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Anisotropy of the Solid-State Epitaxy of Silicon Carbide in Silicon

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Abstract—A new method for the solid-state synthesis of epitaxial layers is developed, in which a substrate participates in the chemical reaction and the reaction product grows not on the substrate surface, as in traditional epitaxial methods, but inside the substrate. This method offers new opportunities for elastic-energy relaxation due to a mechanism operating only in anisotropic media, specifically, the attraction of point defects formed during the chemical reaction. The attracting point centers of dilatation form relatively stable objects, dilatation dipoles, which significantly reduce the total elastic energy. It is shown that, in crystals with cubic symmetry, the most favorable arrangement of dipoles is the ⟨111⟩ direction. The theory is tested by growing silicon carbide (SiC) films on Si (111) substrates by chemical reaction with carbon monoxide CO. High-quality single-crystal SiC-4*H* films with thicknesses of up to 100 nm are grown on Si (111). Ellipsometric analysis showed that the optical constants of the SiC-4*H* films are significantly anisotropic. This is caused not only by the lattice hexagonality but also by a small amount (about 2–6%) of carbon atoms remaining in the film due to dilatation dipoles. It is shown that the optical constants of the carbon impurity correspond to strongly anisotropic highly oriented pyrolytic graphite.

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1. INTRODUCTION

The fabrication of high-quality films of wide-gap semiconductors, such as silicon carbide SiC, aluminum nitride AlN, and gallium nitride GaN, on silicon substrates is one of the major problems of microelectronics and optoelectronics [1]. Solving this problem will allow the integration of a variety of novel semiconductor materials in silicon electronic devices. The main obstacle to growing high-quality low-defect SiC, AlN, and GaN films on Si is the elastic stresses caused by a ~20% mismatch between the lattice parameters of these semiconductors and the Si lattice parameter [2, 3]. At present, a number of costly techniques are being developed in which elastic stresses are reduced by a variety of masks and buffer layers; nevertheless, the wide-gap semiconductor films obtained contain a large amount of misfit dislocations, which significantly degrade the electrical characteristics of the semiconductors.

In this study, we propose a fundamentally new approach to thin-film heteroepitaxy, in which elastic stresses relax on account of the very high attraction of different defects, specifically an atomic vacancy and a foreign atom located at the interstitial position. Both of these point defects are centers of dilatation; due to mutual attraction, they form a relatively stable state, i.e., a dilatation dipole, so called in analogy with an electric dipole. It is demonstrated that the formation of an ensemble of dilatation dipoles ensures the highly effective relaxation of elastic stresses, much more so than with the use of masks or buffer layers. In particular, during the growth of SiC on Si with a lattice-mismatch parameter of ~20%, elastic stresses completely relax and misfit dislocations do not form. This allows thick SiC, AlN, and GaN layers, which have almost the same lattice parameters, and heterostructures on their basis to be grown on Si substrates.

In this study, we propose that the SiC films be grown directly in the bulk of a Si substrate and not on its surface, in contrast to traditional growth [4]. The material of the Si substrate participates directly in the chemical reaction with the formation of SiC. In this case, bulk ordering of the crystal structure of SiC by the entire initial Si matrix occurs. If a Si substrate is treated with a carbon-containing gas, such as C_2H_4, CH_4, CCl_4, CO, or CO_2, then in all cases at a certain temperature and pressure, the SiC film will grow. Our goal, however, is to obtain a high-quality SiC film with the effective relaxation of elastic stresses due to the interaction of point defects, which emerge during the chemical reaction. Therefore, from the variety of reactions, we choose the reaction with the participation of carbon monoxide CO:

$$2\text{Si(solid)} + \text{CO(gas)} = \text{SiC(solid)} + \text{SiO}\uparrow\text{(gas)}. \quad (1)$$

