignment of the laser. The alignment status of the lasers change over time, affecting the quality of the measurements. Moreover, the transparency of the substrate also adds to the noise for the back side measurements. The transparency is dependent on wavelength and therefore the green laser results in relatively higher noise levels. This is also the reason why the intensity is given in relative values instead of absolute values. Nevertheless, the more noise in the measurements, the more difficult it is to compare the results with each other.

The crystallinity is also investigated by means of XRD. The results of the XRD measurements are plotted in 5.3. In the graph the XRD results for RT sputtered  $BaSi_2$  are shown for 3 different substrates: p-type polycrystalline silicon (pc-Si) on top of a c-Si wafer, n-type pc-Si on top of a c-Si wafer and silicon-oxide (SiO<sub>2</sub>) obtained by thermally oxidizing the surface of a c-Si wafer. It is observed that there is no difference with respect to crystal growth for these 3 substrates. More specifically, the RT deposited  $BaSi_2$  is amorphous for the 3 tested substrates and is explained as follows. The very broad intensity peak in the graph, is the result of a broad range of distances between atoms in the lattice, which results constructive interference for a broad range of angles. For a crystalline material, sharp narrow peaks (diffraction lines) at specific angles would be observed, since distances between atoms in a crystal lattice are much more ordered, as explained by Bragg's law in section 3.2.4. The 3 sharp peaks at 2 $\theta$  angles of 31.5, 39 and 42 °are diffraction lines originating from the c-Si substrate. Conclusively, the XRD results agree with the Raman spectroscopy results.



Figure 5.3: XRD pattern for RT sputtered BaSi<sub>2</sub> on a SiO<sub>2</sub>, p-type and n-type pc-Si substrate

Auger electron spectroscopy was performed in order to determine the composition of the material deposited at a TSD of 135 mm. The resulting composition as function of depth is plotted in figure 5.4. The purple line on the right of the figure, denoted as Si(sub), represents the silicon wafer. On top of the wafer the thermal oxide (SiO<sub>2</sub>) of approximatly 90 nm thick is observed in terms of the red and pink line designated as Si(ox) and O, respectively. Thereafter, the RT sputtered BaSi<sub>2</sub> is distinguished by the purple and yellow line indicated with the Ba and Si for the barium and silicon atoms, respectively.

First of all, the results show that the ratio of barium to silicon is 1:2, which is the ratio that corresponds with orthorhombic  $BaSi_2$ . Interestingly, there is a 10% oxygen content throughout the sputtered  $BaSi_2$  film. The reason for the presence of this high amount of oxygen is not known. However, it is speculated that this oxygen is introduced into the material after deposition. It is reasoned that it is unlikely that this amount of oxygen is present in the deposition chamber, which operates at ultra high vacuum levels prior to deposition (<  $1 \cdot 10^{-6}$  Torr) and there is a 100% argon flow at a pressure of 10 µbar through the chamber during deposition. This implies that the material should be porous enough for oxygen to diffuse into after deposition. Thermodynamically it is favourable for barium and silicon to react with oxygen to form BaO and SiO<sub>2</sub> as is evident from the reactions Gibb's free energies of:  $\Delta G_{\rm f} = -525.1$  kJ/mol [93] and  $\Delta G_{\rm f} = -856.5$  kJ/mol [93], respectively. Therefore, it is recommended to investigate the source of this high oxygen content, as it is suspected to be detrimental for the material quality.

At the surface of the material it is noticed that the amount of oxygen increases rapidly. This is attribute to the formation of a surface oxide layer. The time between deposition and measurements was on the order of weeks, therefore it is concluded that the surface oxide formation is self-passivating. The surface oxide layer is approximately 10 nm thick.



Figure 5.4: Elemental composition as function of material thickness of RT sputtered  $BaSi_2$  for a TSD of 135mm, derived from AES

## **5.3.** Electrical properties

In this section the electrical properties of RT deposited (TSD: 135 mm)  $BaSi_2$  are discussed. The fundamental properties of interest, are the charge carrier concentration at thermal equilibrium ( $n_0 / p_0$ ), the mobility ( $\mu_n / \mu_p$ ) and whether the material is p-type or n-type. The Hall setup is able to derive these properties, as explained in section 3.2.6. However, the material is also characterised in terms of sheet resistance, dark and illuminated conductivity and activation energy. From the sheet resistance, the resistivity/conductivity of the material is calculated by using equation 3.13. The conductivities/resistivities obtained by the 3 different measurement methods, are compared with each other for verification. Furthermore, the charge carrier concentration calculated from the activation energy, by using equations 3.20 - 3.22, is compared to the charge carrier concentration obtained by the Hall setup for verification. Finally, the dark conductivity and the illuminated conductivity are compared with each other, to see whether the illuminated conductivity is higher, which would indicate semiconducting behaviour of the material.

In the results of Hall measurements, it is observed that there is an alternating plus and minus sign in the charge carrier concentration. The sign of the charge carrier concentration determines the majority charge carrier type and thereby denotes if the material is p-type or n-type. In literature this phenomena is known as the sign anomaly [94-96]. The phenomena is known to appear in most (tetrahedrally coordinated) amorphous semiconductors [95, 96]. Theories have been developed to explain this effect [95, 96], although none of these theories provide an adequate explanation [94]. Therefore it is difficult to determine the material properties via the hall setup for these materials [94]. That is the reason why, in this work, the results from the hall setup are verified, where possible, with the results from other electrical measurements. Furthermore, it was observed that the charge carrier concentration derived by the hall setup, showed a relatively large spread. Therefore it was chosen to measure the same sample multiple times and present the results in terms of arithmetic mean (AM), minimum and maximum values, standard deviation ( $\sigma$ ) and median (M). The results of the charge carrier concentration are presented in table 5.1 and in table 5.2 for the mobility. The arithmetic mean is determined by taking the absolute values of the charge carrier concentration, in order to avoid addition and subtraction of values due to the alternating plus and minus signs. The AM is calculated by equation 5.2 [97], while for the standard deviation ( $\sigma$ ) equation 5.3 [98] is used.

$$\overline{x} = \frac{\sum_{i=1}^{n} (x_i)}{n} \tag{5.2}$$

$$\sigma = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - \overline{x})^2}$$
(5.3)

Charge carrier concentration							
	TSD: 135 mm						
Nr. of Nr. of	Median	Standard	Arithmetic	Minimum	Maximum		
Positive signs inegative signs	( 2)	deviation	mean	( 2)	( 2)		
(-) (-)	(cm <sup>-</sup> <sup>3</sup> )	(cm <sup>-</sup> 3)	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )		
20 19	9.61E+20	2.78E+22	7.37E+21	1.72E+19	1.71E+23		
TSD: 80 mm							
12 10	1.15E+21	2.91E+21	2.19E+21	1.78E+20	1.16E+22		
Nr. of Nr. of Positive signs Negative si (-) (-) 20 19 12 10	Median (cm <sup>-3</sup> ) 9.61E+20 <b>mm</b> 1.15E+21	TSD: 135           Standard           deviation           (cm <sup>-3</sup> )           2.78E+22           TSD: 80           2.91E+21	Arithmetic mean (cm <sup>-3</sup> ) 7.37E+21 2.19E+21	Minimum (cm <sup>-3</sup> ) 1.72E+19 1.78E+20	Maximum (cm <sup>-3</sup> ) 1.71E+23 1.16E+22		

Table 5.1: Charge carrier concentration of room temperature deposited BaSi<sub>2</sub> measured by the Hall setup

Table 5.2: Mobility of room temperature deposited BaSi<sub>2</sub> measured by the Hall setup

Mobility						
TSD: 135 mm						
Maximum	Minimum	Arithmetic	Standard	Median		
Maximum	Philippin	mean	deviation	riculari		
$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$		
4.3	0.00044	0.28	0.70	0.079		
TSD: 80 mm						
3.0	0.047	0.65	0.64	0.46		

In which  $\overline{x}$  is the AM,  $x_i$  is the  $i^{\text{th}}$  value of the total amount of measured values n and  $\sigma$  denotes the standard deviation.

Although the measured charge carrier concentration shows a relatively large spread, it is determined that the material is degenerate, as can be seen by the very high charge carrier concentration for both TSDs. Furthermore, the sign anomaly is clearly present at both TSDs, as can be seen by the (roughly) same amount of positive and negative signs for the charge carrier concentration. There is also a large spread in the measured mobility. In general the mobility is relatively low for both TSDs. Upon comparison of the two TSDs, it is observed that the measured values of the TSD: 80 mm material have less spread than of the TSD: 135 mm material.

In contrast to the large spread observed for the charge carrier concentration and for the mobility, the resistivity measured with the hall setup, is much more stable, with values ranging between 0.0862 - 0.0824  $\Omega$  cm for a TSD of 135 mm and 0.0124 - 0.0116  $\Omega$  cm for a TSD of 80 mm. These results indicate that the TSD 80 mm material is a better electrical conductor than the TSD 135 mm material. This agrees with the previous speculation that the barium content is larger for the TSD 80 mm material than for the TSD 135 mm, since barium is a(n) (Alkali earth) metal and a better electrical conductor than silicon. The material has a sheet resistance of 1307 - 1561  $\Omega$ /sq and 178 - 204  $\Omega$ /sq for a TSD of 135 and 80 mm, respectively. This corresponds to a resistivities measured by the four-point-probe, are somewhat lower than the resistivities determined by the Hall setup. A possible reason could be that the four-point probe measures at the centre of the sample, while the hall setup has the probes positioned at the corners. Nevertheless, the values are of the same order of magnitude, indicating the correctness of the hall measurements.

**Dark and Illuminated conductivity** The resistivity is also determined by dark and illuminated conductivity measurements with the Wacom machine. The dark and illuminated conductivity are presented in table 5.3. The dark conductivity is 0.840 S/cm and 6.26 S/cm for the TSD 135 mm and TSD 80 mm material, respectively. This corresponds to a resistivity of 1.19  $\Omega$  cm and 0.160  $\Omega$  cm, respectively. The resistivity measured by Wacom, is an order of magnitude larger than the resistivities determined by the hall setup and by the four-point-probe. However, as explained in section 3.2.7, a four point probe technique is more accurate than a 2 point probe technique, due to the influence of the extra contact resistance for the 2 point probe techniques. Furthermore, the measured resistivity can vary upon placing the two contacts, due to the varying contact resistance. In order to have the same contact resistance for the Dark and illuminated conductivity, care was taken to ensure that the contacts were not shifted

Dark and illuminated conductivity						
	Т	SD: 135 mi	m			
Dark Illuminated Rat						
Resistivity	Conductivity	Resistivity	<u>σilluminated</u> Ødark			
(Ωcm)	(S/cm)	(Ωcm)	(-)			
1.19 0.840 1.20 0.836				0.996		
TSD: 80 mm						
0.160	6.26	0.160	6.24	0.995		

Table 5.3: Dark and illuminated conductivity of room temperature deposited material

in between these measurements. Also, care must be taken with respect to heating of the sample upon measuring the illuminated conductivity, since the sample heats up upon illumination, which affects the charge carrier concentration. Therefore, it is recommended to not measure the illuminated conductivity several times in succession.

The illuminated conductivity is determined to be 0.836 S/cm for the TSD 135 mm material, resulting in an illuminated over dark conductivity ratio of: 0.996. For the TSD 80 mm material, the illuminated conductivity is 6.24 S/cm, resulting in an illuminated over dark conductivity ratio of 0.995. This indicates that the illuminated and dark conductivity are approximately the same. It should be noted that the conductivity increases relatively less for material with a high thermal equilibrium charge carrier concentration compared to a material with a low thermal equilibrium charge carrier concentration, when illuminated by the same light source. Nevertheless, the ratio of illuminated over dark conductivity is smaller than unity and this is another indication that the RT deposited  $BaSi_2$  does not exhibit semiconducting properties.

**Activation energy** Lastly, the charge carrier concentration determined by the hall setup, is compared with the activation energy measurements. The activation energy is -4.35 meV for the TSD 135 mm material and -4.75 meV for the TSD 80 mm material. Both these activation energies indicate that the material is degenerate and that the Fermi level is positioned slightly above the edge of the conduction band. Although the results show that the material is not orthorhombic BaSi<sub>2</sub>, the charge carrier concentrations, corresponding to the measured activation energies, are calculated by using equations 3.21, 3.22 and the effective density of states in the conduction and the valence band of orthorhombic BaSi<sub>2</sub> from literature [16], as discussed in section 2.1.2. This results in a carrier concentration of  $n_0 \approx 3.1 \cdot 10^{-19} \text{ cm}^{-1}$  in the case of n-type material and  $p_0 \approx 2.4 \cdot 10^{-19} \text{ cm}^{-1}$  in the case of p-type material for both TSDs. This corresponds with the lower range of charge carrier concentration determined by the hall setup. Although the values of the Hall setup and the ones determined by the activation energy are different, both measurement methods indicate a high charge carrier concentration and degenerate material.

