Gas-phase synthesis of nano-structured semiconductors

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ABSTRACT.- A short review is given of current research activities in the field of nanostructured semiconductors. The utilisation of advanced gas-phase techniques is highlighted and it is indicated that those methods are very promising and open up scarcely explored opportunities for the synthesis of this class of materials. Vapour-liquid-solid (VLS) growth of boron phosphide, particle precipitation aided CVD (pp-CVD) of titanium dioxide, and Laser CVD of the ternary system Si-C-N are briefly discussed as good examples of gas-phase synthetic routes towards nano-structured semiconductor surfaces.

INTRODUCTION

Nanometer-scale engineering of semiconductor materials has become state-of-the-art in semiconductor science and technology. At present, with the aid of advanced lithographic techniques, sub-micrometer-scale patterns are routinely produced which gave access to very-large integrated circuits on silicon wafers. Not only the
processing of Si wafers, however, has encountered a tremendous miniaturisation, also the synthesis of semiconductor materials itself was subject of sub-micron engineering, and led to novel nano-scale morphologies with fascinating properties. Among the best known materials in this class is, of course, nano-porous silicon. This morphology of Si is best known for its direct bandgap in the visible region, which aroused expectations for utilisation of this material in electroluminescence displays, in photovoltaic solar cells, and in chemical sensors. It seems quite justified to speak of nano-porous Si as a new material, despite of the fact that its "bulk" consists of nothing but monocrystalline silicon, since fundamental properties such as the size and nature of its bandgap depend strongly on the characteristic length scale of the specific morphology.

In this paper, we review several possibilities, which especially gas-phase deposition techniques offer for synthesis of nano-porous semiconductor thin films. The discussed examples are taken from current research activities in our laboratory but it should be noticed that at many different locations around the world, similar type of research is in progress. Current developments in this area are very rapid, hence any attempt to provide a more-or-less complete review is prone to be caught up by the latest developments.

**WET-CHEMICAL SYNTHESIS**

In order to synthesise nano-scale semiconductors, two wet-chemical strategies have been developed. First, as in the well-known case of porous silicon, a single crystal is etched in aqueous solution in order to create chaotic etch patterns. In the special case of porous Si, an HF containing etchant is required, as well as a large number of holes at the semiconductor/electrolyte interface. For p-type silicon, porous material forms when polarised in the forward direction, whereas for n-type silicon, the polarisation direction needs to be reverse and band gap illumination must be applied. Reviews of the synthesis of porous silicon can be found in [1].

Semiconductor nano-sized particles can also be formed by a conventional sol-gel technique [2]. In this method, precursors are mixed in a controlled ratio to form a colloid. Subsequently, this colloid is coagulated by changing the conditions such as the temperature or the composition of the liquid. Normally a heat treatment is required after deposition of the particles on a substrate because of the poor attachment of the films. Such thermal anneal improves the attachment of the particles but the sinter process also is prone to change the shape, the crystallographic phase, and the doping density of the particles.
GAS-PHASE SYNTHESIS

As an alternative for wet-chemical techniques, gas-phase reactions have enjoyed increasing interest because of the following advantages, i) gas-phase reactions can usually be better controlled because of the convenient way in which the reactants are supplied and mixed, ii) the composition of the environment is better controlled so that contamination is reduced, and iii) the rate of reaction and the reaction mechanism are conveniently controlled by the temperature of the substrate and of the reacting gases.

As result of this better control, the quality of the product, that is to say the dispersion in the particle size and the chemical composition of the particles, i.e. the doping level and the crystallographic phase, are more reproducible and usually closer to the desired properties than is obtainable with wet-chemical techniques.

In the following paragraphs a few selected pathways for gas-phase formation of nano-structured semiconductor surfaces are introduced but first some general aspects of gas-phase synthesis are highlighted. In a conventional chemical vapour deposition (CVD) experiment, gaseous precursors react either homogeneously or heterogeneously, depending on the specific experimental conditions. In the former case, particles form in the gas phase and diffuse toward a surface onto which they may precipitate and sinter to form a porous film. In the latter case, the substrate surface catalyses the reaction and a dense film is formed. These two alternatives are, however, not the only possibilities. In more dedicated CVD experiments, smart conditions can be set in order to circumvent the usually encountered limitation in the range of possible morphologies. A few of the “tricks” which are applied in our laboratory and elsewhere shall be discussed.

VLS-growth

In a vapour-liquid-solid (VLS) growth experiment, the substrate is activated by nano-sized metal seeds. This activation is usually achieved by dipping the substrate for a few seconds in a metal-ion containing solution and (if necessary) subsequent heating. The metal spots catalyses the heterogeneous reaction by a specific action. For instance, the reactants may dissolve in the metal and crystallisation occurs after supersaturation is reached leading to the formation of a whisker. This is, however, not the only possible reaction mechanism and the interested reader is referred to the following reviews [3].