This reaction ensures the formation of point defects of two types in the Si matrix, specifically a silicon vacancy caused by the output/release of silicon-monoxide gas from the system, and a carbon atom,

which is located in the interstitial position in the Si crystal after the loss of oxygen. These defects form in Si in pairs and cause dilatation strains, i.e., play the role of centers of dilatation in the cubic Si crystal. If a medium is infinite and isotropic, the spherically symmetric centers of dilatation in it do not interact [5]. In real crystals with cubic or hexagonal structure, the interaction of the spherically symmetric dilatation centers is determined by the direction of the straight line connecting them. Depending on the direction and sign of dilatation strains, they can both attract and repulse. This result, along with rough estimations of the interaction energy, was obtained as early as in 1955 in Eshelby's study of crystals with cubic symmetry [6]. Bythat time, it was understood that the energy of the interaction of the dilatation centers in anisotropic crystals can be very large, but it was not used for the relaxation of elastic stresses in the growing heteroepitaxial films. In the approach described here, it is made for the first time.

2. THEORETICAL MODEL OF THE SOLID-STATE EPITAXY OF SiC IN Si AND THE FORMATION OF DILATATION DIPOLES

First, we estimate the dilatation component of the elastic stresses in the SiC film growing directly from the Si matrix by reaction (1). We remove some atoms from the Si matrix and transform the latter to SiC by adding one C atom in the place of each removed atom. The atomic density in Si is $N^{Si} \approx 5.0 \times 10^{28}$ m^{-3} and the density of Si atoms in SiC is $N^{SiC} \approx 4.83 \times 10^{28}$ m^{-3}. Thus, the volume per SiC molecule in the SiC crystal grows by about $\delta = 3.4\%$. If there is no coherence between SiC and Si, then the elastic stresses will only be caused by dilatation. The Si shear modulus is $\mu^{Si} =$ 52 GPa and the SiC compression modulus is $K^{SiC} =$ 250 GPa. Then, using the standard technique, we can estimate the value of the occurring elastic stresses. In particular, the radial component of the shear stresses is

$$\sigma_{rr} \approx -\frac{\mu^{Si} K^{SiC}}{K^{SiC} + \mu^{Si}}\delta \approx -1.5 \text{ GPa}, \quad (2)$$

i.e., ~0.18 eV/atom. Upon coherent conjugation of the film and the substrate, these stresses are larger by several times and have the other sign:

$$\sigma_{rr} \approx \frac{\mu^{Si}}{1 - \nu^{Si}}(\delta_1^2 + \delta_2^2 + 2\nu^{Si}\delta_1\delta_2) \approx 7 \text{ GPa}, \quad (3)$$

where $\nu^{Si} = 0.26$ is Poisson's ratio and δ_1 and δ_2 are the parameters of lattice mismatch between the film and substrate in two directions at the film–substrate interface.

We now consider another growth mechanism in which a C atom is embedded into the Si matrix and a neighboring Si atom is removed by the gas product of reaction SiO (1), i.e., a vacancy is formed. Let us describe the interaction of two point defects, the C atom at the interstice and the silicon vacancy in the crystal. According to the classical theory of elasticity, the energy of the interaction of two point defects, I and II, in a solid can be presented as the interaction of one defect with an elastic-stress field induced by the other defect. The defects in themselves are simulated by the dilatation centers with the powers Ω^{I} and Ω^{II}. In this case, the potential energy of the pair interaction of dilatation centers I and II is [5]

$$E_{int}(r) = -K\Omega_{ij}^{I}\varepsilon_{ij}^{II}(r), \quad (4)$$

where $K = (c_{11} + 2c_{12})/3$ is the compression modulus of the crystal material ($K^{Si} = 98$ GPa), c_{ij} are the elasticity moduli of the crystal, Ω_{ij}^{I} is the dilatation tensor of the first defect located at the origin of coordinates, and ε_{ij}^{II} is the strain tensor caused by the second defect located at point r. Hereinafter, summation is made by repeating indices. The contribution of the terms quadratic in the strains to the interaction energy is disregarded, since in the anisotropic media they posses the second order of smallness as compared with (4). We assume that the point defects are spherically symmetric and incompressible, i.e., $\Omega_{ij}^{I, II} = \Omega^{I, II}\delta_{ij}$, where δ_{ij} is the Kronecker symbol. Then, to calculate E_{int}, it is sufficient to find the principal invariant of the deformation tensor $\varepsilon_{ij}^{II} = \partial u_i/\partial x_i$, where u_i is the shift vector,