## 5.4. Conclusions: room temperature deposited barium disilicide

The results of this chapter show that sputtering  $BaSi_2$  at room temperature does not yield orthorhombic  $BaSi_2$  for both TSDs. The R-T-A plots do not indicate a bandgap for the material, while in the Raman spectrum, no peaks corresponding with the silicon tetrahedra structure of the orthorhombic crystal, are observed. More specifically, the Raman spectrum and the XRD analysis demonstrate that the room temperature sputtered material is amorphous. The R-T-A comparison between 2 thicknesses reveal that the transmittance increases for the thinner sample, which is also expected from the theory. Moreover, the samples that show transmittance, suffer from constructive and destructive interference patterns, which affect the R-T-A results. The Raman spectra are affected by the alignment status of the green and red lasers, complicates the comparison between the spectra. The substrate induces even extra noise in the measurements. Nevertheless, the spectra have a similar shape for both lasers, are similar between the front measurements through the substrate.

Positively, the elemental composition shows that the barium to silicon ratio is the required 1:2 for the TSD 135 mm material. It is reasoned that the material is barium rich for a TSD of 80 mm, since this material shows less transmittance and higher conductivity. However, it should be noted that these are

indirect indicators and it is therefore recommended to verify this by an elemental composition analysis. Furthermore, it is argued that there is a self passivating surface oxide formation, of approximately 10 nm thick. On the other hand, there is 10 atomic % oxygen content throughout the deposited layer. Although it is speculated that the oxygen diffuses into the material after deposition, it is recommended to investigate its origin, since it is thermodynamically favourable for oxygen to react with barium and silicon to form BaO and SiO<sub>2</sub>.

The electrical characterization for both TSDs reveals that room temperature  $BaSi_2$  has a relatively large carrier concentration in the region of  $10^{20}$  cm<sup>-1</sup> up to  $10^{22}$  cm<sup>-1</sup>, making it degenerate. The mobility is relatively low, with values in the region of 0.1 - 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. These properties are given in a broad range due to the large spread in the values determined by the hall setup. For this reason, the resistivity determined by the Hall setup, is compared with with the resistivity determined by other electrical measurements. The results are in the same order of magnitude, implying that the measurements from Hall setup are correct. Furthermore, the dark and illuminated conductivity are approximately the same, thus demonstrating that the material does not exhibit semiconducting properties. Finally, the activation energy measurements agree with the Hall setup. The position of the Fermi level is slightly above the bottom of the conduction band, meaning that the material is degenerate.

## 6

## Properties of high-temperature deposited barium disilicide

The properties of high temperature (HT) deposited  $BaSi_2$  is discussed in this chapter. High temperature deposition is of interest since literature indicate that this can result in crystalline and orthorhombic  $BaSi_2$ , as elaborated in chapter 2.2. In order to determine the optimal temperature for deposition, a temperature series was performed. The material of the temperature series is compared in terms of optical and structural properties. Although in chapter 4 the TSD of 135 mm is determined to be optimal in terms of thickness uniformity, the TSD was reduced in this work in order to increase the substrate temperature even further. The smallest TSD was 80 mm in this work, since this is the smallest TSD for which the substrate temperature has been calibrated previously. The most promising recipe is further researched in terms of its electrical properties and is compared to the room temperature sputtered material.

In this chapter the methodology is first discussed. Thereafter, the material properties of the temperature series is compared in terms of reflectance transmittance and absorbance (R-T-A) and Raman spectroscopy for optical and structural comparison. Next, the electrical properties of the most promising material from the temperature series are reviewed. In the final part of the chapter, conclusions are treated.

## 6.1. Methodology

The same substrate and cleaning procedure was applied, as described in section 4.2. The RF magnetron recipe, as described in appendix B, was used, with the following changes. The substrate was Corning EAGLE XG<sup>®</sup>, the deposition time was 75 minutes for all samples, while the TSD was reduced to 110 mm and 80 mm to obtain a substrate temperature of approximately 400 °C and 450 °C, respectively. Consequently, the film thickness varies between the various samples. The thickness at a TSD of 135 mm is approximately 500 nm, while the thickness at a TSD of 80 mm is approximately 660 nm. In order to have a fair comparison of the electrical properties, the deposition time was reduced to 60 min for a TSD of 80 mm, which corresponds to a thickness of approximately 500 nm. After deposition, the samples were cooled the whole night in the load-lock of the machine by natural convection instead of forced cooling, to eliminate thermally induced stresses in the material. The high temperature deposition series compares the properties of material deposited at a substrate temperatures of <310 °C (TSD:135 mm), <390 °C (TSD:135 mm),  $\approx$  400 °C (TSD:110 mm),  $\approx$  450 °C (TSD:80 mm). These temperatures are obtained by setting the temperature controller at a temperature of: 500 °C, 600 °C, 615 °C, 615 °C, respectively. The substrate temperatures have only been calibrated for a TSD of 110 mm and 80 mm in previous works. For this reason, the temperatures at a TSD of 135 mm are given as: 'lower than' the temperature it would have been at a TSD of 110 mm. After deposition, characterization is carried out by spectrophotometry and Raman spectroscopy. The material deposited at a substrate temperature of  $T_{\rm s} \approx 450$  °C, with a thickness of 500 nm, is thereafter characterized with the Hall setup, four-point probe, dark IV, illuminated IV and activation energy.

## **6.2.** High Temperature deposition series

The material properties of the high temperature deposition series is compared in terms of the optical and structural properties. The optical properties are first discussed in terms of reflectance, transmittance and absorbance. Thereafter, the Raman spectrum is treated, which sheds light on the structural properties.

### 6.2.1. Reflectance, Transmittance and Absorbance

The R-T-A plot of the substrate temperature series is presented in figure 6.1. The transmittance and absorbance are plotted in 6.1a, while the reflectance is depicted in 6.1b. In these graphs, the substrate temperature corresponding with the plotted data, is denoted between brackets. The computer simulated absorbance of 500 nm thick a-Si:H and nc-Si:H is plotted in the graph for comparison. The data is plotted for a wavelength range of 300 nm up to 2500 nm.

First of all, it is observed that none of the samples in this series exhibits a bandgap, especially not near the expected bandgap in the range of 1100 - 900 nm. It appears that the material deposited at a substrate temperature smaller than 310 °C has a bandgap around 1500 nm. However, it is suspected that this is not the result of a bandgap. In particular, this material has a significantly higher transmittance in the whole infrared (IR) range, while it also has more interference than the other samples, resulting in a relatively high reflectance between 1500 an 2400 nm. These effects appear to be very similar to the effect of reducing the sample thickness for the room temperature sputtered material, which is discussed in section 5.2.1. This behaviour is therefore expected to be the result of a thinner material layer, which could have been caused by a plasma failure during deposition. Plasma failures were observed more often for high temperature depositions. Nevertheless, this recipe does not result in orthorhombic BaSi<sub>2</sub> material as will be evident from the Raman spectroscopy. For this reason this behaviour is not further investigated.

There is a noteworthy difference in the reflectance of the samples. The reflectance of the lowest substrate temperature is only 12% in the region without interference effects. This is much lower than the 20% to 26% of the samples deposited at a higher substrate temperature. This difference in reflectance indicates that the material differs in terms of the real part of the complex refractive index, which can be seen in equation 5.1. Since the substrate is the same for these samples  $(n_1 \text{ in equation } 5.1)$ , the difference in reflectance is then due to a difference in refractive index  $(n_2)$  of the deposited material.

There is no transmittance of light for the material with a substrate temperature of 400 °C and 450 °C, while there is transmittance for the material deposited at  $T_{\rm s}$  < 310 and  $T_{\rm s}$  < 390 °C. The high transmittance of the material deposited at  $T_{\rm s}$  < 310 °C is expected to be the result of a thinner material thickness, as discussed previously in this section. The transmittance of the  $T_{\rm s}$  < 390 °C material shows a similar trend as the TSD: 135 mm material sputtered at room temperature, which is reviewed in section 5.2.1. The differences are (partially) attributed to the difference in interference. The zero transmittance of the higher temperature depositions, are mostly attributed to the thicker material thickness due to the decreased TSDs.



Figure 6.1: Comparison of the reflectance (right) and transmittance and absorbance (left) for varying substrate temperatures



Figure 6.2: R-T-A comparison between the high temperature ( $T_s$ : 450 °C) and room temperature sputtered material. Also the high temperature material is compared in terms of thickness.

The influence of the thickness on the R-T-A values is also examined for the high temperature deposited material. The R-T-A is plotted in figure 6.2 for a wavelength range of 300 - 2500 nm. Also, the computer simulated absorbance of a-Si:H and nc-Si:H is plotted in the figure for comparison.

The influence of the thickness of the material on the R-T-A is very similar to the room temperature case, as described in section 5.2.1. The thinner material also does not exhibit a bandgap, which is similar as seen for the room temperature samples. Furthermore, the transmittance increases for a thinner material, which agrees with Lambert-Beer law, as explained in section 5.2.1. However, the transmittance does not increase as much in this case, compared to the RT case. This is attributed to the slightly thicker material for the high temperature deposited sample due to the lower TSD. Furthermore, it is argued in chapter 5 that the material deposited at lower TDS has a higher barium content, which results in a lower transmittance in the infrared range. Moreover, the thinner material suffers from a different interference pattern, which makes it difficult to compare the the R-T-A above a wavelength of 900 nm with each other. Nevertheless, it is observed that the absorbance is overall lower compared to the thicker sample, which is a direct result of the reduced material thickness, which also agrees with Lambert-Beer's law.

Furthermore, the high temperature material is compared with the room temperature (RT) sputtered material, indicated by the red lines in the graph. The RT sputtered  $BaSi_2$  has a lower transmittance, almost no interference effects and a higher absorbance in the infrared range. Since both material are deposited with the same recipe except for the temperature, the difference has to be attributed to the increased substrate temperature during deposition. More specifically, these changes could be the result of the crystallization of the material, which is discussed in the following section.

#### 6.2.2. Structural properties

The effect of substrate temperature on the crystal structure is discussed in this section of the report. The crystallinity of the material is determined by Raman spectroscopy. The Raman spectra of the high temperature deposited material is presented in figure 6.3. In the left side of this figure (6.3a), the Raman spectra is shown for the front side measurements, while on the right side (6.3b), the Raman spectra is plotted for the measurements through the substrate. All measurements are performed with the red laser ( $\lambda = 633$  nm), since it measures further into the material and thereby it can characterize more of the bulk of the material instead of the surface. The red laser is also better for measurements



Figure 6.3: Raman spectra of the substrate temperature series of the front (left) and back (right) side of the material, measured by the  $\lambda = 633$  nm laser. The result of a high temperature deposited sample obtained from the Nagoya university and the room temperature sputtered results are plotted for comparison.

through the substrate, for the same reason. Results are plotted in a stacked graph for better comparison. In the graphs, the position of the fundamental frequencies of the  $[Si_4]^{4-}$  tertrahedra and of c-Si, as explained in section 3.2.3, are plotted as dashed lines. The peak at 486 cm<sup>-1</sup> is quantitatively compared by its full width at half maximum (FWHM) value. This frequency is chosen because it has the highest intensity compared to the other frequencies, as mentioned in section 3.2.3. Furthermore, this peak is the least affected by neighbouring peaks, resulting in a better fit. The peak is fitted by a nonlinear Gaussian curve fit in the OriginPro <sup>®</sup> software package. Lastly, a sample obtained from Nagoya university was also measured for comparison and is plotted in the figure. This material has a thickness of 400 nm and was deposited by RF magnetron sputtering on a quartz substrate.

