Simulation of quality of SiC/Si interface during MBE deposition of C on Si

Simulation der SiC/Si – Grenzflächenqualität während der MBE – Abscheidung von C auf Si

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In the present paper we simulate the processes accompanying the SiC/Si epitaxial growth. The model suggested describes the formation and growth of voids at SiC/Si interface. These voids are sources of Si atoms for SiC growth. According to the model the size distribution function was obtained being in good agreement with experimental data. The influence of surfactants on the nucleation and growth of SiC nanoislands on Si was studied as well.

Keywords: silicon carbide, nanoislands, voids, rate equations, Monte Carlo

Im vorliegenden Beitrag wurden die Prozesse, die bei epitaxialem Wachstum von SiC auf Si während der Molekularstrahlepitaxie von C auf Si – Oberflächen ablaufen, simuliert. Das vorgeschlagene Model beschreibt die Bildung und das Wachstum von Hohlräumen and der SiC/Si – Grenzfläche. Diese Hohlräume fungieren als Quelle für Si – Atome die einen Beitrag zum SiC – Wachstum liefern. Auf der Grundlage des Models wurden die Größenverteilung der Hohlräume berechnet, die sich in guter Übereinstimmung mit den experimentellen Daten befindet. Desweitern wurde der Einfluß von Surfactanten auf die Nukleation und das Wachstum von SiC Nanoclustern auf Si – Oberflächen untersucht.

Schlüsselworte: Siliziumkarbid, Nanocluster, Hohlräume, Rategleichung, Monte Carlo Methode

Introduction

The growth of silicon carbide on silicon allows to combine the benefits of SiC physical properties with the well-developed silicon technologies. The SiC/Si heterostructure could be used as a material for sensors operating at high temperatures, for implementation as substrates for the III-nitride epitaxy, etc. The main technical problem of creating a SiC/Si device is the fact that the lattice and thermal expansion constants mismatches for these materials are as high as 20 % and 8 %, respectively. It leads to creation of multiple nano-islands on the surface. Also the quality of SiC/Si heterojunction suffers because of the presence of voids at the interface. These voids are formed due to the flow of Si atoms from substrates to the growing SiC film and reduce the quality of the interface that makes difficulties for many practical applications of the SiC/Si structure. To improve the interface quality it is important to understand the physics of formation of these voids. The formation of voids was experimentally observed in various studies [1–4] that showed mainly triangular (or more precisely) pyramidal form of the voids on Si (111) substrate with {111} facets [1,3]. In this paper we present the simulation study of void formation and growth in order to have a deeper insight into the evolution processes. The comparison of simulation results with data extracted from TEM images is made to confirm and validate the suggested model.

Pre-deposited impurities can be used to decrease the interface strain and as a consequence the rate of three-dimensional cluster formation and the rate of voids formation. They act as nucleation sites and can increase the concentration of the clusters suppressing the transition form two-dimensional to three-dimensional growth. This transition starts if the SiC clusters reach the critical size [5]. Ge impurity could be easily introduced to the SiC/Si interface, but they act also as anti-surfactants. In the current investigation Monte Carlo simulation was used to determine the effects of impurity which has negative effective binding energy with SiC.

Simulation of void formation

During the growth of SiC film on Si substrate by MBE carbon deposition, the only source of Si atoms is the silicon substrate. Therefore, simultaneously with SiC film growth a system of voids (vacancy clusters in silicon) appears in the substrate. These voids might have rather large sizes (up to several micrometer) [3]. A simple physical model is proposed to describe the processes of nucleation and growth of the void system. We use in our investigations the experimental results obtained by transmission electron microscopy (TEM) observations of such a void system [3]. The size distribution function of voids was extracted from TEM images which allows direct comparison with simulation results.

