

Mechanisms of epitaxial growth of SiC films by the method of atom substitution on the surfaces (100) and (111) of Si single crystals and on surfaces of Si films grown on single crystals Al₂O₃

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Abstract. The structure and morphology of silicon carbide (SiC) films formed by a new method of atom substitution on the surfaces (100) and (111) of silicon substrates (Si) were investigated. It is shown that the singular faces (100) of Si in the process of substitution of silicon atoms for carbon atoms are transformed into a face of SiC, consisting of an ensemble of facets resembling saw-tooth structures, the side surfaces of which are covered with planes (111) and (110) and (210). Theoretically, a fundamentally different mechanism of atom substitution on the faces (111) and faces (100) is described and experimentally confirmed. It was found that on the vicinal surface of Si, deviated 4° or more from the singular face (100), during the synthesis of SiC, an ordered phase of SiC is formed, the surface morphology of which appears as of facets (scales) consisting of faces (111). It is shown that the method of topochemical substitution of atoms can grow epitaxial SiC layers not only on a silicon substrate, but also on substrates of other materials, in particular, on single-crystal sapphire substrates.

1. Introduction

In papers [1–4] a new method of obtaining of nano-SiC epitaxial films on Si, the so-called method of atom substitution, was theoretically predicted and experimentally discovered. This method of growth of nano-SiC is fundamentally different from all existing methods and technologies of growing single crystals, films and nanostructures. This method is based on the “assembly” of a new silicon carbide matrix on the basis of the old silicon matrix by partial substitution of silicon atoms in the crystalline matrix of the substrate with carbon atoms. The “assembly” of the SiC matrix is carried out by chemical reaction (1)



In [2–4] it was proved that the reaction (1) proceeds in two stages. In the first stage, an intermediate compound is formed – activated complex “silicon vacancy-carbon atom-matrix-silicon” (C–V_{Si}). Carbon atoms at this stage are located in the interstitial positions of the silicon matrix. At the second stage of the reaction, the activated complex passes into silicon carbide, and the released vacancies merge into pores formed under a layer of silicon carbide. In a cubic symmetry crystal, these two centers of dilatation (a carbon atom and a silicon vacancy) interact elastically with each other. If



dilatated dipoles are perpendicular to the plane (111) of silicon, they are attracted to each other [2–5]. At the same time, almost all dilatated elastic energy, which arose due to the introduction of a carbon atom and the formation of a vacancy, relaxes [2–5].

It should be noted that the strict quantum mechanical calculation of the rate of chemical reaction (1) and the interaction of a silicon vacancy with a carbon atom was described in [6, 7]. After the chemical transformation is complete, the mechanical dipoles that have fulfilled their role disintegrate into a film of silicon carbide and pores under its surface. The orientation of the film is determined by the "old" crystal structure of the original matrix of Si, and not only the surface of the substrate, as it usually occur in traditional methods of films growing.

2. Structural and morphological features of formation of SiC films on singular surfaces Si (111) and Si (100)

A distinctive feature of the method of substitution of atoms is that, regardless of the initial crystallographic plane of Si on which SiC was synthesized, a plane [111] is necessarily formed as one of the planes. This effect is due to the fact that the elastic dipoles carbon atom – silicon vacancy, which was mentioned above, are always perpendicular to the direction [111] and lie in the plane [110] perpendicular to the plane (111).

Thus, according to the work [3], the nucleation rate of SiC embryos on a smooth densely packed face $I(n_{cr}, \beta_{cr})$ can be found from the expression (2)

$$I(n_{cr}, \beta_{cr}) = \frac{2D_{cr}}{\sqrt{\pi}} (N_d + N^{Si}) \exp(-R_{cr}/k_B T), \quad (2)$$

and the rate of SiC nucleation on the Si vicinal face $I(n_{cr}, \beta_{cr})$ from the expression (3)

$$I(n_{cr,V}) = \frac{2D_{cr,V}}{\sqrt{\pi}} N_d \exp\left(-\frac{R_{cr,V}}{k_B T}\right), \quad (3)$$

where $R_{cr}(\cos \varphi(x, y, z)) = \frac{\Gamma_1 \Gamma_2 (4\pi \Gamma_2 - \Gamma_3 \varepsilon)}{[\zeta - \Lambda(\cos(\varphi(x, y, z))) N_d]^2} + \frac{\pi \Gamma_2 \Gamma_3^2}{\mu^{Si} \varepsilon [\zeta - \Lambda(\cos(\varphi(x, y, z)))]}$ is the work of formation of the embryo SiC containing n_{cr} molecules of SiC and etching pits on the closely packed faces, depending on the location of dilatation dipoles, relative to the crystallographic coordinate of the cubic crystal, i.e.