Firstly, the Raman spectra shows that there is crystal growth for high temperature depositions with temperatures of 400 °C and above. On the other hand, the substrates deposited at a temperature less than 390 °C, indicate the growth of amorphous material for both the front and back side measurements, similar to the room temperature deposited material. More specifically, for the  $T_{\rm s}$  > 400 °C, there is crystalline material detected for the front side measurements, while this is not the case for the measurements through the glass. This suggests that the sample is amorphous directly on top of the substrate, while there is crystal growth in the latter layers. The transition point is not know, while it is clear that this transition point is at a distance further away from the substrate than the penetration depth of the laser. Furthermore, the transition is a function of the substrate temperature, since there is a very weak peak detected for the  $T_c$ : 450 °C material, while this is not detected for the lower substrate temperatures. Therefore, it is reasoned that the better quality at the surface of the material, is partially attributed to the heating up of the substrate and target during the deposition. While heating up the installation, the shutter is closed and the target is behind the shutter. When removing the shutter to start the deposition, the temperature could drop to lower values until the target and substrate are heated up again to its (new) equilibrium temperature. Another reason could be that the substrate affects the material. This would mean that the material first grows amorphous on the glass substrate and crystallizes during deposition. Epitaxial growth has been achieved in literature on Si(111) and Si(100) wafer orientation, as discussed in the literature review in chapter 2. For future research it could be interesting to investigate if the material is able to grow epitaxial on these c-Si wafers.

Furthermore, the FWHM values are determined of the peaks at a Raman shift of 486 cm<sup>-1</sup>. The FWHM is 15.4 and 15.1 for the material with a substrate temperature of 400 and 450 °C, respectively. This, together with the appearance of a peak at the back side of the  $T_s$ : 450 °C material, suggests that the material grows more crystalline for higher substrate temperatures. Moreover, with the recipe used for the  $T_s$ : 450 °C material, a 500 nm thick sample was made on quartz. This corresponds

with the pink spectrum in the figure. It is observed that the FWHM value is lower for the material deposited on guartz than for the same deposition on Corning EAGLE XG<sup>®</sup>. It is suspected that the thinner thickness of the guartz enables a (slightly) higher temperature on the substrate. The guartz substrate has a thickness of 0.5 mm, while the Corning EAGLE XG® has a thickness of 0.7 mm. On the other hand, the Raman spectrum measured through the substrate, appears slightly more crystallized for the Corning EAGLE XG<sup>®</sup> sample than for the quartz sample. Unfortunately, the setup is only able to reach a maximum substrate temperature of approximately 450 °C, which is already pushing the apparatus to its limits. It would be very interesting to see how the material would perform if it could be deposited at higher substrate temperatures. Therefore, it is recommended to either upgrade the machine or switch to another machine capable of reaching higher substrate temperatures, if that lies within the possibilities. The sample from Nagoya university is more crystallized than the samples in this work, which is observed by its smaller FWHM of 11.6 for the front side and even 10.9 for the back side measurements. This sample is probably deposited at a higher substrate temperature, which would explain this result. Noteworthy are the two peaks observed at a Raman shift of 262  $cm^{-1}$  and  $309 \text{ cm}^{-1}$ . The origin of these peaks is unknown and was also never observed for the in-house made samples of this work.

Final remark is regarding the Raman spectrum of the  $T_{\rm s}$  < 310 °C material, which is rather different compared to all other Raman spectra. Therefore, this Raman spectroscopy measurements was performed a second and third time for verification, with similar results. Normally, this Raman spectra is observed when measuring the glass substrate rather than the BaSi<sub>2</sub> material. Nevertheless, no further research was performed, since the front side measurements indicate no crystallization of the material.

## **6.3.** Electrical properties

In this section, the electrical properties of the material deposited at a substrate temperature of 450 °C are treated, similarly to section 5.3 of the previous chapter. However, the four-point-probe apparatus was unable to measure the sheet resistance of this material, which was previously used used for verification of the resistivity determined by the Hall setup. It is reasoned that the apparatus was not able to measure the sheet resistance due to the higher resistivity of the material, as a result of the lower charge carrier concentration. The charge carrier concentration and the mobility determined by the Hall setup, are presented in table 6.1 and 6.2, respectively. The same large spread in the values is observed for this material. Therefore, the charge carrier concentration and the mobility are both presented in terms of the minimum and maximum values, AM, standard deviation and median, similar to section 5.3.

Also, this high temperature deposited material suffers from the sign anomaly. It is suspected that this occurrence of the sign anomaly can be explained by the structural properties, as follows. The structural properties indicate that the material is deposited amorphous on the substrate, while it grows crystalline further away from the substrate. Thus the material is not fully crystallized throughout the layer. This presence of an amorphous phase in the material is expected explain the sign anomaly in the Hall measurements.

The charge carrier concentration of the  $T_s$ : 450 °C material is lower than of the room temperature deposited material. More specifically, the charge carrier concentration is of the order of  $10^{-17}$  cm<sup>-3</sup> up to high in the  $10^{-18}$  cm<sup>-3</sup> for the high temperature deposited material, while the charge carrier

Charge carrier concentration						
		Ce	ntre of the	substrate		
Maximum	Minimum	Arithmetic	Standard	Median	Nr. of	Nr. of
Maximum	Pininiani	mean	deviation	riculari	Positive signs	Negative signs
(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(-)	(-)
2.83E+17	2.99E+16	1.00E+17	7.37E+16	9.59E+16	7	4
1 cm out of the centre of the substrate						
9.44E+18	1.55E+17	1.52E+18	2.67E+18	4.84E+17	8	3

Table 6.1: Charge carrier concentration of high temperature deposited (substrate temperature: 450 °C, TSD: 80 mm) BaSi<sub>2</sub>, measured by the Hall setup.

Mobility							
	Centre of the substrate						
Maximum	Minimum	Arithmetic	Standard	Median			
Maximum	Pinning	mean	deviation	riculari			
$(cm^2V^{-1}s^{-1})$	$m^2 V^{-1} s^{-1}$ ) (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )		$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$			
26.6	2.80	12.6	8.03	8.23			
1 cm out of the centre of the substrate							
19.8	0.32	7.69	5.43	6.20			

Table 6.2: Mobility of high temperature deposited (substrate temperature: 450 °C, TSD: 80 mm) BaSi<sub>2</sub>, measured by the Hall setup.

concentration is 2-5 orders of magnitude larger for the room temperature deposited material of section 5.3. This suggest that the  $T_s$ : 450 °C material is not degenerate, which is in contrast to the case for the room temperature material. The mobility also shows a great improvement with respect to the room temperature material. The mobility of the high temperature material is on average an order of magnitude larger, with an arithmetic mean of the mobility in the range of 7.69 - 12.6 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Both these results indicate that the material is better suited as an absorber layer in a photovoltaic device than the room temperature deposited material.

Furthermore, it is observed that the charge carrier concentration depends on the position from which the sample is taken. The charge carrier concentration is on average lower in the centre of the sample in comparison to 1 cm out of the centre. For this reason it is recommended to further research which area of the sample exhibits which properties at this recipe, which is important to know if the material is used for solar cells in future research. This difference is also seen in the measured resistivity. In the centre, the resistivity is between 7.84  $\Omega$  cm and 7.96  $\Omega$  cm, while it is between 2.04  $\Omega$  cm and 2.08  $\Omega$  cm for the sample taken 1 cm out of the centre. It is speculated that these differences could be a result of varying barium to silicon ratio, varying material thickness, a difference in substrate temperature during deposition, affecting the crystallinity of the material, or a combination of these.

**Activation energy** The activation energy of the material is -2.96 meV. This suggests that the Fermi level is just above the bottom of the conduction band and that the material is degenerate, similar to the results of room temperature sputtered BaSi<sub>2</sub>. The charge carrier concentration corresponding with this activation energy, is  $n_0 \approx 2.9 \cdot 10^{-19}$  cm<sup>-3</sup> and  $p_0 \approx 2.2 \cdot 10^{-19}$  cm<sup>-3</sup> in the case of n-type and p-type material, respectively. These values are derived as explained in section 5.3. It can be seen that the charge carrier concentration determined by the Hall setup. However, as already mentioned in this section, the charge carrier concentration appears to increase significantly when it is measured out of the centre. The contacts for the activation energy are deposited roughly 0.5 cm out of the centre of the sample and have a width of 2 cm, which is determined by the available mask. The position and size of the contacts are expected to be (partially) the reason for this large discrepancy in charge carrier concentration measured by the Hall setup and the activation energy. However, there is not sufficient data available to make solid conclusions, therefore it is recommended to further investigate this matter.

**Dark and illuminated conductivity** The dark and illuminated conductivity is determined for the contacts facing the light source and for the case that the light enters through the substrate. The dark and illuminated conductivity are presented in table 6.3.

The dark conductivity is 0.319 S/cm and 0.321 S/cm, while the illuminated conductivity is 0.322 S/cm and 0.322 S/cm for the case of contacts facing the light source and light coming through the substrate, respectively. This corresponds to a resistivity of 3.13  $\Omega$  cm and 3.11  $\Omega$  cm (dark) and 3.11  $\Omega$  cm (illuminated), for respectively contacts facing the light and light through the substrate. The ratio of illuminated over dark conductivity for contacts facing the light is 1.008 and it is 1.003 for the other case. Although the increase in conductivity is relatively small, for both these cases there appears to be an increase in charge carrier concentration due to light induced charge carrier generation, leading to an increase in conductivity. However, for these measurements the same samples are used as for the activation energy. Therefore, in these measurements the contacts are

Dark and illuminated conductivity						
C	ontacts facin	g towards t	he light sour	ce		
C	Dark	Illun	ninated	Ratio		
Resistivity	Conductivity	Resistivity Conductivity		$\frac{\sigma_{illuminated}}{\sigma_{dark}}$		
(Ωcm)	(S/cm)	(Ωcm)	(S/cm)	(-)		
3.13	0.319	3.11	0.322	1.008		
Light entering through the substrate						
3.11	0.321	3.10	0.322	1.003		

Table 6.3: Dark and illuminated conductivity of high temperature deposited (T<sub>s</sub>: 450 °C) BaSi<sub>2</sub>

also not exactly in the centre. Thus the conductivity is measured in the region where the charge carrier concentration is high relative to the centre. For this reason, the light induced charge carriers are small compared to the thermal equilibrium charge carrier concentration, which could (partially) explain the small increase in conductivity upon illumination. Another reason for the small increase in the conductivity, could be due to the presence of an amorphous phase along with the crystalline phase. This amorphous material does not exhibit semiconducting properties and thereby does not generate light induced charge carriers that would otherwise increase the illuminated conductivity of the material.

### **6.4.** Conclusions: high temperature deposited barium-disilicide

The first thing that can be concluded is that depositing  $BaSi_2$  at high substrate temperatures improves the material quality. More specifically, the high substrate temperature enables the growth of orthorhombic  $BaSi_2$ , which is the semiconducting material of interest in this work. Moreover, the material deposited at a substrate temperature of 450 °C, is the most crystalline material of the high temperature deposition series. However, the high temperature deposited sample from Nagoya university, indicates an even higher crystallization. This result suggests that higher crystallinity can be achieved at even higher substrate temperatures. Unfortunately, the apparatus is not able to reach higher substrate temperatures. For this reason, it is recommended to investigate the possibility to either upgrade the machine in order to reach higher substrate temperatures or to change to another machine that is capable of reaching higher substrate temperatures.

Furthermore, the Raman spectra measured from the back side of the samples, indicate that the material is amorphous directly on top of the substrate. The material is thus a combination of amorphous and crystalline material. Also, there is no bandgap observed in the R-T-A plot of the high temperature material. This result is attributed to the presence of this amorphous material in the samples. Therefore, the material can be improved much further in terms of crystallization. It is expected that a more crystallized material will lead to the observation of a bandgap in the R-T-A plot.

The electrical properties of the high temperature deposited material, are also improved with respect to the room temperature deposited material. The charge carrier concentration is in the region of 10<sup>17</sup> cm<sup>-3</sup> up to 10<sup>18</sup> cm<sup>-3</sup>, which is a significant decrease of 2-5 order of magnitude with respect to the room temperature material. This means that this material is not degenerate, although the charge carrier concentration is still rather high compared to (intrinsic) charge carrier concentrations reached in literature. On the other hand, the results from the activation energy:  $E_a = -2.96$  meV, do not agree with the charge carrier concentration results from the Hall setup. However, it is observed that the measurement results depend on the position of the measurement. For this reason it is suspected that the position and dimensions of the contacts affect the results of the activation energy measurements. Therefore, it is recommended to further research this behaviour. Moreover, the mobility has increased up to 7.69 - 12.6 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, which is an increase of an order of magnitude with respect to the room temperature sputtered material. Furthermore, the ratio of illuminated over dark conductivity indicates that the material exhibits semiconducting properties, although the illuminated conductivity is only slightly larger than the dark conductivity. These improvements are also attributed to the improved crystallinity of the high temperature deposited material with respect to the amorphous room temperature sputtered material.