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The following assumptions were applied to describe the voids formation and evolution during MBE growth of silicon carbide on Si:

1. On a free silicon surface there is a number of Si adatoms and surface vacancies which are formed due to thermal oscillations which normally should be in equilibrium state, i.e. the numbers of appearing and disappearing vacancies and adatoms are equal. In the initial stage of SiC growth free Si adatoms diffuse to form SiC clusters since it is energetically favorable for Si to be in the SiC-state and only carbon atoms are deposited on Si surface. Thus a number of excess surface vacancies appear at the surface. These processes, for simplicity, are described in the model by an efficient vacancy formation energy. Implicitly, efficient energy takes into account the formation of a vacancy-atom pair, recombination of this pair, outdiffusion of Si atoms. The situation should not change qualitatively when the silicon surface is completely covered by a SiC layer (i.e. there is no free silicon surface). However it might be more difficult to create a single vacancy under the SiC layer compared to the free surface due to bonding with silicon carbide (the vacancy formation energy should be higher).
2. It is energetically favorable for a new vacancy to be formed near a already existing one (see, for example [6]), i.e. to create di-, three-vacancy clusters and so on, in other words new vacancies are formed in already existing voids. Thus a system of vacancy clusters appears on the Si surface which is a source of Si atoms to form the SiC layer. These vacancy clusters (or voids) proceed to appear and grow under the SiC layer too.
3. The total rate of vacancies generation (i.e. the rate of vacancy generation in all voids) corresponds to the rate of carbon deposition, in other words the silicon substrate provides a number of silicon atoms for the SiC film which is equal to the number of deposited carbon to maintain stoichiometry. In principle, there are two competing processes: generation of new vacancies (single vacancy or vacancies in voids) and Si atoms as well as recombination of this pairs. In equilibrium the rates of these two processes are equal. In the case of MBE some part of Si atoms are spent for SiC growth. Hence, the rate of recombination is lower comparing to equilibrium. Therefore the number of vacancies increases and the rate of this increase is called the rate of vacancies generation. We also suppose that the rates of vacancy–atom pair generation and recombination are sufficient to provide the necessary amount of Si atoms for SiC growth.
   For a single void it is assumed that the rate of evaporation for a Si atom from a void is proportional to the surface of the void. Thus the rate of vacancies generation for a single void is normalized to the coverage of a silicon surface by voids as well as proportional to the void surface and to the carbon deposition rate.
4. The vacancy diffusion was neglected, i.e. we suppose that the rate of vacancy generation for a certain void (in other words, the rate of void growth) is higher than rate of possible vacancy diffusion to this void.
5. All voids are suggested to have pyramidal form, according to experimental data [3].
   To describe the time evolution of voids we use a Rate Equations approach (see e.g. [7]). According to this method we write balance equations for the mean surface concentrations of vacancy clusters consisting of one, two or three vacancies as well as an equation for the size distribution function of voids for larger sizes. The distribution function shows the number of voids with a certain size per unit surface area. The equation set is as follows:

$$\frac{\partial N_V(t)}{\partial t} = a \cdot \varrho_{Si} \cdot (1-\theta) - g_V \cdot S_1/\theta \tag{1}$$

$$\frac{\partial N_{2V}(t)}{\partial t} = g_V \cdot S_1/\theta - g_V \cdot S_2/\theta \tag{2}$$

$$\frac{\partial N_{3V}(t)}{\partial t} = g_V \cdot S_2/\theta - g_V \cdot S_3/\theta \tag{3}$$

$$\frac{\partial f(L,t)}{\partial t} = f_0 - \frac{\partial}{\partial L}\left[f(L)\frac{dL}{dt}\right] \tag{4}$$

$$\frac{dL(t)}{dt} = a_q(L) \cdot a^3 \frac{g_V}{\theta} \;\; and \; f_0 = \left.\frac{g_V \cdot S_3}{\theta}\right|_{L=L_{min}} \tag{5}$$

Here $N_{jV}(t)$ (j=1,2,3) are the mean surface concentrations of vacancy clusters consisting of one, two or three vacancies respectively;

g_V is the rate of vacancies generation (which is equal to the rate of carbon deposition, see assumption 3);

$S_j = j^*a^2$ (j=1,2,3) – "surfaces of the base" of the clusters consisting of one, two or three vacancies respectively, a – is mean interatomic distance in Si;

$$\theta = N_V(t) \cdot S_1 + N_{2V}(t) \cdot S_2 + N_{3V}(t) \cdot S_3 + \int_{L_{min}}^{\infty} f(L,t) S(L) dL \tag{6}$$

is the part of the substrate surface, covered by voids; here $S(L) = \frac{\sqrt{3}}{4}L^2$ is the surface of pyramidal void's base; L is the length of the edge of the pyramid's base; $a = v_V \cdot exp(\varepsilon_f^V/kT)$ - is the rate of a single vacancy generation, v_V is the frequency of surface atom thermal oscillation, ε^V_f is the efficient formation energy of a stable single vacancy; $f(L,t)$ is the size distribution function of voids; f_o is the rate of voids generation with minimal size ; $\alpha_q(L)$ is the efficiency of growth for a void with a edge length (it shows how efficiently a void may emit Si atoms or how efficiently new vacancies may appear in a void).

