Drift mechanism of mass transfer on heterogeneous reaction in crystalline silicon substrate

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ABSTRACT

This work aims to study the pressure dependence of the thickness of the epitaxial silicon carbide film growing from crystalline silicon due to the heterogeneous reaction with gaseous carbon monoxide. It turned out that this dependence exhibits the clear maximum. On further pressure increasing the film thickness decreases. The theoretical model has been developed which explains such a character of the dependence by the fact that the gaseous silicon monoxide reaction product inhibits the drift of the gaseous reagent through the channels of a crystal lattice, thus decreasing their hydraulic diameter. In the proposed hydraulic model, the dependences of the film thickness both on the gas pressure and time have been calculated. It was shown that not only the qualitative but also quantitative correspondence between theoretical and experimental results takes place. As one would expect, due to the Einstein relation, at short growth times the drift model coincides with the diffusion one. Consequences of this drift mechanism of epitaxial film growing are discussed.

1. Introduction

One of the possible mechanisms of epitaxial film growing on crystalline substrates is the chemical reaction between the gas and substrate itself. The evident advantage of such a topochemical mechanism is the opportunity to control elastic stresses, arising due to lattice mismatching of the film and substrate, using point defects accompanying inevitably these reactions [1–3].

As it is known, the heterogenic reaction is called topochemical when, at least, one solid initial component participates, and not less than one solid reaction product is formed. The important subclass of topochemical reactions is composed by reactions in which the solid initial component and solid reaction product are crystalline [4,5]. In this case the primary particle configuration in the crystalline lattice of initial substance (substrate) determines unambiguously the particle configuration in the crystalline lattice of the product (the film). This relates to the fact that intermolecular interactions in the lattice hinder the reorientation of reacting particles at the displacement of the chemical subsystem along the reaction coordinate. In the cycle of studies [1–3,6] there has been developed the new mechanism of silicon carbide (SiC) film epitaxy on silicon (Si) substrates due to topochemical reaction of substitution of the portion of Si atoms by carbon atoms (C). The key role in this reaction is played by an ensemble of point defects formed by pairs of silicon vacancies and carbon atoms. The method of

topochemical epitaxy has been applied for growing of high quality SiC layers of thickness 20–300 nm on Si substrates. It has been shown that SiC films do not contain misfit dislocations in spite of huge difference in lattice parameters of Si and SiC [2]. The buffer layers of SiC on Si thus obtained were then used for the epitaxial growth of various semiconductor films such as AlN, GaN ZnO, CdS, CdTe, Ga_2O_3, which grow directly on Si substrate only in polycrystalline form [2,3]. The authors of studies [6,7] have developed the thermodynamic and kinetic models of topochemical transformation as the first-order phase transition through the intermediate phase. They elucidated the nature of intermediate phase, which plays the role of intermediate state in two-stage topochemical formation of SiC from C

$$CO(gas) + Si(crystal) = C(point\ defect\ in\ \text{Si}) + V_{\text{Si}} + SiO(gas) \qquad (1)$$

$$Si(crystal) + C(point\ defect\ in\ \text{Si}) + V_{\text{Si}} = SiC(crystal), \qquad (2)$$
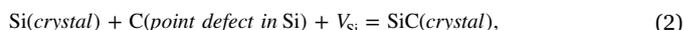
where V_{Si} is the silicon vacancy. This intermediate state is so called "pre-carbide" silicon, i.e. silicon saturated with pairs of C+V_{Si} defects. In fact, this is silicon where each second atom is substituted by C atom. Thus, the pre-carbide silicon is fully ready to be transformed into silicon carbide. This phase transition is accompanied by the formation of voids, since the volume of the SiC cell twice less the volume of the initial Si cell. This transformation (2) occurs layer by layer (a few layers transform simultaneously) with a film shift normal to the substrate surface. The stage (2) occurs significantly later than the stage of the

substitution reaction (1), since the formed SiC film is sufficiently uniform in thickness and has no noticeable voids. In [1–3] the bound pairs of $C+V_{Si}$ point defects were denoted as dilatation dipoles by analogy with electric dipoles. The theory of dilatation dipoles based upon the Green function for point defects in a crystal with a cubic symmetry has been developed in [1,8]. The key result of this theory is the fact that point defects of C and V_{Si} are strongly mutually attracted to one another along the direction $<111>$, providing the relaxation of elastic energy of the intermediate state. This just explains the lack of misfit dislocations in the finite reaction product which is the SiC film.

Despite the progress in the description of topochemical transformation, up to now, a number of experimental results have no proper theoretical explanation. First, the real process of the film growth terminates too fast (in ~10^3 s), further on, the film thickness is not increased (even decreased) [2], whereas the standard diffusion model [9] predicts the thickness growth at large times as $\sqrt{t}$. Second, some islands of SiC phase, ribbon-shaped, as a rule, are found being very deep in the Si substrate under the SiC film. At the depth of ~1 mkm the fraction of SiC consists $3-4\%$ at growth temperature 120 °C and growth time 10^3 s. At temperature 1350 °C, single SiC islands were found at the depth of ~10 mkm. Not clearly, how the standard diffusion process provides so fast penetration of a large amount of CO molecules into such a significant depth. These islands have the form of long, self-intersecting ribbons, which does not correspond to the characteristic behavior of diffusion. Third, with increasing CO pressure near Si surface, the thickness of SiC decreases essentially until full disappearance of the film, while at conventional diffusion the situation should occur visa versa, i.e. the film should become thicker.