# 7

## Effects of post-growth annealing on the properties of barium disilicide

In chapter 6, it is discussed that depositing at increased substrate temperatures improves the material properties with respect to room temperature deposited material. Nevertheless, the properties of the high temperature deposited material can still be improved. In literature, it is demonstrated that amorphous BaSi<sub>2</sub> material can be crystallised into orthorhombic BaSi<sub>2</sub> by post-growth annealing. For both these reasons, the effect of post-growth annealing on the optical, structural and electrical material properties was researched in this work. The optimal annealing strategy for obtaining the best material quality, is a combination of both annealing temperature and annealing time. First, the optimal temperature range is determined by an annealing temperature series at a fixed annealing time. For the two most promising temperatures, the annealing time is varied to investigate the effect on the material quality. Furthermore, post-growth annealing is also researched for material deposited at a TSD of 80 mm. Moreover, the combination of high temperature deposition and post-growth annealing is presented in this work, which is compared with the room temperature deposited material.

This chapter is structured as follows. First the methodology is treated. Thereafter, the effect of annealing temperature on the optical and structural properties is discussed. This is followed by the section, which reviews the influence of annealing times on the optical and structural properties. In the same section, the properties of post-growth annealed material deposited at a TSD of 80 mm is examined. In the next section, the results of combining high temperature deposition and post-growth annealing are presented. Thereafter, the electrical properties of the best annealing results are treated. Finally, conclusions with respect to post-growth annealing are discussed.

## 7.1. Methodology

The Hereaus Spectrosil<sup>®</sup> 2000 fused silica was used as substrate in this experimental work, since it is able to withstand the relatively high annealing temperature up to 750 °C used in this work. The same cleaning method was used as described in section 5.1. Also, the same wafer substrates were used for the AES measurements as explained in 5.1. The parameters used for researching the optimal annealing temperature, are the same as presented in appendix B. The room temperature deposited samples were thereafter annealed in a Carbolite AAF 11/7 furnace, with a nitrogen backing gas flow of 25 L/min. The researched annealing temperatures are: 550 °C, 600 °C, 650 °C, 700 °C and 750 °C. These annealing temperatures were based on previous research on post-growth annealing, which is treated in chapter 2.2. The annealing time was kept constant at 90 minutes for these annealing experiments, also based on previous experimental research found in literature. In the Carbolite furnace, the temperature ramp up rate was set to 400 °C/hr. All annealing experiments were performed in a furnace that was at room temperature prior to annealing. The samples were measured by spectrophotometry and Raman spectroscopy. Also in this work, samples were send to the university of Bratislava in Slovakia for AES analysis and to the new technologies research centre of the university of West Bohemia in Pilsen for XRD analysis.

For the annealing time experiments, the same procedure as described above was utilized. The examined annealing time and temperature combinations are: 650 °C for 90 min and 180 min for TSD: 135 mm material and 700 °C for 90 min and 30 min for TSD: 135 mm and 80 mm. The sample where the combination of high temperature deposition and annealing was investigated, was annealed at 700 °C for 90 min. These samples were all measured by spectrophotometry and Raman spectroscopy.

The most promising samples were the following combinations. Room temperature (TSD: 135 mm) deposited material, post-growth annealed at 700 °C for 30 min and 90 min, and the RT and high temperature (TSD: 80 mm) deposited samples, annealed at 700 °C for 90 min. These samples were characterized in terms of electrical properties by hall setup, activation energy and dark IV and illuminated IV. It was also attempted to measure the sheet resistance with the four-point probe, however the apparatus was unable to measure the annealed samples.

## **7.2.** Effect of annealing temperature on RT deposited material properties

The effect of post-growth annealing for various annealing temperatures is reviewed in this section. First, the optical properties are discussed in terms of absorbance, transmittance and reflectance. This data is used to determine the absorption coefficient, indirect and direct bandgap Tauc plots. Secondly, the structural properties of the annealed material are discussed by Raman spectroscopy, XRD and AES.

#### **7.2.1.** Optical properties

The R-T-A of the RT deposited, post-growth annealed samples are plotted in figure 7.1. Figure 7.1a shows the transmittance and absorbance of the samples, while the reflectance is presented in figure 7.1b. The absorbance, transmittance and reflectance are denoted as A, T and R in the graph, respectively. The annealing temperature is indicated between brackets in the legend. The absorbance of a-Si:H and nc-Si:H is plotted in the graph for comparison.

In figure 7.1a, it is observed that the absorbance decreases in the IR range for higher annealing temperatures. This decrease in absorbance is accompanied by an increase in the transmittance. The transmittance is the largest for the samples annealed at 700 °C and 750 °C, while the transmittance of the samples annealed at 550 °C and 600 °C is zero throughout the whole spectrum. The transmittance of the material annealed at 650 °C is in between these regions, with a transmittance of approximately 15% in the IR range. The absorbance and transmittance results of the high annealing temperatures, indicate the presence of a bandgap in the material. This apparent bandgap appears at a longer wavelength than the bandgap of the a-Si:H and nc-Si:H materials, thus the material has not resulted in either a-Si:H or nc-Si:H after annealing.

The material change due to annealing, is accompanied by a reduction of reflectance, as can be seen in figure 7.1b. The reflection of the material annealed at 550 °C and 600 °C is between 20% and 30%, depending on the interference. This is in the same range as the RT material exhibited.



Figure 7.1: Reflectance (right), transmittance and absorbance (left) of RT deposited (TSD: 135 mm) BaSi<sub>2</sub>, post-growth annealed at varying annealing temperatures for 90 minutes.

Therefore, it appears that the material changes little for these annealing temperatures. However, the material annealed at 650 - 750 °C shows a reduction of the reflection in the low wavelength range. The reflection is in the range of 10 - 20%, also depending on interference. Therefore, it is concluded that the material changes for annealing temperature of 650 °C and higher, annealed for 90 minutes.

The optical bandgap of the material can be estimated by a Tauc plot, as explained in section 3.2.2. The Tauc plot requires the absorption coefficient of the material. For this reason the absorption coefficient is determined for the annealed samples of 650 °C and higher. The absorption coefficient is calculated using equation 3.3. The absorption coefficient presented here, is only valid in the high absorption region, where the material is optically thick. At the point where the material is optically thin, interference effects and internal reflection affect the absorption coefficient. The absorption coefficient of the material annealed at 650 - 750 °C is presented in figure 7.2. In the figure, the absorption coefficient of 1  $\mu$ m thick BaSi<sub>2</sub> deposited at a substrate temperature of 600 °C, obtained from Latiff et al. [11], is plotted for comparison.

In the figure, it is observed that the absorption coefficient is relatively constant for high photon energies for the material annealed at 650 °C and 700 °C, similar to the reference of Latiff et al. At photon energies below 1.8 eV, the absorption coefficient decreases rapidly for the material of Latiff et al. However, for the samples in this work the absorption coefficient decreases less rapidly. This indicates that the material created in this work, is more defective and not a perfect crystal. This is also evident by the Raman spectra, XRD analysis and AES, which are discussed in the following section of this chapter.



Figure 7.2: Absorption coefficient plot of room temperature deposited  $BaSi_2$  at a TSD of 135 mm, post-growth annealed for 90 min at 650, 700 and 750 °C, respectively. In the graph the absorption coefficient of 1 µm thick barium disilicide deposited at a substrate temperature of 600 °C is plotted for comparison. Source: Latiff et al. [11]



Figure 7.3: Tauc plot of the RT deposited (TSD: 135 mm) material, annealed at 650 - 750 °C, for an indirect bandgap (left) and for a direct bandgap (right). Tauc plot of Latiff et al. [11] plotted as a reference for the indirect bandgap.

The absorption coefficient of the annealed material is used to derive the Tauc plots for a direct and indirect bandgap. The results are presented in figure 7.3. The Tauc plot for an indirect bandgap is plotted in figure 7.3a and the direct bandgap is shown in figure 7.3b. The optical bandgap is derived by extrapolating the linear region. These are depicted as the black lines in the graph. The point at which the linear fit intersects the x-axis, is the optical bandgap.

The reference material of Latiff et al. [11], has an estimated optical indirect bandgap of 1.25 eV, which agrees with the indirect bandgap in literature of 1.1 - 1.35 eV [2, 16, 18]. The material of this work has a lower indirect bandgap of 0.70 eV, 0.99 eV and 0.81 eV, for the material annealed at 650 °C, 700 °C and 750 °C, respectively. The indirect bandgap of the material annealed at 700 °C, is the closest to the literature reported values. The direct bandgap derived for the material of this work, is 1.72 eV, 1.91 eV and 2.34 eV for the material annealed at 650 °C, 700 °C and 750 °C, respectively. It is observed that the material of this work, exhibits a larger direct bandgap than the bandgap reported in literature.

### 7.2.2. Structural properties

In figure 7.4, the Raman spectra for the annealed samples are presented. The red laser ( $\lambda = 633$  nm) is used for measurements, since it is able to measure deeper into the material compared to the green laser ( $\lambda = 514$  nm). The results are compared to the high temperature material, deposited on quartz with a substrate temperature of 450 °C. Also, the Raman spectrum of the RT deposited material is plotted in the graphs. In figure 7.4a, the front side measurements are plotted and figure 7.4b shows the back side measurements. In the graphs the FWHM values are depicted for the peak at 486 cm<sup>-1</sup>.

The Raman spectra shows that the material is more crystallized for higher annealing temperatures. This is quantified by the FWHM, which reduces for higher annealing temperatures. The crystallization of the material thus influences the absorbance and transmittance of the material. The material becomes more transmitting in the IR range for higher crystallization, as can be seen in the R-T-A plot of figure 7.1. The annealed material is also more crystalline than the high temperature deposited material. Furthermore, the annealed material is crystalline on top of the substrate, while this is not the case for the high temperature deposited material.

Moreover, the Raman spectrum shows an increase in c-Si intensity for higher annealing temperatures. The material annealed at 750 °C, does not show any orthorhombic  $BaSi_2$  peaks at all. This material only has a very strong peak corresponding to c-Si. The c-Si peak is less defined for the measurements through the substrate, as can be seen in the red circles in figure 7.4b. From these observations, it is concluded that there is a reaction occurring at the surface of the material during the annealing, which affects the material properties.



Figure 7.4: Raman spectra of the post-growth annealed (90 min) RT (TSD: 135 mm) deposited material. Measurements performed by the red laser on the front (left) and back (right) side of the material. The result of the material deposited at a substrate temperature of 450  $^{\circ}$ C and at RT are plotted for comparison.

The effect of this surface reaction on the structural properties of the material throughout the depth, is further reviewed in figure 7.5. In this figure, the Raman spectra is shown of the material annealed at 650 °C. The material is measured by the green and red laser on the top and by the red laser through the substrate. In order to approximate the depth at which the 2 different lasers penetrate into the material in figure 7.5, the penetration depth of the light is calculated by using the following assumptions. The material properties are uniform throughout depth and the absorption coefficient is given by the orange curve in figure 7.2. The absorption of light is described by Lambert-Beer law:  $I(x) = I_0 \exp(-\alpha x)$ . Furthermore, the penetration depth of light is the distance at which:  $1 - \exp(-1)$  ( $\approx 63\%$ ) of the light is absorbed by the material. The penetration dept  $x_p$  is calculated by:  $x_p = \frac{1}{\alpha}$ , resulting in a  $x_{p-514nm} = 86$  nm and a  $x_{p-633mm} = 120$  nm for this specific case.



Figure 7.5: Raman spectra as function of depth of RT deposited BaSi<sub>2</sub> annealed at 650 °C

In the Raman spectrum of figure 7.5 it is observed that the material properties change throughout the depth. The closer to the surface of the material, the less orthorhombic barium disilicide is present. On the other hand, the c-Si peak becomes more prominent closer to the surface. This material change is attributed to oxidation of the surface, which is evident from the AES analysis, presented in figure 7.9. The AES indicates that there is preferential oxidation of barium, resulting in a silicon rich material. The preferential oxidation of barium was also described in literature [80]. This silicon rich material forms c-Si, as can be seen in the Raman spectrum. The reaction proposed in literature is:  $2BaSi_2 + O_2 \rightarrow 2BaO + 4Si$  [99, 100]. From figure 7.4, it is concluded that this oxidation reaction has higher kinetics for higher temperatures. Therefore, it is recommended to research the crystallinity for samples annealed at 750 °C (and possibly higher), in the case that oxidation of the material can be prevented.