This equation set (1)-(6) was solved numerically using the experimental parameters of the carbon deposition from [3]. The size distribution function for voids were obtained for different times of deposition t and compared with experimental results for time $t \asymp 2100$s which corresponds to the deposition time in [3] (see *fig.1*). One can see a rather good agreement of simulated and experimental curves which is achieved by using fit parameters. There are two fit parameters in our simulation, namely, efficient formation energy of a single vacancy (ε^V_f) and efficiency of a void growth ($\alpha_q(L)$). To get a satisfactory agreement with experiment the following values of these parameters were use: $\varepsilon^V_f = 5.8$ eV for deposition time $t < 100$ s, $\varepsilon^V_f = 6$ eV for deposition time $t > 100s$ and $\alpha_q(L) = 0.002 \cdot L^{0.8}$. The change of the value of the formation energy of a single vacancy with time is believed to be connected to the full coverage of the substrate surface with SiC approximately at this moment. When the surface is fully covered by the SiC layer it is more difficult for a Si atom to leave the Si-substrate and to move to the surface of the SiC layer. Hence, under this conditions it is more difficult to create a vacancy. It is worth to note that this efficient values are much higher than the normal value of the surface vacancy formation energy (about 2 eV).). This is due to the fact that efficient values for stable vacancy

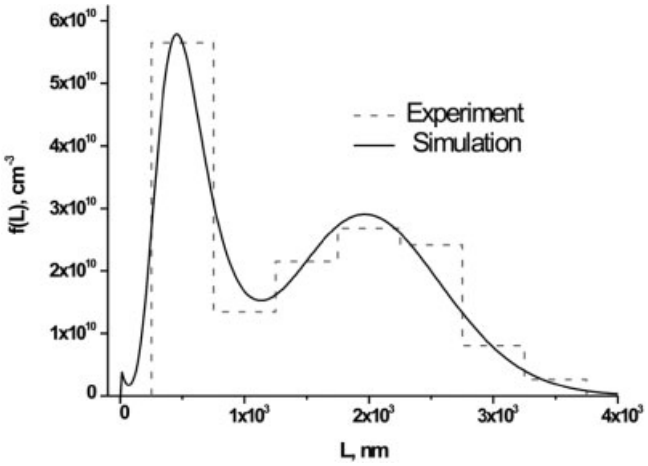

Fig. 1. Size distribution function of voids in the silicon substrate (solid lines – simulation results, dashed line – data extracted from TEM images [3]).

Fig. 1. Größenverteilungsfunktion der Hohlräume im Siliziumsubstrat an der SiC/Si - Grenzfläche (durchgezogene Linie – Simulationsergebnisse, gestrichelte Linie – experimentelle Verteilung bestimmt aus TEM – Untersuchungen aus [3]).

formation (i.e. the value of ε^V_f) take into account the number of vacancies remaining on the surface not only after the vacancy formation itself but also after possible vacancy recombination with Si atom (cf. assumption 1). The changes in the formation energy led to a two-peaks function which was obtained in [3]. Therefore, these two peaks may be connected with a switching of the growth mode: from free Si-substrate surface to a fully covered SiC substrate.

The efficiency of the void growth ($\alpha_q(L)$) reveals the size dependence: the larger the void is, the easier the voids growth (it is easier to create a new vacancy in this void). This dependence may be due to the influence of internal stress in silicon around the void. With increasing void size the surface to volume ratio of the void decreases and the influence of the formation of a single vacancy at void surface is relatively weaker than in the case of smaller voids. However one may suppose that this dependence may change for very large voids since the layer which the surface has no contact with the substrate (i.e. which is in contact with voids) increases and for a large single void the energy of the void-SiC interface may become sufficient to prevent rapid void growth.

It is possible to use the developed approach for the analyses of the main features of voids nucleation and growth. The obtained knowledge can be used for technological applications to prevent (or reduce) the void formation. However this is the topic of further studies.