That to explain the above mentioned experimental data, we advanced the completely different model of epitaxial topochemical film growing, suggesting that the growth is due to the drift of molecules of the CO gaseous reagent and SiO gaseous reaction product along channels of the crystalline lattice, first, in pre-carbide silicon and, later on, in SiC. The drift or gas flow (which is suggested to be polytropic in this case) is caused by a pressure difference between outside and inside boundaries of the crystal. The driving force of the diffusion is the gradient of gas concentration, which also takes place. The theory of chemical transport reactions shows that the ratio of masses of gaseous substances, transported by pressure-driven drift and by diffusion is proportional to the squared gas pressure [10]. This is the reason why at low pressures the predominant mechanism of mass transfer is the diffusion, whereas at high pressures it is the drift. On the basis of mentioned experimental data we suppose that in this case the pressure is high enough and transfer of CO gas into the reaction zone and SiO gas from the reaction zone is predominantly via the drift, caused by pressure difference. It is possible, that high drift mobility of CO and SiO molecules in SiC crystal is caused by polarization of CO and SiO molecules.

First part of the paper presents the experimental results on the growth mechanism, namely, the measured dependence of the maximal thickness of the SiC film on CO pressure. The second part deals with the theoretical model describing the SiC film growth due to the drift of molecules along crystal channels. The reduction of the film thickness with increasing CO pressure is explained by the fact that the CO molecule flow encounters the rising flow of the SiO molecule reaction products moving along the same channels, which decreases the crystal channel throughput (so called hydraulic diameter). The qualitative and quantitative agreement of theoretical and experimental results has been exhibited.

2. Material and methods

The topochemical synthesis of silicon carbide films has been carried out in a specially equipped vacuum oven, whose construction is described in details in the review [2]. Substrates of Si(111) and Si(100) were held at the temperature T=1270 °C in the CO atmosphere
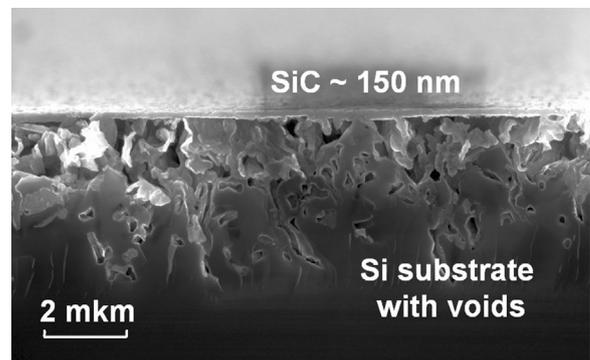
Fig. 1. The image of the SiC/Si(111) sample cut, obtained scanning electron microscope (SEM). Under the SiC~150 nm thick film in the volume of the Si substrate one can see pores and voids partially filled with SiC.

at various pressures p_{CO} in the range 6–600 Pa. The gas flow was changed in a small range within the value of 25 sccm. The synthesis of silicon carbide has been carried out according to the two-stage reaction (1), (2). The summation of these stages gives the synthesis ultimate reaction

$$2Si(crystal) + CO(gas) = SiC(crystal) + SiO(gas) \qquad (3)$$
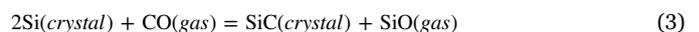
The time of synthesis at such conditions is usually $10-15$ min, therefore that to complete fully the topochemical synthesis, the substrates were held in the CO atmosphere for 30 min. The micrograph of the SiC/Si(111) sample cut, obtained at p_{CO}=95 Pa, is shown in Fig. 1. Clearly seen is the ~150 nm thick SiC epitaxial film. The film thickness for every CO pressure has been determined by the VUV-Vase J.A. Woollam ultraviolet ellipsometer with a rotating analyzer functioning in a range 0.5–9.3 eV. Fig. 2 shows the typical ellipsogramm of the SiC/Si(111) sample obtained at $p_{CO} = 200$ Pa. The thickness of SiC corresponds to 90 nm. Oscillations of the dielectric function are caused by the interference of beams reflected from the SiC surface and SiC/Si interface. At energies exceeding 6 eV the SiC film is opaque, and so there is no interference. However, the transparency of the SiC epitaxial film, retaining up to 6 eV, points to the small concentration of defects (first of all, twins) and to high quality of epitaxy.

In Fig. 1 one can see, below the SiC film, a large amount of pores and voids in the Si substrate down to 4 mkm depth. The analysis carried out by channeling of the sample with ions of hydrogen and helium, has revealed a great amount of carbon atoms in the Si substrate down to 4 mkm depth. In particularly, at the depth of 2 mkm a fraction of C
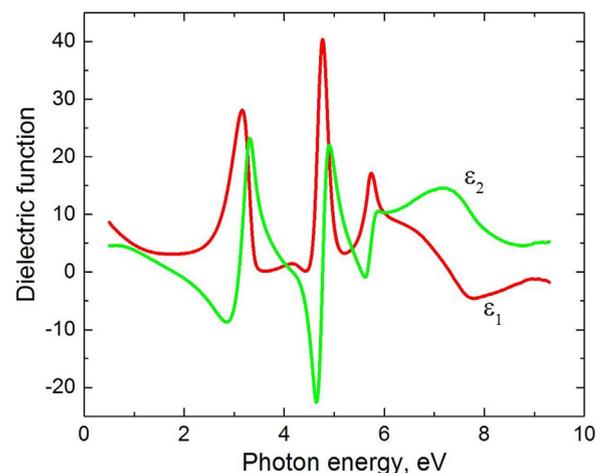
Fig. 2. The typical dependence of the real ε_1 and imaginary ε_2 parts of the dielectric function on the photon energy for the sample SiC/Si(111), which was measured using the VUV-VASE J.A. Woollam ellipsometer with a rotating analyzer. Interference oscillations in the energy range below 6 eV correspond to the SiC film thickness ~90 nm.