The structural properties of the post-growth annealed, RT (TSD: 135 mm) deposited material were measured by XRD and the results are presented in figure 7.6. In the figure, the XRD pattern is plotted for the tested annealing temperatures. These XRD spectra are compared to the theoretical diffraction lines of orthorhombic BaSi<sub>2</sub>, BaSi and Ba<sub>5</sub>Si<sub>3</sub>, obtained from literature [11, 80, 101]. In the graph, the diffraction lines corresponding with orthorhombic BaSi<sub>2</sub>, BaSi and Ba<sub>5</sub>Si<sub>3</sub>, are depicted with a black, red and blue dashed line, respectively. In figure 7.6, it is observed that orthorhombic BaSi<sub>2</sub> is obtained for all annealing temperatures. This is evidenced by the diffraction peak at:  $2\theta = 30.5 - 31^{\circ}$  for all samples. Although, the intensity at this diffraction peaks corresponding with BaSi and Ba<sub>5</sub>Si<sub>3</sub>, which are located at  $2\theta = 26.1^{\circ}$ ,  $29.9^{\circ}$  and  $2\theta = 21.5^{\circ}$ ,  $24.1^{\circ}$ , respectively. Thus the XRD spectra agree with the Raman spectra with respect to the presence of orthorhombic BaSi<sub>2</sub>, while the XRD spectra also indicates the presence of other barium silicide phases.



Figure 7.6: XRD pattern of post-growth annealed RT (TSD: 135 mm) deposited material

The new technologies research centre of the university of West Bohemia were able to estimate the crystal grain sizes by XRD measurements. The results are presented in figure 7.7.

In the figure, it can be seen that the crystallite size is between 30 nm and 100 nm for the annealed samples. The material annealed at 650 °C, has the largest crystallite size. There is no clear trend visible for the crystal size as function of the annealing temperature. It was expected that higher annealing temperature would result in larger crystal sizes, since the Raman spectra indicates higher crystallinity. However, the Raman spectra only indicates the crystallinity of orthorhombic  $BaSi_2$  and c-Si, while the XRD analysis indicates that there are also other barium silicon phases present. This could explain the difference between expected and measured crystal sizes.



Figure 7.7: Crystal size estimated by XRD analysis

Furthermore, XRD analysis was also performed to investigate the influence of the substrate on the crystallization, which was also researched for the RT material in section 5.2.2. The investigated substrates are: p-type and n-type pc-Si and  $SiO_2$ . Results are presented in figure 7.8. In the graph, the results of the RT deposited material, which is also depicted in figure 5.3, is plotted with dashed lines for comparison.

It is observed that there is actually very little difference in the XRD spectra for the 3 different substrates. The broad peak for RT material changes to a crystallised spectrum with multiple intense diffraction peaks upon annealing. The material has the same diffraction peaks for post-growth crystallisation on p-type pc-Si, n-type pc-Si and SiO<sub>2</sub>. There is only a slight difference in the intensity for the diffraction spectra. The intensity is in general the highest for the SiO<sub>2</sub> substrate, while it is the lowest for the n-type pc-Si substrate.



Figure 7.8: Effect of substrate on crystallisation of RT deposited barium disilicide



Figure 7.9: Effect of post-growth annealing on the elemental composition of RT (TSD:135 mm) deposited barium disilicide

The elemental composition of post-growth annealed RT (TSD:135 mm) deposited  $BaSi_2$ , is determined by AES and depicted in figure 7.9. The figure shows the elemental composition throughout depth for the sample annealed for 90 minutes at 650 °C. The silicon bonded with oxygen, is indicated with the red line, while the yellow/orange line designates silicon bonded to other elements. The oxygen is represented by the pink line and barium by the purple line.

As previously mentioned in this section, the elemental composition shows an increase of oxygen in the first 200 nm from the surface. This oxygen is the result of surface oxidation during the annealing. The Carbolite furnace with nitrogen backing gas flow, used for post-growth annealing in this work, is thus not suitable for annealing the material without any protective measures. Furthermore, the graph indicates a higher percentage of barium than of silicon in this oxidized region. From the non-annealed composition analysis, it was seen that the silicon to barium ratio was 2:1 throughout the whole layer. Thus, it is concluded that there is preferential oxidation of barium, which agrees with other studies [80]. Due to this preferential oxidation, the ratio of silicon to barium is barium and oxygen rich in the oxidized layer. As a consequence, the material below the oxidized layer is silicon rich. This explains the detection of c-Si peak in the Raman spectra. Nevertheless, the oxidation of the material is detrimental for material properties. Therefore, it is recommended to investigate methods that are able to protect the material against surface oxidation.

## **7.3.** Influence of the annealing time on the optical and structural properties

In this section of the report, the effect of annealing time on the material properties is discussed. The most promising material from the previous section is obtained by annealing at 650 - 700 °C. The effect of annealing time, is researched by annealing a RT (TSD: 135 mm) deposited sample for 180 minutes at 650 °C and at 700 °C for 30 min. These results are compared with the results obtained by annealing for 90 min, which is treated in the previous section.

The transmittance and absorbance of these samples are plotted in figure 7.10a, the absorbance is depicted in figure 7.10b. The reflectance plot of the samples is omitted, since the reflectance is approximately the same for all samples. The temperature and annealing time are indicated between brackets in the legend of the figures.

In figure 7.10, it can be seen that the absorbance in the IR range decreases significantly when annealing for 180 minutes instead of 90 minutes at 650 °C. This is accompanied by a significant increase in the transmittance and with an improved absorption coefficient plot. The absorption coefficient plot, shows a sharper decrease in the absorption coefficient, resembling more the shape of the reference



Figure 7.10: Transmittance, absorbance (left) and absorption coefficient (right) plotted of RT deposited (TSD: 135 mm) BaSi<sub>2</sub>, post-growth annealed at varying annealing temperatures and times.

material of Latiff et al. On the other hand, the material annealed for 30 min at 700 °C, behaves optically very similar to the material annealed for 90 min at the same temperature. The absorbance is slightly larger for all measured wavelengths, while the transmittance is very similar, apart from interference. The absorption coefficient is also similar, although it is slightly larger for the low photon energies. These results indicate that similar properties of the material can be obtained by different combinations of annealing times and temperatures.

In figure 7.11 the Tauc plots are presented. Figure 7.11a shows the Tauc plot for indirect bandgap, while figure 7.11b depicts the Tauc plot for a direct bandgap. In the Tauc plot for indirect bandgap, the data of Latiff et al. is shown for comparison. The annealing recipe is denoted in the legend by first the annealing temperature in degree Celsius, while the second number represents the annealing time.

The indirect optical bandgaps are estimated to be 0.70 eV, 0.89 eV, 0.99 eV and 0.99 eV for the material annealed 90 minutes at 650 °C, 180 minutes at 650 °C, 90 minutes at 700 °C and 30 minutes at 700 °C, respectively. The indirect bandgap thus increases when annealing the material for 180 minutes instead of 90 minutes at 650 °C. On the other hand, the indirect bandgap of the sample annealed for 30 minutes at 700 °C, is the same as the sample annealed for 90 minutes at this temperature. The indirect bandgaps of these samples are still lower than the in literature reported bandgaps for this material.



Figure 7.11: Tauc plot for indirect bandgap (left) and direct bandgap (right) of RT deposited (TSD: 135 mm) material, annealed at 650 and 700 °C for varying times. In the indirect Tauc plot the data of Latiff et al. [11] is plotted for comparison.



Figure 7.12: Raman spectra of RT deposited (TSD: 135 mm) material, annealed at 650 and 700 °C for varying times. Raman spectra measured by the red laser ( $\lambda = 633$  nm) at the front (left) and back side of the material (right). The results of the sample deposited at a substrate temperature of 450 °C and the room temperature deposited material are plotted for comparison.

The direct optical badgaps are 1.72 eV, 2.12 eV, 1.91 eV and 1.87 eV for the samples annealed for 90 minutes at 650 °C, 180 minutes at 650 °C, 90 minutes at 700 °C and 30 minutes at 700 °C, respectively. The direct bandgap thus increases when annealing for longer times at the same temperature. It is reasoned that the increase in direct bandgap for longer annealing times, is due to the higher oxidation and thus the larger fraction of c-Si in the material. All direct bandgaps are higher than literature reported direct bandgaps.

The structural properties of the samples are compared by Raman spectroscopy. The Raman spectrum of the specimens are presented in figure 7.12. The Raman spectra measured from the front side of the film are shown in 7.12a. The measurements through the substrate are depicted in 7.12b. In the graphs, the results from the material deposited at a substrate temperature of 450 °C and the RT material are shown for comparison. Furthermore, the FWHM of the peak at a Raman shift of 486 cm<sup>-1</sup> is indicated in the graph.

It is observed in the Raman spectra that the material is more crystallized when annealed for 180 min, compared to the material annealed for 90 min, both at a temperature of 650 °C. For the material annealed at 700 °C, the opposite behaviour is observed, although the FWHM of both samples are very similar. However, it can be seen that the c-Si peak increases for longer annealing times for both temperatures. Therefore, it is reasoned that there is a trade-off between better material properties due to higher crystallization as a result of longer annealing times, while on the other hand the material properties degrade as a result of more surface oxidation. For this reason, it is recommended to investigate what the best way is to prevent this surface oxidation, since it is expected that it will highly benefit the material quality.

## **7.4.** High temperature deposition and post-growth annealing

In this section, the effect of post-growth annealing on the optical and structural properties of high-temperature deposited  $BaSi_2$  is discussed. The material is deposited at a substrate temperature of 450 °C and post-growth annealed at 700 °C for 30 minutes and 90 minutes, respectively. The same annealing is performed for RT (TSD: 80 mm) deposited material for comparison.

The transmittance and absorbance of the samples are shown in figure 7.13a and the absorption coefficient is presented in figure 7.13b. In the legends of figure 7.13, the RT and HT denotes if the sample is deposited at room temperature or high temperature prior to post-growth annealing. The number thereafter, indicates the annealing time in minutes.


Figure 7.13: Transmittance, absorbance (left) and absorption coefficient (right) of RT and HT deposited material at a TSD of 80 mm, post growth annealed at 700 °C for 30 and 90 minutes, respectively.

In figure 7.13a, it is observed that the absorbance of post-growth annealed samples deposited at a TSD of 80 mm, for both RT and HT grown material, is higher in the IR range compared to the TSD: 135 mm annealed samples. This is accompanied by a lower transmittance for the TSD: 80 mm samples. It is speculated that this is caused by either the higher (expected) barium content or because the deposited material is more dense at this shorter TSD. Furthermore, it can be seen that the RT deposited material has a higher absorbance and lower transmittance in the IR range, compared to the HT deposited material. This is attributed to the higher crystallization of the HT deposited sample prior to the annealing step. The transmittance of the material increases for longer annealing times. As a result of the higher absorbance and lower transmittance, the absorption coefficient of this material is also higher compared to the TSD: 135 mm material. There are only small differences in absorption coefficient between the 4 samples. Although the absorption coefficient is relatively large throughout the material, the shape of the absorption coefficient is comparable to the one from literature.

The absorption coefficient results in the improved Tauc plots for direct and indirect optical bandgap, which are pictured in figure 7.14. The Tauc plot for indirect bandgap is depicted in figure 7.14a and the Tauc plot for direct bandgap is shown in figure 7.14b. The results from Latiff et al. are plotted for comparison in the Tauc plot for indirect bandgap.

The indirect bandgaps estimated from the Tauc plot in figure 7.14a are: 1.00 eV, 1.10 eV, 1.02 eV, 1.05 eV corresponding with: RT material annealed for 30 minutes, HT material annealed for 30 minutes, RT material annealed for 90 minutes and the HT material annealed for 90 minutes, respectively. These results thus show that the indirect bandgap of these samples are closer to the literature reported values than the samples made at a TSD of 135 mm. This improvement is also seen in the direct bandgaps derived in figure 7.14b. The direct bandgaps are: 1.42 eV, 1.42 eV, 1.41 eV, 1.55 eV for the RT 30 minutes, HT 30 minutes, RT 90 minutes and HT 90 minutes, respectively. The direct bandgaps of the first 3 samples are very similar, while it is slightly larger for the HT 90 minutes sample. Nevertheless, these direct bandgaps are very close to the literature reported value of 1.37 eV [2]. The values of the direct bandgap are again affected by surface oxidation for the HT sample annealed for 90 minutes, resulting in a decrease of the indirect bandgap and an increase of the direct bandgap, compared to the HT sample annealed for 30 minutes. Thus also for RT and HT material deposited at a TSD of 80 mm, there is surface oxidation during post-growth annealing, which is detrimental for the material properties.