to the $\cos((x, y, z))$; $R_{cr,V} = \frac{4\pi \Gamma_1' \Gamma_2^2}{[\zeta - W(\cos((\varphi(x, y, z))) N_d]^2} + \frac{4\pi a \Gamma_2^2 (\frac{\Gamma_2^2}{\Gamma_2} + \cos \theta / \sqrt{3})}{[\zeta - W(\cos((\varphi(x, y, z))) N_d]} (R_{cr,V}) = 4\pi \Gamma_1$ is the work of formation of the embryo SiC containing n_{cr} molecules on SiC vicinal faces, which depends both on displacement of dilatation dipoles, which depends on its location relative to the crystallographic coordinate of the cubic crystal $\cos(x, y, z)$, and the angle of deviation of vicinal faces from faces (111) θ ; $\beta_{cr} = R_{cr}/H_{cr}$, the ratio of the critical dimension of the formed shrinkage pore to the critical layer thickness of SiC; $\zeta = k_B T \frac{(V^{SiC} + V^{Si})}{(V^{SiC} V^{Si})} \ln \left[\frac{P_{CO} K^{eq}}{P_{SiO}} \right]$; $\Lambda(\cos(\varphi(x, y, z))) = W(\cos((\varphi(x, y, z))) N_d + Y_{SiC}$; V^{SiC} , volume per atom in a cubic lattice of SiC; V^{Si} , volume per atom in the cubic lattice of Si; k_B is the Boltzmann constant; T , temperature of synthesis of SiC, depends on the process and lies in the range 1000–1400 °C (that not to exceed the melting point of silicon); K^{eq} is the equilibrium constant for the formation of SiC from Si under its processing by gas CO; P_{CO} , pressure of carbon monoxide in the vapor phase over the surface of the Si substrate, and P_{SiO} , pressure of silicon monoxide in the reaction zone; $W(\cos((x, y, z)))$, elastic energy of the crystal in the formation of dilatation dipoles in its volume, depending on their location relative to the crystallographic coordinates of the cubic crystal $\cos((x, y, z))$.

The energy $W(\cos((x, y, z)))$ can take both positive and negative values depending on the direction of the face; approximately it equals zero for the direction $W([111]) \approx 0$ eV at the arrangement of elastic dipoles along the direction [111] and is maximal at the arrangement of dipoles along the direction [100] $W([100]) \sim 1$ eV; N_d is the density of elastic dipoles in the volume of the intermediate

complex in silicon, the rate of chemical reaction of SiC formation is determined, on average, $N_d \approx 1,6 \cdot 10^{28} \text{ m}^{-3}$; $Y_{\text{SiC}} = \mu^{\text{Si}} K^{\text{SiC}} \varepsilon^2 / 2(K^{\text{SiC}} + \mu^{\text{Si}})$; $\mu^{\text{Si}} = 0,52 \cdot 10^{11} \text{ N/m}^2$ is a shift module of Si; $K^{\text{SiC}} = 2,5 \cdot 10^{11} \text{ N/m}^2$ is the compression module of SiC; ε is the strain in the surface layer of the substrate that occurs due to the difference in distance between the atoms in Si and SiC along the planes (111), $\varepsilon \approx 0,2$; since $K^{\text{SiC}} \gg \mu^{\text{Si}}$, then $Y_{\text{SiC}} \approx \mu^{\text{Si}} \varepsilon^2 / 2$; a is the interatomic distance in silicon matrix; Γ_1 describes the change of the total surface energy of the upper and lower faces of the disc-shaped SiC embryo and the pore in the conversion of Si in SiC [8]; Γ_2 is the total surface energy of the side faces of the embryo and of etching pit, bordering the shrinkage pore; Γ_3 is the total surface energy of the lateral surfaces of the embryo of SiC and of the pore in the Si; Γ_1'' is the total surface energy of the embryo of SiC and of the pore on the vicinal crystal face; Γ_2' is the total surface energy of the embryo and of the etching pit, formed on vicinal faces; specific estimates of values Γ_1 , Γ_2 , Γ_1'' and Γ_2' can be found in [3]; D_{cr} and $D_{\text{cr,v}}$ are pre-exponential kinetic coefficients calculated in [3]. From the formulas (1) and (2) it follows that the nucleation of SiC can occur only if $\zeta > \Lambda(\cos(\varphi(x, y, z)))$ or, what is the same, the pressure of CO must satisfy the condition (4)