$$u_i = \frac{K\Omega^{II}\partial G_{ij}(x, x')}{(\partial x'_j|_{x'=0})}. \quad (5)$$

Here, G_{ij} is the tensor Green's function of a point defect in the crystal. Finally, we obtain the energy of the interaction of spherically symmetric incompressible defects [7–9]:

$$E_{int} = -K^2\Omega^{I}\Omega^{II}\frac{\partial^2 G_{ij}}{\partial x_i \partial x'_j|_{x'=0}}. \quad (6)$$

Since silicon satisfies the weak anisotropy condition

$$\eta = \left|\frac{c_{11} - c_{12}}{2c_{44}}\right| < 1,$$

for $G(x, x')$ we can use the approximate Green's function for the case of infinitely weak anisotropic crystals with cubic symmetry, which was derived by Lifshits and Rozentsveig [10]. Substituting it into (6) and making transformations, we arrive at

$$E_{int} = E_0\left(\cos^4\varphi_x + \cos^4\varphi_y + \cos^4\varphi_z - \frac{3}{5}\right), \quad (7)$$

$$E_0 = \frac{15K(1-\eta)}{4\pi}\frac{3c_{11} - 4c_{44}}{c_{12} + 2c_{44}}\frac{\Omega^{I}\Omega^{II}}{r^3}, \quad (8)$$

where $\cos\varphi_i = x_i/r$ are the cosines between the axes x, y, and z and the direction of the straight line connecting the interacting defect centers. The value of $\cos^4\varphi_x + \cos^4\varphi_y + \cos^4\varphi_z - 3/5$ has a minimum in the $\langle 111\rangle$ direction, which amounts to -0.27 and corresponds to the attraction of the same defects, when, e.g., they both compress the lattice, as a vacancy and a small interstitial atom, a maximum in the $\langle 100\rangle$ direction, which amounts to 0.4 and corresponds to the repulsion of the same defects, and the saddle point -0.1 in the $\langle 110\rangle$ direction. Therefore, the most energetically favorable location of the same defects is in the $\langle 111\rangle$ direction, when a C atom is located at the interstice under the (111) plane along the (011) plane and a vacancy formed simultaneously with this atom as a result of reaction (1) is located along the $\langle 111\rangle$ direction relative to the C atom. In this case, the interaction of point defects decreases the total elastic energy, which makes these defect pairs relatively stable. We call them dilatation dipoles by analogy with electric dipoles.

The powers of dilatation centers of the vacancy and the carbon atom Ω_v and Ω_a can be estimated using Eshelby's classical results and data on the carbon atomic radius and silicon-vacancy effective radius [6]: $\Omega_a = -0.29V^{\mathrm{Si}}$ and $\Omega_v = -0.68V^{\mathrm{Si}}$, where $V^{\mathrm{Si}} = 2.0 \times 10^{-29}\ \mathrm{m}^{-3}$ is the volume per atom in Si. This yields the following estimate for the energy of attraction of defects in the $\langle 111\rangle$ direction; $E_{\mathrm{int}} = -1.0$ eV. The energies E_v and E_a of elastic distortion of the lattice by the vacancy and carbon atom can be estimated assuming that the medium is isotropic and the defects are incompressible [6]. In this case, $E_v = 0.73$ eV and $E_a = 0.14$ eV. Thus, if the carbon atom simply participates in dilatation, then, as was shown above, the elastic energy per SiC molecule is $W_{\mathrm{dil}} = \sigma_{rr} = 0.18$ eV and, if it is a component of a dilatation dipole, then the elastic energy per SiC molecule is $W_{\mathrm{dip}} = E_v + E_a + E_{\mathrm{int}} = -0.13$ eV. Since no more than five dilatation dipoles can correspond to eight SiC molecules, the maximum value of the elastic-energy relaxation on account of the formation of dilatation dipoles is $\Delta W = (5/8)(W_{\mathrm{dil}} - W_{\mathrm{dip}}) \approx 0.19$ eV per SiC molecule. Thus, the dilatation elastic energy can completely relax on account of the dilatation dipoles only, since $W_{\mathrm{dil}} - \Delta W \leq 0$. In other words, this relaxation mechanism is highly effective.