Figure 7.14: Tauc plot for indirect bandgap (left) and direct bandgap (right) of HT and RT (TSD: 80 mm) deposited material, post-growth annealed at 700 °C for 30 and 90 minutes.

The Raman spectra of the samples are presented in figure 7.15. The Raman spectra is used to compare the structural properties between the samples. The spectra measured at the front side of the film, are plotted in figure 7.15a, while figure 7.15b depicts the measurements of the back side of the samples. The FWHM is determined of the peak located at a Raman shift of 486 cm<sup>-1</sup>, to quantify the crystallinity of the material. The spectra of the non-annealed RT and HT samples are shown for comparison.

In figure 7.15, it is observed that the crystallinity of the HT deposited material increases upon annealing. The material changes from amorphous to more crystalline on the back side of the material. These structural changes improve the material quality. Furthermore, the crystallinity of the RT deposited material is comparable or better than the HT deposited material, after going through the same annealing procedure. This is in contrast with was expected. Also, the transmittance and absorbance suggest that HT deposited material is more crystalline than the RT counterpart. Nevertheless, the postgrowth annealing results in the formation of c-Si, as is evidenced by the peak in the Raman spectrum at a Raman shift of 520.5 cm<sup>-1</sup>. This effect is discussed previously in this chapter and is related to the surface oxidation of the material. Thus also for this recipe, the importance of surface oxidation preventive measures is evident.



Figure 7.15: Raman spectra of the HT and RT (TSD: 80 mm) samples, post-growth annealed at 700 °C for 30 and 90 minutes. Raman spectrum measured at front side (left) of the film and through the substrate (right) by the red laser ( $\lambda = 633$  nm).

## **7.5.** Electrical properties of post-growth annealed barium disilicide

The electrical properties the 4 most promising samples of this chapter were determined. The tested samples are: RT deposited at a TSD of 135 mm and post-growth annealed at 700 °C for 30 minutes and 90 minutes, respectively and the RT and HT samples deposited at a TSD of 80 mm, post-growth annealed at 700 °C for 90 minutes.

The results from the Hall setup are presented in table 7.1 and table 7.2. The charge carrier concentration is presented in the same way as in the previous chapters, which is explained in section 5.3. The charge carrier concentration of the RT (TSD: 135 mm) deposited material, annealed for 30 minutes and 90 minutes at 700 °C, are in the low to high  $10^{16}$  cm<sup>-3</sup> region, in which the material annealed for 30 minutes shows a slightly higher charge carrier concentration compared to the 90 minutes annealed material. The charge carrier concentration is 3 - 6 orders of magnitude lower for the annealed material than for the non-annealed RT material in chapter 5. This endorses the importance of post-growth annealing of amorphous RT deposited material, to obtain non-degenerate orthorhombic barium disilicide.

Post-growth annealing HT deposited material, results in a charge carrier concentration that is comparable to the non-annealed HT sample. However, the annealed sample has a higher maximum value, resulting in a relatively high arithmetic mean and a large standard deviation. This could be the result of the presence of small craters in the samples, increasing the error of the measurement. Nevertheless, the median is in the high  $10^{16}$  cm<sup>-3</sup> range, which corresponds with the activation energy measurement, which is treated below. Furthermore, the sign anomaly seems to have almost disappeared for the material (RT and HT) annealed for 90 minutes, while this is not the case for the sample annealed for 30 minutes. This agrees with the literature, in which it is reported that the sign anomaly disappears upon crystallization of the amorphous phase by post-growth annealing [94]. Unfortunately, the Hall setup was unable to measure the RT (TSD: 80 mm) deposited sample, annealed at 700 °C for 90 min. Therefore, the only results on the charge carrier concentration are derived from the activation energy measurements, which are discussed below.

The mobility of the annealed samples is presented in table 7.2. There is a quite significant difference in the mobility between the 3 annealed samples. The mobility is the largest for the RT (TSD:135 mm) deposited material annealed for 90 min at 700 °C, with an arithmetic mean of 47.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The same material annealed for 30 minutes, has a lower mobility, with a AM value of 7.31 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. Both are 1 - 2 orders of magnitude larger than the RT values. The mobility of the high temperature annealed sample shows a relatively low mobility, with an AM of  $1.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . This value is considerably lower than the mobility of the non-annealed HT material, which has a mobility in the range of AM: 7.69 - 12.6 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. This is in contrast to what was expected. It is expected that higher crystallization and lower charge carrier concentration increases the mobility. Therefore, this result is attributed to errors induced by the non-uniformity (craters) of the material.

Charge carrier concentration						
TSD: 135 mm, RT, Annealed: 700 C, 90 min						
Maximum	Minimum	Arithmetic	Standard	Median	Nr. of	Nr. of
		mean	deviation		Positivie signs	Negative signs
(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )	(-)	(-)
3.31E+17	1.94E+15	2.45E+16	5.96E+16	9.23E+15	3	26
TSD: 135 mm, RT, Annealed: 700 C, 30 min						
4.45E+17	1.50E+16	8.16E+16	1.12E+17	3.89E+16	15	7
TSD: 80 mm, RT, Annealed: 700 C, 90 min						
Unable to measure: Sample contact error						
TSD: 80 mm, HT, Annealed: 700 C, 90 min						
1.55E+19	5.49E+16	1.65E+18	4.41E+18	8.42E+16	0	11

Table 7.1: Charge carrier concentration of the annealed samples, measured by the Hall setup

		Mobility				
TSD: 135 mm, RT, Annealed: 700 C, 90 min						
Maximum	Minimum	Arithmetic mean	Standard deviation	Median		
$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$	$(cm^2V^{-1}s^{-1})$		
201	0.68	47.1	40.9	37.7		
TSD: 135 mm, RT, Annealed: 700 C, 30 min						
24.2	0.66	7.31	7.48	4.56		
TSD: 80 mm, RT, Annealed: 700 C, 90 min						
Unable to measure: Sample contact error						
TSD: 80 mm, HT, Annealed: 700 C, 90 min						
1.7	0.006	1.01	0.51	1.12		

Table 7.2: Mobility of the annealed samples, measured by the Hall setup

**Activation energy** The results of the activation energy measurements are shown in table 7.3. The charge carrier concentration is calculated from the activation energy by using equations 3.21, 3.22, as explained in section 3.2.9, and the effective density of states in the conduction and the valence band taken from literature [16].

The activation energy of the annealed samples, indicate that the material is non-degenerate, except for the post-growth annealed RT (TSD: 80 mm) deposited material. However, for this sample the Hall setup was unable to measure the charge carrier concentration and thus a comparison between the two measurements cannot be made. The results of the TSD: 135 mm material agrees with the charge carrier concentration results obtained from the Hall setup. The only difference is that the material annealed for 30 minutes has a slightly lower charge carrier concentration compared to the material annealed for 90 minutes, while this was opposite for the Hall results. The HT annealed sample shows the largest activation energy, which corresponds to the lowest charge carrier concentration. This is in contrast to the results from the Hall setup, which indicated the largest charge carrier concentration for this material compared to the others. Aside for the differences, the activation energy confirms that the material is non-degenerate after post-growth annealing, which is important for potentially using this material in solar cells.

Table 7.3: Activation energy of annealed sample, with the corresponding calculated charge carrier concentration in the case of n-type and p-type material

Activation energy					
TSD: 135 mm, RT, Annealed: 700 C, 90 min					
Activation operav	Corresponding	Corresponding			
Activation energy	n <sub>o</sub>	p <sub>0</sub>			
(meV)	(cm <sup>-3</sup> )	(cm <sup>-3</sup> )			
186	1.85E+16	1.43E+16			
TSD: 135 mm, RT, Annealed: 700 C, 30 min					
214	6.23E+15	4.79E+15			
TSD: 80 mm, RT, Annealed: 700 C, 90 min					
-5.12	3.17E+19	2.44E+19			
TSD: 80 mm, HT, Annealed: 700 C, 90 min					
279	4.95E+14	3.81E+14			

**Dark and illuminated conductivity** The dark and illuminated conductivity results are presented in table 7.4. The conductivity is measured for the sample with contacts facing towards the light source and for the case where the light enters through the quartz substrate. The ratio of illuminated over dark conductivity is larger than 1 for the samples, except for the post-growth annealed RT (TSD: 80 mm) deposited sample. These results correspond with the measured activation energies, indicating that the material exhibits semiconducting properties. The ratio for the post-growth annealed RT (TSD: 135 mm) deposited sample shows a value smaller than one in the case that the contacts are facing towards the light source, while it is larger than 1 in the case that the light enters through the substrate. This difference is unexpected and cannot be explained.

The relatively small difference between dark and illuminated conductivity is attribute to 2 reasons. First of all, the material has a large oxide layer on top, which acts as an electric insulator. This insulator has a large resistivity and therefore dominates the total resistivity between the metallic contacts. In the case that the conductivity of the semiconductor material increases, the resistivity of this layer reduces. However, the resistance of the oxide layer remains the same. When the resistance due to the oxide layer is much larger than the resistance of the semiconductor layer below, the total resistance between the metal contacts varies little upon illumination. Another reason is that the charge carrier concentration at thermal equilibrium is still relatively large compared to, for example intrinsic c-Si, which has a charge carrier concentration as low as  $1.5 \cdot 10^{10}$  cm<sup>-3</sup> [43]. The number of light induced charge carriers is therefore several orders of magnitude larger in the case of intrinsic c-Si, while it is of the same order of magnitude for the material of this work.

Table 7.4: Dark and illuminated conductivity of the annealed samples

$\begin{tabular}{ c c c c c } \hline \hline Dark and illuminated conductivity \\ \hline \hline Contacts facing towards the light source \\ \hline \hline TSD: 135 mm, RT, Annealed: 700 C, 90 min \\ \hline \hline TSD: 135 mm, RT, Annealed: 700 C, 90 min \\ \hline \hline Dark & Illuminated & Rational \\ \hline Dark & Illuminated & Rational \\ \hline \hline Dark & Illuminate & Illuminate \\ \hline \hline Dark & Illuminate & Illuminate \\ \hline \hline Dark & Illuminate & Illuminate & Illuminate \\ \hline \hline Dark & Illuminate & Illuminate & Illuminate & Illuminate & Illuminate \\ \hline \hline Dark & Illuminate & Illuminat$	0 uated					
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	0 ated					
TSD: 135 mm, RT, Annealed: 700 C, 90 minDarkIlluminatedRatiResistivityConductivityResistivityConductivity(Ωcm)(S/cm)(Ωcm)(S/cm)(-)	0 <u>ated</u>					
DarkIlluminatedRatiResistivityConductivityResistivityConductivity $\frac{\sigma_{illumin}}{\sigma_{dar}}$ (Ωcm)(S/cm)(Ωcm)(S/cm)(-)	<b>0</b> uated					
ResistivityConductivityResistivityConductivity $\frac{\sigma_{illumin}}{\sigma_{dar}}$ ( $\Omega$ cm)(S/cm)( $\Omega$ cm)(S/cm)(-)	<u>ated</u>					
$(\Omega \text{cm})$ (S/cm) ( $\Omega \text{cm}$ ) (S/cm) ( <sup>-</sup> )						
	r					
1.01E+4 9.94E-5 9.78E+3 1.02E-4 1.02	<u>'9</u>					
TSD: 135 mm, RT, Annealed: 700 C, 30 min						
9.61E+3 1.04E-4 9.84E+3 1.02E-4 0.97	'8					
TSD: 80 mm, RT, Annealed: 700 C, 90 min						
2.37 0.422 2.38 0.420 0.99	14					
TSD: 80 mm, HT, Annealed: 700 C, 90 min						
1.28E+4 7.80E-5 1.20E+4 8.30E-5 1.06	64					
Light entering through the substrate						
TSD: 135 mm, RT, Annealed, 700 C, 90 min						
1.02E+4 9.82E-5 9.675E+3 1.03E-4 1.05	52					
TSD: 135 mm, RT, Annealed, 700 C, 30 min						
2.78E+4 3.60E-5 2.61E+4 3.83E-5 1.06	53					
TSD: 80 mm, RT, Annealed, 700 C, 90 min						
2.38 0.419 2.39 0.419 0.99	19					
TSD: 80 mm, RT, Annealed, 700 C, 90 min						
1.24E+4 8.04E-5 1.17E+4 8.56E-5 1.06	5					