$$P_{\text{CO}} > \frac{P_{\text{SiO}}}{K^{\text{eff}}}, \quad (4)$$

where $K^{\text{eff}} = K^{\text{eq}} \exp\{-[\Lambda(\cos(\varphi(x, y, z))) V^{\text{SiC}} V^{\text{Si}} / (V^{\text{SiC}} + V^{\text{Si}}) k_B T]\}$ is the generalized equilibrium constant K^{eq} , taking into account the elastic energy $\Lambda(\cos(\varphi(x, y, z)))$.

An important feature of the formulas (2) - (4) describing the nucleation of the SiC layer on Si is that the work of the formation of the SiC embryo significantly depends on the direction along which the chemical bonds in the intermediate complex are broken. According to the formulas (2) and (3), along the direction [111], the term $\Lambda(\cos(\varphi(x, y, z))) = [W(\cos(\varphi(x, y, z))) N_d + Y_{\text{SiC}}]$ in the denominator of the work of formation $R_{\text{cr}}(\cos(\varphi(x, y, z)))$ in the formula (2) or the term $[W(\cos(\varphi(x, y, z))) N_d]$ in the denominator of the work of formation $R_{\text{cr,v}}$ in formula (3), take the minimal values. That means that the nucleation rate will be maximal only along the direction [111]. Namely, these faces (111) are formed primarily in the process of SiC synthesis by the substitution method.

In the case of a vicinal surface deviated from the plane (111) by a small angle, as follows from equation (3), the growth begins already at pressure P_{CO} at which $\ln \left[\frac{P_{\text{CO}} K^{\text{eq}}}{P_{\text{SiO}}} \right] > 0$; for example, for $T = 1250^\circ\text{C}$ this pressure must be $P_{\text{CO}} \geq 0.03 \cdot P_{\text{SiO}}$. In the case of other low-index faces, the situation is changing essentially. According to the calculations carried out in [3] $W([100]) \sim 1$. It follows that the value $\Lambda(\cos(\varphi(x, y, z)))$ for the face (100) will be $\Lambda(\cos(\varphi(x, y, z))) \approx 3.4 \cdot 10^9 \text{ J/m}^3$. This value of $\Lambda(\cos(\varphi(x, y, z)))$ leads to the fact that the formation of the SiC film by the method of atom substitution on the face (100) becomes possible only if CO pressure in the reaction zone is $p_{\text{CO}} > 0.5 \cdot p_{\text{SiO}}$, i.e. ten times higher than the stable film growth pressure [3] $P_{\text{CO}} \geq 25 \text{ Torr}$. That is why, SiC can't nucleate on the smooth surface (100) of silicon. However, the nature bypasses such a high value of $\Lambda(\cos(\varphi(x, y, z)))$ transforming the face (100) into a SiC face consisting of a set of facets resembling saw-tooth structures, the side faces of which are covered with planes (111) and (110), and (210). The angle between the face direction (100) and the faces (111) is $54^\circ 44'$. Any small deviation of the face (100) from this direction makes it vicinal, which leads to the instantaneous formation of a very thin layer (several atomic layers) of the film. The growth of thick SiC layers at this pressure is not possible, since a thin SiC layer will close all main pores, through which CO enters the inner layers of Si substrate during the synthesis.