Thus, at the first stage of the chemical reaction, the metastable compound forms, the composition and structure of which differ from those of Si and SiC (Fig. 1). The compound consists of layers of silicon and carbon, with the latter being bivalent, separated by layer of vacancies. The dipoles stabilize this structure, replacing the broken chemical bonds with elastic interaction (Fig. 1). In chemistry, such intermediate states are called transition phases [11]. They are usually formed because, during the preliminary stage, the reaction requires a weakening of the chemical bonds in the initial reactant by extending them. Such an extension allows the reactants to pass to the final state of reaction products with minimum energy consumption. Such a transition is often a first-order phase transition with the barrier height close to the thermal energy $k_{\mathrm{B}}T$. In this case, the elastic dipoles located along the $\langle 111\rangle$ direction lead to anisotropy of the chemical reaction, extend the chemical bonds in silicon, and favor the formation of silicon carbide with minimum energy consumption (Fig. 1). The breaking of the dipoles due to thermal fluctuations leads to the formation of dislocationless SiC, and mobile silicon vacancies released during this process either go to the surface or gather together under the SiC film with the formation of pores in Si [7]. Immobile carbon atoms arising during breaking of the dipole mainly transform into SiC and those not transformed remain in SiC as an impurity.

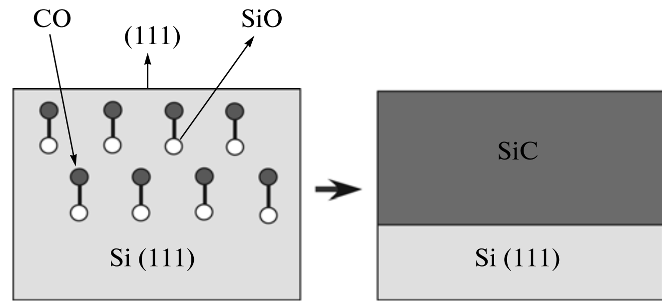

Fig. 1. Schematic representation of the SiC solid-phase epitaxy within the Si (111) substrate by chemical reaction between the substrate material and CO gas. Point dilatation defects form due to the chemical reaction in Si in pairs: C atom at the interstice (dark circle) and a silicon vacancy (light circle). Strong attraction between them leads to the formation of dilatation dipoles, which ensure the relaxation of elastic stresses and orientation of the SiC layer. The SiC layer in itself forms from Si by a low-barrier first-order phase transition through an intermediate phase consisting of Si saturated with dilatation dipoles.

The phase transition from the intermediate phase to the final state is often accompanied by another first-order phase transition in the initial matrix. This second transition is impossible without the formation of a final phase, i.e, the first transition; therefore we can speak about the master and slave phase transitions. For example, in solids the master phase transition often causes elastic stresses between the initial and new phases and the elastic stresses, in their turn, lead to the other, slave, phase transition in the initial phase. In this case, the phase transition from Si to SiC leads to the formation of shrinkage pores in Si, which is also a phase transition. This process will be studied elsewhere.