Monte Carlo Simulation of growth with impurity

Pre-deposited impurities could be used to control the nucleation of SiC nanoislands and voids [8–10] and to further improvement of the structural quality. In experiments Ge impurity atoms were added at the surface to modify the growth conditions. To study the influence of the impurity on SiC growth on Si simulations with a developed kinetic Monte Carlo (KMC) simulation code [11] were performed.

At first simulation of SiC cluster growth without the predeposition of impurity was performed and the cluster concentration was obtained. Then the simulation of the growth in presence of mobile and immobile pre-deposited impurity atoms was carried out. Two types of interaction were studied: an attractive, to simulate the growth in a presence of surfactant, and a repulsive. The latter one corresponds to the growth with antisurfactants (like Ge impurity during SiC/Si growth). Ge atoms have attractive interaction with Si atoms and repulsive interaction with C atoms, hence reducing the rate of SiC formation, because they bind Si adatoms needed to form silicon carbide molecules.

For an attractive impurity it was shown that the resulting cluster density strongly depends on the surfactant mobility at the surface, as the impurity tends to aggregate (because of thermal enhanced diffusion during the growth). The cluster concentration in all cases shows Arrhenius behavior, but the presence of a impurity dramatically increases the cluster concentration. Generally, the cluster concentration is lower then the initial impurity concentration due to aggregation. If the impurity diffusion is high enough, the cluster concentration may even not be affected (*fig. 2*).

In the case of immobile impurity with repulsive interaction with the growing SiC it was shown, that within the developed atomistic KMC physical model the repulsive interaction with SiC led to a slight increase of the concentration of the growing clusters (See *fig. 3*). This figure shows a part of a simulation cell with an area equal to the mean cluster area and so only one cluster would nucleate at that cell. In contrary the simulation shows that multiple nuclei appear in-between of impurity atoms. The reason for this is that repulsive impurity decorates growing clusters and prevents new adatoms to be incorporated into existing clusters, forcing them to nucleate new ones. At the same time the nuclei are highly unstable and so at longer deposition times the overall cluster concentration would decrease, because the repulsive interaction with impurity effectively increases the diffusion coefficient, making the migration length of C adatoms larger.

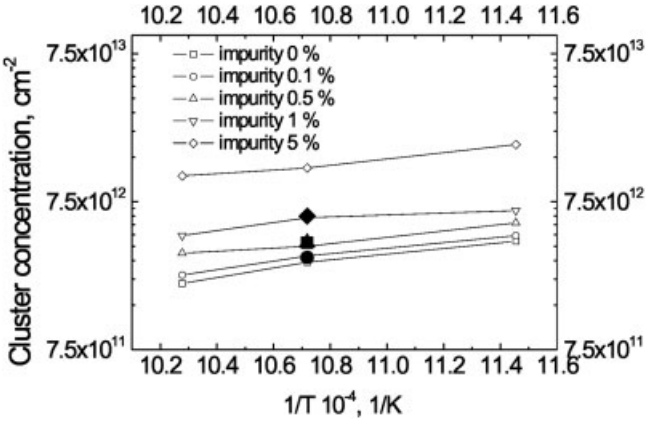

Fig. 2. Simulation of cluster growth in presence of impurity with attractive interaction. Impurity concentration was varied form 0.1 % ML up to 5 % ML. Solid symbols show the same data for highly diffusive impurity.

Fig. 2. Simulation des Einflusses von Oberflächenverunreinigungen mit attraktiven Eigenschaften zu C auf das Clusterwachstums. Die Verunreinigungskonzentration wurde von 0.1 % bis 5 % einer Monolage variiert. Gefüllte Symbole gelten für Verunreinigungen mit hohem Diffusionskoeffizienten.

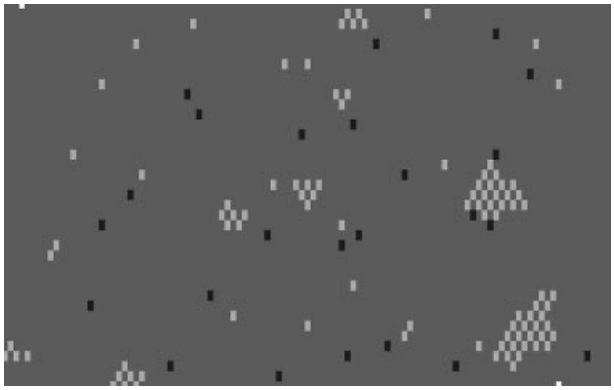

Fig. 3. Growth with impurities with repulsive interactions. Black dots – impurities, dark grey dots – silicon substrate, light gray dots – silicon carbide. Cluster density is increased (substrate size is selected in such a way that only one cluster should appear).