As an example of this type of synthesis, VLS-growth of boron phosphide (BP) shall be discussed. Boron phosphide is a rather unknown III-V semiconductor with an indirect bandgap of 2.0 eV [4]. It crystallises in the zincblende structure and can be grown epitaxially on (100) silicon [5]. With VLS growth, whiskers of BP can be formed on graphite, silicon or other substrates. As catalyst, either nickel or silver has been used employing a 0.1 molar Ni or Ag-acetate solution. In Figure 1, a SEM magnification of a wood of BP nano-sized wires on graphite is shown. Without the metallisation, a dense polycrystalline BP
film would have been formed, but the presence of metal catalyst seeds completely changes the reaction mechanism and the concomitant morphology. A TEM micrograph of a single BP whisker is shown in Figure 2 on which it is clear that nano-scale dimensions are readily achieved. The length of these whiskers is about 3 orders of magnitude larger than their thickness, but this aspect ratio depends strongly on the deposition temperature and the duration of the formation reaction. Moreover, as is always the case in VLS growth, the whiskers are monocristalline and have preferred growth in a certain direction.

Figure 1 - SEM micrograph of a carbon substrate covered with BP whiskers obtained with VLS growth. The thickness of the whiskers is approximately 50 nm.
Particle-precipitation-aided CVD (pp-CVD) is another possibility to synthesise nano-porous semiconductor films [6]. In this method, the CVD reaction conditions are set such that homogeneous particle nucleation in the gas-phase takes place. In order to collect these particles on a substrate, a driving force in the right direction is applied which can be achieved by either thermophoresis or electro-phoresis. In thermophoresis-driven pp-CVD the substrate temperature is set slightly below the temperature of the reacting gasses, which induce a particle concentration gradient such that directed diffusion towards the substrate takes place. Usually temperature differences between 10 and 50 degrees C suffice for an appreciable precipitation rate, which can be as high as 50-100 μm per hour. Figure 3 shows a nano-porous TiO₂ film on an indium tin oxide (ITO) coated glass substrate. As alternative, also electrophoresis can be employed. In that case the small electrical charge carried by the formed particles is utilised by applying an electric field which induces a Lorentz force acting on the particles and accelerating them in the right direction. Electrophoresis-driven pp-CVD thus requires a conducting substrate onto which electrical contact is made. In case the charge of the particles is too low, additional UV excitation can be applied to strip few electrons from the particles.
Figure 3 - SEM micrograph of nano-porous TiO₂ on ITO coated conductive glass obtained with pp-CVD. On this graph the smallest details that can be discerned are approximately 500 nm in size but the actual surface roughness is much smaller than that.

It appears that both types of pp-CVD give rise to unpredictable chaotic morphologies because of the fact that the driving force for particle precipitation is determined by the morphology of the surface which in its turn is continuously changing by the precipitation process. A mathematical description thus requires several coupled differential equations so that oscillating or chaotic behaviour can be expected [7]. The use of non-linear dynamics in the description of pp-CVD processes is further supported by the observation that the obtained morphologies appear to be extremely sensitive to the reaction conditions as well as to the history of the CVD reactor. For instance, small amounts of reaction products of previous experiments on the reactor walls may influence the outcome of the pp-CVD reaction significantly.

Laser-CVD
At present, laser-CVD is among the most advanced methods for synthesis of nanostructured surfaces [8]. Since powerful CO₂ (continues wave) or excimer (pulsed) lasers are required, only laboratory-scale facilities are operational to date, but since the quality of the CVD products is very high, laser-CVD seems to have good potential for future industrial application. In conventional CVD experiments,
particles which are formed in the gas phase usually have plenty of time to collide, while still present in the hot reaction zone and sinter together to form aggregates. In contrast, by applying a laser beam as energy source, the reaction zone is reduced to a few millimetres or less and when the reactant gases are injected into the beam a very short residence time is achieved. When the residence time is close or below the average collision time, the sinter rate of the particles is strongly suppressed, which results in the formation of monodisperse nano-sized particles. By mounting a substrate just outside the reaction zone, the formed particles will precipitate (because of the previously discussed thermophoresis process) and form a nano-porous film. A SEM image of laser-CVD-synthesised ternary Si-C-N particles (i.e. a mixture of SiC and Si₃N₄) deposited on a copper surface is shown in Figure 4. Here a tuneable CO₂ laser was utilised and an organo-silicon compound together with ammonia were employed as precursors. The organo-silicon precursor as well as NH₃ absorbs the CO₂ laser radiation of 10.6 μm which corresponds to Si-N and N-H vibration excitations. This type of minute experimental control over the excitation of specific chemical bonds in the precursors discloses fascinating pathways to advanced gas-phase synthesis. By simply tuning the laser wavelength, reaction mechanisms and concomitant morphologies of the CVD products can be manipulated in great detail which offers great opportunities for exploration of a whole new range of materials with unexpected properties.

Figure 4 - SEM micrograph of nano-porous Si-C-N composit on copper obtained with laser-CVD. On this graph the smallest details that can be discerned are approximately 500 nm in size but the actual surface roughness is much smaller than that.

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SUMMARY AND CONCLUSIONS

Advanced gas-phase deposition techniques can be successfully employed for synthesis of nano-porous semiconductors. Because of the excellent control over the supply and mixing of reactant gasses, the environment, and the reaction mechanism, nano-structured materials with reproducible properties can be synthesised with these methods. VLS growth can be employed to form dense collection of nano-wires on a variety of surfaces, whereas nano-porous thin semiconductor films can be obtained from particle precipitation aided (pp-) CVD. Finally, the utilisation of lasers for material synthesis offers unsurpassed control over chemical synthesis of semiconductors and other materials in the gas phase and offer, therefore, new challenges for material scientists.

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