3. RESULTS AND DISCUSSION

To verify the main results of the above model, we carried out a number of experiments on growing SiC

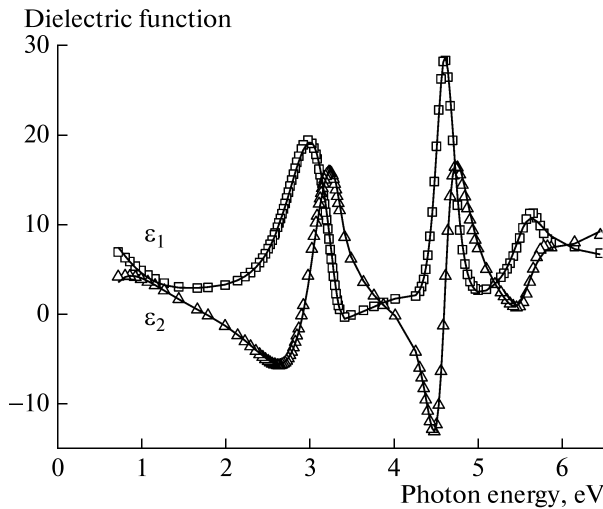

Fig. 2. Permittivity of the SiC/Si (111) sample vs the photon energy measured with a J.P. Woollam ellipsometer. ε_1 is the real part and ε_2 is the imaginary part. Points correspond to the experiment and the solid line, to theoretical spectra obtained with the use of the anisotropic bilayer model.

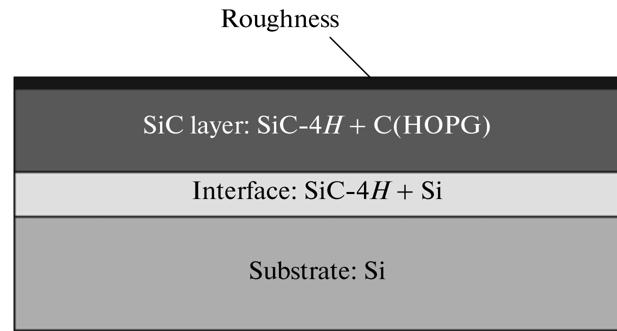

Fig. 3. Anisotropic bilayer model describing the ellipsometric spectra of the SiC/Si (111) samples. The bottom layer is the Si substrate, the first layer is the 9-nm-thick buffer consisting of 85% SiC-4*H* and 15% Si, and the second layer is the basic SiC layer consisting of 94% SiC-4*H* and 6% HOPG. On top is the 5-nm roughness. The optical constants of SiC-4*H* and HOPG are anisotropic.

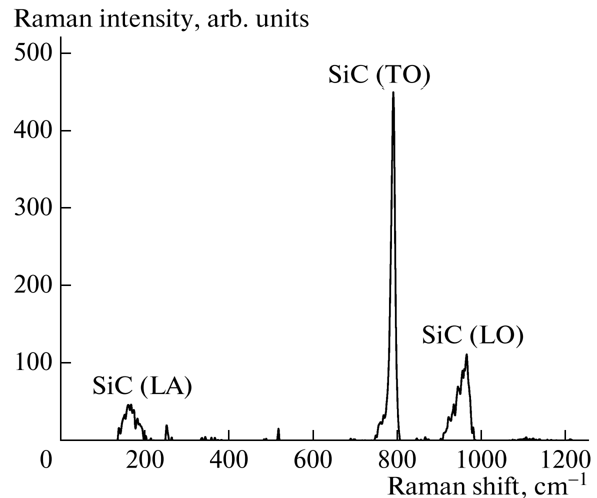

Fig. 4. Raman spectrum of the SiC layer obtained from the spectrum of SiC/Si (111) by subtracting the Si (111)-substrate spectrum. The lines of the longitudinal optical (LO), transversal optical (TO), and longitudinal acoustic (LA) oscillations are marked.