3. Structural and morphological peculiarities of formation of a film of SiC on a vicinal surface of Si (100)

A completely different picture will be observed if SiC is grown by the method of substitution of atoms on the surface (100), disoriented to $2-7^\circ$ in the direction $\langle 011 \rangle$. If you heat the surface to temperatures in excess of 600°C , the plane (100) of silicon, according to thermodynamics, will be covered with

steps. The terraces of this structure will be planes (100), and the steps will be limited by planes (011). Along the directions $\langle 011 \rangle$ there are “channels” in the silicon lattice, which are associated with the peculiarities of the crystallographic structure of the lattice. Therefore, the CO molecules are rushing in direction perpendicular to the steps inside Si. The Si surface is saturated with CO and, as described above, the interaction reaction between Si and CO occurs, as a result of which the intermediate state is formed that is converted to SiC. In this transformation the part of Si from the step (011) is evaporated and forms the step (111) of SiC. This process removes the “degeneracy” inherent to the non-deviated face (100) and leads to the formation of facets consisting of faces (111) of Si, which are located on the former steps (011), but not randomly displaced as on the face (100). Naturally, these faces make up the same angle of $\sim 55^\circ$ with the face (100) and an angle of $\sim 35^\circ$ with the face (011).

Since the attraction between the silicon vacancy and the carbon atom in the silicon matrix is maximal along the direction $\langle 111 \rangle$, part of the step (011) of Si can turn into a fracture (112) of SiC. As is known, the angle between the planes (112) and (100) in a cubic crystal with a diamond lattice is ~ 35 degrees. As a result, a lateral wedge-like protrusion of silicon carbide is formed, which has an apex protruding above the site of the step and an tilted face reaching the site of the lower step, with the formation of a slope. The surface of Si (100) is covered by an array of wedge-like parallel steps representing themselves triangular prisms (lateral faces of pyramids) [3, 12].

4. Structural and morphological features of the SiC film formation on the surface (100) of the epitaxial Si film grown on Al₂O₃

Using the method developed in [1–4], one can obtain the epitaxial layers of SiC not only on a silicon substrate, but also on substrates of other materials. To do this, a single-crystal layer of Si must be deposited on the working surface of the substrate, and then synthesized the SiC layer using the reaction (1). If the initial silicon carbide is epitaxial, the SiC layer would be epitaxial as well. Figure 1 shows the image of the surface and of the cleavage of a single-crystal substrate Al₂O₃ with a layer of epitaxial SiC obtained with a scanning raster microscope (SEM). This structure was obtained as follows. At the beginning, an epitaxial Si layer with a thickness of the order of 610–630 nm and of orientation (100) was deposited on the surface of the R-cut sapphire by CVD. Further, the sapphire substrate with a layer of Si was placed in a special device for the growth of SiC and was annealed at temperature 1250°C in the atmosphere of CO. As a result, an epitaxial layer of SiC was grown. The structure of the SiC layer is clearly visible in figure 1. It consists of a solid layer of SiC of a thickness about 58 nm and of the porous Si layer covered with a layer of SiC. In addition, it can be seen that the SiC layer has a greater degree of roughness.

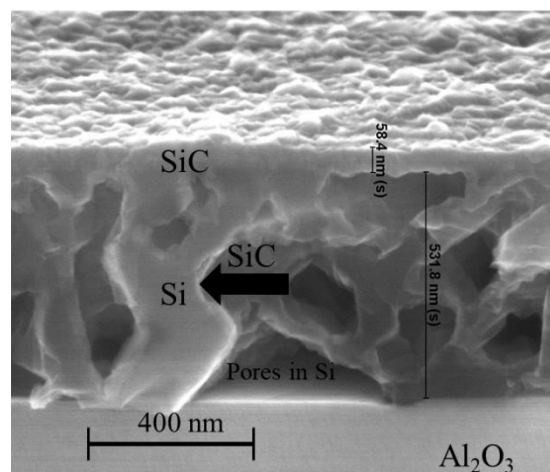


Figure 1. SEM-image of a cross-section cut of sapphire with a formed SiC layer and porous silicon covered with SiC with a thickness of about 532 nm.

The increased degree of SiC surface roughness is due to the fact that, as shown in the above, during the transformation of Si (100) into SiC, the SiC layer of orientation (100) is covered with saw-tooth faces (111). This is that is observed as SiC is growing on sapphire by the method of atom substitution.

5. Conclusions

Thus, it is theoretically and experimentally shown that SiC layers are growing as epitaxial layers on the orientation (111) of Si as well as on (100) orientation. However, the growth mechanism of SiC is fundamentally different. This leads to a significant difference in the surface morphology of SiC layers grown on Si substrates of these orientations. The surface (111) of Si remains smooth when transforming into a surface of SiC, while the surface (100) is covered with facets consisting of faces (111). It is shown that a similar mechanism is observed as SiC is growing from the Si layer grown on sapphire.

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