#### 7.6. Conclusions: post-growth annealing barium disilicide

In this section of the report, the effects of post-growth annealing on the optical, structural and electrical properties of BaSi<sub>2</sub> are reviewed. In general, the absorbance in the IR range of the spectrum reduces upon annealing, which is accompanied by an increase in the transmittance. More specifically, annealing at 550 °C and 600 °C for 90 minutes, only marginally changes the absorbance. The minimum annealing time and temperature to see an increase in the transmittance is 650 °C for 90 minutes. Furthermore, this increase of transmittance is attributed to the crystallization of the material, as evidenced by the Raman spectra. The crystallized material exhibits an optical indirect bandgap of 0.7 eV up to 0.99 eV and a direct bandgap of 1.72 up to 2.34 eV for the material deposited at a TSD of 135 mm, postgrowth annealed for 90 minutes. The best result is obtained for annealing the material for 90 minutes at 700 °C. Nevertheless, the elemental analysis indicated that there is surface oxidation upon annealing. Barium is preferentially oxidized at the surface, resulting in a barium oxide rich top layer and a silicon rich bottom layer, with respect to the optimal barium to silicon ratio of 1:2. It is therefore concluded that surface oxidation during annealing is detrimental for the material properties. The effect of the surface oxidation is visible in the Raman spectrum by the formation of peaks at a Raman shift of 520.5 cm<sup>-1</sup>, which corresponds to c-Si. The XRD analysis also confirmed the formation of orthorhombic BaSi<sub>2</sub> alongside with other unwanted barium silicide phases. From the XRD analysis, the crystallite sizes are estimated to be in the range of: 30 - 100 nm for the annealed material.

Furthermore, it is shown that annealing for longer times at lower temperatures can result in similar material properties as annealing at higher temperatures for shorter times. Nevertheless, the optical bandgap that is closest to the values reported in literature, is 0.99 eV for the indirect bandgap and 1.72 eV for the direct bandgap, corresponding to the material annealed at 700 °C for the indirect bandgap and annealed at 650 °C for 180 minutes for the direct bandgap. The Raman shift shows that the material crystallizes upon annealing. The lowest FWHM obtained is 9.5 cm<sup>-1</sup>, for the material annealed at 700 °for 30 minutes. It is reasoned that longer annealing times enhance the crystallinity of the material, while at the same time the longer annealing times also increase surface oxidation, which is detrimental for the material.

The material deposited a TSD of 80 mm was also researched for both post-growth annealed RT and HT deposited samples. The absorbance in the IR range reduces less and the transmittance increases less for these samples, compared to the TSD 135 mm material. Nevertheless, the optical bandgaps estimated by the Tauc plots are closer to literature, with values ranging from 1.41 - 1.55 eV for the direct bandgap and 1.00 - 1.10 eV for the indirect bandgap. However, this material also suffers from the detrimental surface oxidation. Therefore, it is recommended to investigate preventive measures for surface oxidation.

The charge carrier concentration decreases upon annealing the material. This is true for the RT material deposited at a TSD of 135 mm, while the results are not conclusive for the material deposited at a TSD of 80 mm. The reduced charge carrier concentration is attributed to the crystallization of the material, which is generally accompanied by an increase in the mobility. The activation energy agrees with the results from the hall setup with respect to the reduced charge carrier concentration, which is in the range of  $10^{16}$  cm<sup>-3</sup>. Post-growth annealing has thus shown to be an effective way to obtain crystallized non-degenerate material, which exhibits semiconducting behaviour as evidenced by an illuminated over dark conductivity ratio larger than 1.

## 8

#### **Conclusions and Outlook**

#### 8.1. Conclusions

The aim of the thesis was to contribute to the development of high quality orthorhombic barium disilicide suitable for thin film solar cell applications, by utilizing the radio frequency magnetron sputtering deposition technology. This study has shown that it is evident that this high quality layer cannot be obtained by mere room temperature deposition. There are 2 strategies that can be followed for obtaining crystallized orthorhombic barium disilicide. Both these strategies require high temperatures in part of the production process. The first strategy is to deposit the material at high substrate temperatures. The other strategy is post-growth annealing of the room temperature sputtered material. Obviously, a combination of high temperature deposition followed by post-growth annealing is also possible.

First, the properties of state-of-the-art orthorhombic barium disilicide were researched by means of a literature review. These properties provided the direction and reference for the material properties throughout this work.

The development of high quality layers started with researching the optimal target to substrate distance (TSD) for obtaining the most uniform material thickness. Theory predicts that the material thickness uniformity increases (more uniform) for larger TSDs, which is accompanied by a reduction in the deposition rate. The experimental work agrees with these predictions and the best thickness uniformity is obtained at a TSD of 135 mm. The deposition rate at this TSD, for the specified deposition recipe, is 6.63 nm/min.

In the following part of the thesis, the properties of room temperature (RT) deposited barium disilicide are reviewed. The results indicate that sputtering at room temperature without any post-growth annealing treatment, results in an amorphous material for both a TSD of 80 mm and 135 mm. This is evidenced by the relatively high absorbance and low transmittance in the IR range and the broad continuous diffraction peaks measured by both Raman spectroscopy and XRD.

Furthermore, the transmittance is lower for the material deposited at a TSD of 80 mm than for the material deposited at a TSD of 135 mm. Also, the TSD: 80 mm deposited material exhibits a higher conductivity. It is reasoned that this is both the result of a larger barium to silicon ratio. Nevertheless, it is recommended to verify this prediction by an elemental composition analysis of this material.

Moreover, the elemental composition obtained by Auger electron spectroscopy (AES), demonstrates that the barium to silicon ratio is the required 1:2 for the material deposited at a TSD of 135 mm. In this RT deposited material there is 10% oxygen present throughout the layer. It is speculated that oxygen diffuses into the material after deposition. It is recommended to verify this.

The RT deposited material is found to be degenerate, as is evidenced by a charge carrier concentration in the order of  $10^{19}-10^{22}$  cm<sup>-3</sup>. This is accompanied by a relatively low mobility of 0.28 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and 0.65 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the material deposited at a TSD of 135 mm and 80 mm, respectively. The activation energy measurements of this material endorses this conclusion. The material does not exhibit any semiconductor behaviour in terms of light induced charge carrier generation, which is seen by a ratio of illuminated over dark conductivity of approximately 1.

In order to improve the material quality, high temperature deposition is investigated. Depositing at a substrate temperature of 400 °C and higher, results in partially crystallized orthorhombic barium disilicide, which is evidenced by the Raman spectroscopy. In the Raman spectra, it is observed that the material is amorphous directly on top of the substrate, while it is crystalline at the surface. The material deposited at the highest substrate temperature resulted in the most crystalline material with a FWHM of 12.9. Nevertheless, the reference sample obtained from Nagoya university, is even more crystallized with a FWHM of 11.6. Unfortunately, the RF magnetron sputtering tool used in this work, was only able to reach a maximum substrate temperature of 450 °C. It is expected that the material quality can improve further for higher substrate temperatures. The combination of crystalline and amorphous material resulted in relatively high absorbance and low transmittance in the IR range, thus the R-T-A plots do not indicate the presence of an optical bandgap. Furthermore, the charge carrier concentration of the material deposited at a substrate temperature of 450 °C, is in the order region of  $10^{17} - 10^{18}$  cm<sup>-3</sup>, which is 2-5 order of magnitude lower than the RT deposited material. The mobility is also significantly larger than of the RT deposited material, with an average value of 7.69 - 12.6  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ . However, these properties depend on the position on the substrate where the measurement is taken. This explains the contradictory result of the activation energy, which indicates that the material is degenerate. The ratio of illuminated conductivity over dark conductivity are slightly larger than 1, which is an indication that the material exhibits semiconducting properties.

The other strategy that is researched in this work, is post-growth annealing of the material. Firstly, the results are compared of RT (TSD: 135 mm) deposited material annealed at different annealing temperatures for 90 minutes. The optical properties improve upon annealing as is evidenced by a reduction in absorbance and an increase in transmittance in the IR range for the material annealed at 650 °C, 700 °C and 750 °C, while there is zero transmittance for the material annealed at 550 °C and 600 °C. This change in optical properties is attributed to the crystallization of the material due to post-growth annealing, which is evidenced by the Raman spectroscopy and the XRD analysis.

These improved optical properties, result in the appearance of an optical bandgap. The absorption coefficients of the material annealed at the 3 highest temperatures, are presented and used for deriving the optical bandgap by plotting the Tauc plots. The indirect optical bandgap ranges from 0.7 eV for annealing at 650 °C up to 0.99 eV in the case of an annealing temperature of 700 °C. The direct optical bandgap ranges from 1.72 eV up to 2.34 eV for the material annealed at 650 °C and 750 °C, respectively.

On the other hand, the elemental composition reveals that the surface oxidizes during post-growth annealing. There is preferential oxidation of barium with respect to the silicon. Consequently, the surface is barium and oxygen rich, while the material below is silicon rich. This is observed in the Raman spectra by the formation of c-Si peaks. The XRD confirms the formation of orthorhombic barium disilicide, while it also reveals the formation of other barium silicide phases.

Furthermore, the influence of the annealing time on the material properties are discussed. The absorbance, transmittance and absorption coefficient data are very similar for the material annealed for 180 minutes at 650 °C and the material annealed for 90 minutes and 30 minutes at 700 °C. This results in an indirect optical bandgap of 0.89 eV, 0.99 eV and 0.99 eV and a direct optical bandgap of 2.12 eV, 1.91 eV and 1.87 eV, respectively. The Raman spectrum shows that the material is more crystallized when annealed for 180 instead of 90 minutes at 650 °C, while on the other hand the material is more crystallize for the shorter annealing time at 700 °C. It is reasoned that the longer annealing time enhances the crystallization of orthorhombic barium disilicide, while the surface oxidation has a negative effect on the crystallization.

Moreover, post-growth annealing of RT and HT samples deposited at a TSD of 80 mm is investigated. The transmittance is less and the absorbance is higher in the IR range compared to the material deposited at a TSD of 135 mm. However, the optical bandgaps of these samples are closer to the values in literature. The direct optical bandgap ranges from 1.41 - 1.55 eV and the indirect bandgap ranges from 1.00 - 1.10 eV. Nevertheless, the Raman spectrum indicates that this material also suffers from surface oxidation.

The electrical properties improve upon annealing of RT material deposited at a TSD of 135 mm. The charge carrier concentration, determined by the Hall setup, is in the in the order region of  $10^{16}$  cm<sup>-3</sup> for material annealed at 700 °C. This agrees with the results from the activation energy. The mobility is increased, compared to the RT material, with a value in the region of 7.31 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the

30 minutes annealed sample and 47.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the 90 minutes annealed sample. The results are inconclusive for the annealed HT material deposited at a TSD of 80 mm, showing a low charge carrier concentration of  $10^{14}$  cm<sup>-3</sup>, derived by the activation energy and a charge carrier concentration of  $10^{16} - 10^{18}$  cm<sup>-3</sup>, determined by the Hall setup. The mobility is relatively low with an average value of  $1.01 \text{ cm}^{2}\text{ V}^{-1}\text{ s}^{-1}$ . Nevertheless, the ratio of dark and illuminated conductivity are larger than 1 for these 3 samples, indicating that the material exhibits semiconducting properties. The post-growth annealed sample deposited at a TSD of 80 mm is degenerate, according to the activation energy, while the Hall setup was unable to measure its properties. This sample has an illuminated over dark conductivity ratio smaller than 1.

Both high temperature deposition and post-growth annealing has proven to increase the material quality. Post-growth annealing is at this point required for both HT and RT deposited material to improve the crystallinity. The main challenge is therefore to research surface oxide preventive measures.

#### 8.2. Outlook

In order to be able to use this material as an absorber material in thin film photovoltaic applications, it is required to prevent surface oxidation during post-growth annealing. There are several strategies that can be followed. In this outlook different strategies are discussed.