films from a Si substrate by reaction (1). Substrates of single-crystal silicon of the (111) and (100) orientations 33 mm in diameter were kept in a vacuum furnace at a temperature of $T = 1200–1300°C$, in a CO atmosphere, at a pressure of $p_{CO} = 10–70$ Pa for 5–60 min. In this time, a 20–200-nm-thick SiC film grew within the Si substrate [7]. On the (100) surface, the elastic energy does not relax. In this case, the film is textured and contains a great number of defects and dislocations. At the same time, as was theoretically predicted, on the (111) surface an ensemble of dislocation dipoles forms, which leads, on the one hand, to the significant relaxation of elastic stresses and, on the other hand, to ordering of the new phase according to the initial silicon structure. As a result, a high-quality SiC film grows, which contains no misfit dislocations [8]. Measurement of the elastic stresses in the SiC/Si (111) films using an FLX-2320-S stress measurement system yields the mean value $\sigma \approx 0.5$ GPa; i.e., in reality, about 2/3 of elastic dilatation stresses relax on account of dipoles. It should be emphasized that the SiC films are compressed, while, if they are grown by the classical mechanism, they would be stretched, since the SiC and Si lattice constants are $a^{SiC} = 4.357$ Å and $b^{Si} = 5.43$ Å.

Studying the ellipsometric spectra of the SiC/Si (111) samples showed that the optical constants of the grown layers are anisotropic; i.e., the optical constants in the sample plane do not coincide with those in the plane perpendicular to the sample. Such an effect is characteristic of the hexagonal SiC polytypes; in this case, however, the anisotropy is stronger. Analysis of the difference in the optical constants of the grown layers and SiC showed the presence of a carbon-atom impurity at an amount of 2–6%; the optical constants of the additional component completely correspond to highly oriented pyrolytic graphite HOPG with very pronounced anisotropy. Figure 2 shows the typical dependence of the permittivity of the SiC/Si (111) sample on the photon energy. The dependence was obtained using a J.A. Woollam ellipsometer. It is described well by the bilayer ellipsometric model (Fig. 3) consisting of a Si substrate, a 9-nm-thick transition layer constituted by 85% SiC-4*H* and 15% Si, and a 71-nm-thick layer of silicon carbide of the hexagonal polytype SiC-4*H* containing additional carbon atoms at interstices in the form of the HOPG phase with a 5-nm roughness. We suggest that these are the remainder of

the dilatation dipoles located in a layer of about the same thickness. As a result, the SiC/Si (111) samples exhibit pronounced optical-constant anisotropy.

Figure 4 shows the Raman spectrum of the SiC layer of the SiC/Si (111) sample obtained with a WITec alpha300 R confocal Raman microscope after subtracting the Si-substrate signal. This procedure is required because the SiC LO line and the Si second-order line positions almost coincide and should be separated. One can clearly see the TA line characteristic of only anisotropic hexagonal SiC polytypes. In this case, the polytype cannot be established reliably because of the small SiC thickness and, consequently, low intensity of the lines.

4. CONCLUSIONS

Thus, in the proposed mechanism of SiC growth in the substrate bulk, first point defects, specifically C atoms at interstices and silicon vacancies, form during the course of the chemical reaction. It should be emphasized that the CO molecule actively diffuses in Si, but after losing an oxygen atom, the remaining C atom is almost immobile. These point defects strongly attract one another with the formation of relatively stable objects, dilatation dipoles. The latter induce long-range elastic-stress fields, which interact with the forming SiC molecules and ensure the effective relaxation of elastic stresses induced by SiC molecules. In the ideal case, all elastic stresses of ~1.5 GPa can relax on account of dipoles only. In the traditional epitaxial growth of a film, the elastic stresses are larger by a factor of about 4 and can relax only due to the formation of lattice and crack misfit dislocations. After the breaking of the dipoles and the formation of SiC, some fraction of C atoms remains in the SiC (~5%), which substantially affects such properties of SiC as the optical constants, conductivity, and even the polytype.

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