Fig. 3. Simulation des Einflusses von Oberflächenverunreinigungen mit repulsiven Eigenschaften zu C auf das Clusterwachstums. Schwarze Punkte – Verunreinigungen, dunkelgraue Punkte – Siliziumsubstrat, hellgraue Punkte – Siliziumkarbid. Die Clusterdichte wächst mit der Präsenz von Verunreinigungen (die Substrategröße in der Simulation wurde so gewählt, dass nur ein Cluster im Fall einer Verunreinigungsfreien Oberfläche entstehen konnte).

Discussion and Conclusions

Computer simulation methods were used to study the growth of SiC film on Si substrate. The main attention was paid on the void formation in the substrate at the Si/SiC interface. A Rate Equation model was suggested which describes void nucleation and growth. This model allows to calculate the void size distribution function and to make a comparison with experimental data which shows a good agreement between TEM observations and calculation results. Kinetic Monte-Carlo was used to investigate the influence of impurities on the growth of SiC clusters on Si surface. Simulations show, that impurities strongly affect the cluster concentrations. Regardless to the interaction type, both surfactants and anti-surfactants lead to higher concentration of nucleation of smaller clusters. This fact is important for the formation of high-quality SiC/Si interfaces, because small clusters create less strain in the substrate and lower the rate of transition of silicon atoms from substrate to SiC clusters. Therefore the void formation is suppressed and high-quality interface could be obtained. At the same time, the SiC growth rate suffers form the presence of impurity, because the silicon incorporation rate lowers. Additional simulation and experiments are needed to determine the pre-deposited impurity concentrations and growth parameters necessary to form a desired SiC/Si interface quality.

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References

1. A.J. Leary, I.H. Khan, *Thin Solid Films* **1970**, *5*, 145.
2. Y. Sun, T. Miyasato, J. K. Wigmore, N. Sonoda, Y. Watari, *J. Appl. Phys* **1997**, *82*, 2334.
3. J. Jinschek, U. Kaiser, W. Richter, *J. of Electron Mycroscopy* **2001**, *50*, 3.
4. F.M. Morales, S.I. Molina, D. Araujo, R. Garcia, V. Cimalla, J. Pezoldt, *Diamond and Rel. Mater.* **2003**, *12*, 1227.
5. Yu. V. Trushin, E. E. Zhurkin, K. L. Safonov, A. A. Schmidt, V. S. Kharlamov, S. A. Korolev, M. N. Lubov, J. Pezoldt, *Tech. Phys. Lett.* **2004**, *30*, 641.
6. Yu. V.Trushin, *Theory of radiation processes in metal solid solution,* Nova Science Publishers Inc., New York, **1996**.
7. K.L. Safonov, A.A. Schmidt, Yu.V. Trushin, D.V. Kulikov, V. Cimalla, J. Pezoldt, *Mater. Sci. Forum* **2003**, *433–436*, 591.
8. F.M. Morales, P. Weih, Ch. Wang, Th. Stauden, O. Ambacher, J. Pezoldt, In: Microscopy of Semiconducting Materials, Springer Proc. in Physics, Eds. A.G. Cullins and J.L. Hutchinson, **2005**, *107*, 135.
9. J. Pezoldt, T. Wöhner, Th. Stauden, J.A. Schaefer, P. Masri, *Mater. Sci. Forum* **2001**, *353–356*, 183.
10. V. Cimalla, K. Zekentes, T. Tsagaraki, Th. Stauden, F. Scharmann, J. Pezoldt, *Mater. Sci. Forum* **2001**, *353–356*, 187.
11. A.A. Schmidt, V.S. Kharlamov, K.L. Safonov, Yu.V. Trushin, E.E. Zhurkin, V. Cimalla, O. Ambacher, J. Pezoldt, *Comp. Mater. Sci.* **2005**, *33,* 375.

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