One strategy is to prevent surface oxidation by using a capping layer. The requirements of this capping layer is that it should be a barrier for oxygen molecules. Ideally the barrier layer enables no interaction between the environment and the barium disilicide layer below. Furthermore, the layer should be (easily) removable after annealing, without damaging the crystallized orthorhombic barium disilicide layer. Besides, it should be stable at the high annealing temperatures and non-reactive with the barium disilicide material. One material that can potentially fulfill these requirements is silicon nitride. This layer can be removed by reactive ion etching after annealing. Another possibility to prevent or reduce surface oxidation could be by placing two samples on top of each other with the barium disilicide material facing towards one another during the annealing process. In this method the material layers protect each other from oxidation. Furthermore, it would be interesting to see how the material behaves when it is annealed in ultra high vacuum. In an ultra high vacuum furnace there would only be a small fraction of oxygen left in the environment, thereby preventing or at least reducing oxidation. Unfortunately, this is not possible in the Carbolite furnace used in this work. Thus an different annealing furnace is needed to investigate this possibility.

Another strategy is by omitting the post-growth annealing step altogether. However, as this work has shown, post-growth annealing is required for further material quality improvement because the maximum substrate temperature is limited to 450 °C. Nevertheless, it would be very interesting to be able to deposit at higher substrate temperatures, since it is expected that the material can grow more crystalline. This can be achieved by two ways. The first is by upgrading/modifying the equipment so that it is able to reach higher substrate temperatures. Another possibility is by installing the target in another machine that is able to reach higher substrate temperatures.

# A

#### Diffusive mass transfer of sputtered barium disilicide

In order to gain insight into the diffusive mass transfer of barium disilicide inside the deposition chamber during sputtering, a simplified analysis of the diffusive mass transfer mechanism was conducted. In particular, in this analysis, the concentration and the mass flux (deposition rate) as function of virtual source distance (VSD) is derived, where-after the implication of the TSD on the uniformity is discussed.

The derivation is based on a microscopic mass balance over the shell of a sphere with radius r and r + dr, as is presented in figure A.1.



Figure A.1: 2 Dimensional representation of the shell of a sphere with radius r and r+dr

It is assumed that the situation is steady state, this means that there is no change in the total mass inside the control volume over time. Furthermore it is assumed that there is solely mass transfer by diffusive means, so other contributions and transport phenomena are neglected here. Moreover, horizontal transport over the substrate is not taken into account. Another assumption is that there is only 1 species and therefor Fick's law applies [102]:

$$\phi_{\rm m}^{''} = -D\frac{{\rm d}c}{{\rm d}r} \tag{A.1}$$

In which  $\phi_m''$  is the mass flux in kg/m<sup>2</sup>s, *D* is the diffusion coefficient in m<sup>2</sup>/s, *c* is the concentration in kg/m<sup>3</sup> and *r* is the radius or the distance from the virtual source in m. With these assumptions, the concentration is derived from the mass balance over the control volume. Thereafter, the concentration profile is used as an input into equation A.1, which results in the mass flux as function of distance from the virtual source. This results is then used to analyse the uniformity for 2 cases with different TSD, from which the effect of the TSD on the uniformity is clarified. This derivation begins with the general equation for a mass balance:

$$\frac{\mathrm{d}}{\mathrm{d}t}M = \phi_{\mathrm{m,in}} - \phi_{\mathrm{m,out}} \tag{A.2}$$

In which *M* is the mass in the control volume,  $\phi_{m,in}$ , *t* is the time and  $\phi_{m,out}$  are the mass flow into and out of the control volume, respectively.

By applying the steady state condition, the left side of equation A.2 is equal to zero. The right side of equation A.2 is elaborated in terms of mass flux ( $\phi_{m}^{"}(r)$ ) and surface area (A(r)):

$$0 = \phi_{m}^{''}(r)A(r) - \phi_{m}^{''}(r + dr)A(r + dr)$$
(A.3)

Dividing both sides of equation A.3 by dr, results in:

$$0 = \frac{\mathrm{d}}{\mathrm{d}r}(\phi_{\mathrm{m}}^{''}(r)A(r)) \tag{A.4}$$

Applying Fick's law (equation A.1) for the mass flux, rewriting the area of a spherical shell in terms of the radius and assuming that the diffusion coefficient is not a function of the radius in equation A.4, gives:

$$0 = -D4\pi \frac{\mathrm{d}}{\mathrm{d}r} \left(\frac{\mathrm{d}c(r)}{\mathrm{d}r}r^2\right) \tag{A.5}$$

Integrating the differential equation in equation A.5 once:

$$\int \frac{\mathrm{d}}{\mathrm{d}r} \left(\frac{\mathrm{d}c(r)}{\mathrm{d}r}r^2\right) \mathrm{d}r = \int 0\mathrm{d}r \tag{A.6}$$

Working out the integral of equation A.6, results in:

$$\frac{\mathrm{d}c(r)}{\mathrm{d}r}r^2 = K_1 \tag{A.7}$$

Integrating equation A.7 once more, gives:

$$\int \frac{\mathrm{d}c(r)}{\mathrm{d}r} \mathrm{d}r = \int \frac{K_1}{r^2} \mathrm{d}r \tag{A.8}$$

Working out the integral of equation A.8 results in the concentration profile:

$$c(r) = -\frac{K_1}{r} + K_2$$
(A.9)

Applying boundary condition (BC) 1, which says that if the radius goes to infinity, the concentration goes to zero, to equation A.9, gives:

$$c(r = \infty) = 0 = -\frac{K_1}{\infty} + K_2$$
 (A.10)

The result of equation A.10 is that constant  $K_2$  is equal to zero. Applying boundary condition 2:  $c(r = r_0) = c_0$ , which represents the condition that at a certain radius  $r_0$  the concentration is equal to  $c_0$ , to equation A.10, to determine the other constant, results in:

$$c(r = r_0) = c_0 = -\frac{K_1}{r_0}$$
(A.11)

The outcome of equation A.11 is therefore:  $K_1 = -c_0r_0$ . By rewriting all constants in equation A.9 results in the following solution for the concentration profile:

$$c(r) = \frac{r_0 c_0}{r} = constant \frac{1}{r} = K_3 \frac{1}{r}$$
(A.12)

The mass flux as function of the radius is now easily obtained by inserting equation A.12 into equation A.1:

$$\phi_{\rm m}^{''} = -D\frac{{\rm d}c}{{\rm d}r} = -D\frac{{\rm d}}{{\rm d}r}(K_3\frac{1}{r}) = K_4\frac{1}{r^2} \tag{A.13}$$

Multiple trends can be identified upon investigating equation A.12 and equation A.13. First of all, both the mass flux and the concentration decrease for increasing radius. Applied to the VSD and the TSD in the sputtering chamber, it means that the deposition rate is higher for shorter VSD (TSD). This also applies to the TSD because the TSD is the VSD plus the thermalization distance as explained in chapter 4. Secondly, the relative decrease of the mass flux and the concentration reduces for increasing radius. This has a consequence on the uniformity, which is illustrated in the following section.

Figure A.2 represents the situation of the substrate position with respect to the virtual source inside the deposition chamber. By applying equation A.13 to 2 cases with different VSD, the effect of VSD/TSD on the uniformity is demonstrated. In the first case the VSD is assumed to be 80 mm, while in the second case the VSD is assumed to be 135 mm. The length (and width) of the substrate is 100 mm as mentined in section 4.2, which corresponds to L in figure A.2. The virtual source distance with respect to the edge of the substrate is denoted as  $VSD_2$  and is calculated by using Pythagoras' theorem:

 $VSD_2 = \sqrt{VSD^2 + (\frac{1}{2}L)^2}$ . The uniformity is evaluated by calculating the ratio of mass flux at the centre

of the substrate over the mass flux at the edge of the surface:  $ratio = \frac{\phi_m^{''}(r=VSD)}{\phi_m^{''}(r=VSD_2)}$ .



Figure A.2: 2 Dimensional representation of the substrate position with respect to the virtual source

**Case 1** In this case the *VSD* is 80 mm, which results in a  $VSD_2 = \sqrt{80^2 + 50^2} \approx 94$  mm. The deposition rate at the centre of the substrate is:  $\phi_m^{"}(r = 80) = K_4 \frac{1}{80^2} \approx 1.56 \cdot 10^{-4} K_4 \text{ kg/m}^2 \text{s}$ , while the deposition rate at the edge of the substrate is:  $\phi_m^{"}(r = 94) = K_4 \frac{1}{94^2} \approx 1.12 \cdot 10^{-4} K_4 \text{ kg/m}^2 \text{s}$ . The ratio of  $\phi_m^{"}(r = VSD)$  over  $\phi_m^{"}(r = VSD_2)$  is therefor:  $ratio = \frac{1.56 \cdot 10^{-4} K_4}{1.12 \cdot 10^{-4} K_4} \approx 1.39$ .

**Case 2** By following the same method as in case 1 gives a  $VSD_2 = \sqrt{135^2 + 50^2} \approx 144$  mm. At the centre of the substrate the deposition rate is:  $\phi_m^{''}(r = 135) = K_4 \frac{1}{135^2} \approx 5.49 \cdot 10^{-5} K_4 \text{ kg/m}^2 \text{s}$ , while at the edge of the substrate the deposition rate is:  $\phi_m^{''}(r = 144) = K_4 \frac{1}{144^2} \approx 4.83 \cdot 10^{-5} K_4 \text{ kg/m}^2 \text{s}$ . This results in a ratio of:  $ratio = \frac{5.49 \cdot 10^{-5} K_4}{4.83 \cdot 10^{-5} K_4} \approx 1.14$ .

In the second case the ratio of  $\phi_{m}^{"}(r = VSD)$  over  $\phi_{m}^{"}(r = VSD_{2})$  is 1.14 while the ratio is 1.39 in the first case. This means that the uniformity in the second case is better over the substrate than the uniformity in the first case. In conclusion, this analysis of the idealized diffusive mass transfer illustrates that the uniformity improves (more uniform) for increasing VSD (TSD), while the deposition rate decreases for increasing VSD (TSD).

# B

### Initial RF magnetron sputtering recipe

The initial recipe used in this experimental research for the RF magnetron sputtering process, as described in section 3.1.1, is listed below:

- RF power: 50 W
- Target diameter: 3 inch
- Target composition: BaSi<sub>2</sub>
- Gas composition: 100% Argon
- Gas flow: 15 SCCM
- Gas pressure: 10 µbar
- Target to substrate distance: 135 mm
- Deposition time: 75 min
- Film thickness: 500 nm
- Substrate: Quartz
- Substrate temperature: Room temperature

## C

#### SE data of uniformity samples

In this appendix the results of the SE measurements of the uniformity experiment samples is presented in table C.1. The table presents the thicknesses and roughnesses obtained after fitting the model with the measured data in the CompleteEASE<sup>®</sup> software package. The CompleteEASE<sup>®</sup> software uses the effective roughness layer approach to model the surface roughness [83]. In this model the effective roughness layer is placed on top of the sample. Consequently, the thickness derived by the model, is the thickness of the sample without the roughness layer. To incorporate the effect of the roughness on the overall sample thickness, the overall thickness (*t*) is calculated as:  $t = Thickness + \frac{1}{2}roughness$ . The relative thickness (*t*<sub>rel</sub>) is then calculated by:  $t_{rel} = \frac{t_r}{t_{centre}}$ , where subscript r stands for the radius at which the thickness is measured and  $t_{centre}$  denotes the thickness at the centre of the sample.

TSD: 160 mm, Sample: L3702						
Radius	Thickness	Roughness	MSF	Overall	Relative	
Radius	Thechess	Rouginess	NJL	thickness	thickness	
(mm)	(nm)	(nm)	(-)	(nm)	(-)	
0	82	12	33	89	1.00	
14	78	12	30	85	0.96	
28	70	13	28	77	0.87	
42	54	15	30	61	0.69	
57	38	16	40	46	0.52	
	TSD	: 135 mm, Sa	mple:	L3703		
0	126	11	28	132	1.00	
14	122	11	28	128	0.97	
28	108	13	33	115	0.87	
42	90	14	33	97	0.74	
57	61	18	42	70	0.53	
TSD: 110 mm, Sample: L3705						
0	217	7	25	221	1.00	
14	212	9	25	216	0.98	
28	179	10	27	183	0.83	
42	131	10	34	136	0.61	
57	93	14	35	100	0.45	
TSD: 85 mm, Sample: L3704						
0	191	3	37	192	1.00	
14	169	1	39	170	0.88	
28	104	1	38	104	0.54	
42	183	4	38	185	0.96	
57	110	10	92	115	0.60	

Table C.1: Uniformity data of samples deposited with a TSD of: 160, 135, 110 and 85 mm, respectively

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