

Topochemical Synthesis of Epitaxial Silicon Carbide on Silicon

Andrey V. Osipov, Sergey A. Kukushkin, Andrey V. Luk'yanov

Abstract—A method is developed for the solid-phase synthesis of epitaxial layers when the substrate itself is involved into a topochemical reaction and the reaction product grows in the interior of substrate layer. It opens up new possibilities for the relaxation of the elastic energy due to the attraction of point defects formed during the topochemical reaction in anisotropic media. The presented method of silicon carbide (SiC) formation employs a topochemical reaction between the single-crystalline silicon (Si) substrate and gaseous carbon monoxide (CO). The corresponding theory of interaction of point dilatation centers in anisotropic crystals is developed. It is eliminated that the most advantageous location of the point defects is the direction (111) in crystals with cubic symmetry. The single-crystal SiC films with the thickness up to 200 nm have been grown on Si (111) substrates owing to the topochemical reaction with CO. Grown high-quality single-crystal SiC films do not contain misfit dislocations despite the huge lattice mismatch value of ~20%. Also the possibility of growing of thick wide-gap semiconductor films on these templates SiC/Si(111) and, accordingly, its integration into Si electronics, is demonstrated. Finally, the *ab initio* theory of SiC formation due to the topochemical reaction has been developed.

Keywords—Epitaxy, silicon carbide, topochemical reaction, wide-bandgap semiconductors.

I. INTRODUCTION

It is well known the enormous elastic stress appearing during the growth of single crystal films with the lattice parameter strongly differing from the lattice parameter of the substrate does not permit us to obtain high quality epitaxial layers of new wide-gap semiconductors without misfit dislocations. It is believed that the most promising of these are SiC, aluminum nitride (AlN), gallium nitride (GaN), gallium oxide (Ga₂O₃), and some others. Integration of these materials into the Si electronics plays a very important role for the development of several industrial technologies; therefore, it is very important to get epitaxial films of these materials just on Si. However, because of the very large difference in lattice parameters of Si and all the mentioned wide-gap semiconductors, during the epitaxial growth of these materials the stress energy rises. This leads to the appearance of an

enormous number of misfit dislocations in growing films and even to complete film cracking.

In this work, we apply a different relaxation mechanism of the elastic energy for growing dislocation-free heteroepitaxial films. The essence of this approach, which differs from all the modern methods of film growth, is based on the idea of preliminary incorporation of point defects into the crystal lattice of the Si matrix. During the growth of the SiC film on the Si substrate, such defects are the carbon atom placed in the Si interstitial position and the vacancy formed due to the fact that silicon monoxide, SiO, removes one of the Si atoms. If these defects are attracted to each other by the elastic interaction in the Si host, the resulting elastic energy caused by their incorporation into the substrate is much lower than the energy of non-interacting defects.

It is known that topochemical reaction is a chemical transformation, wherein there is at least one solid phase both before and after the transformation [1], and the process of transformation is localized at the interface of initial solid phase (host)—final solid phase (guest). An important subclass of topochemical transformations are those reactions in that both initial and final solid phases are monocrystalline or epitaxial [1]. This subclass is particularly important for the epitaxial growth of semiconductor films. In particular, SiC films were epitaxially grown through the topochemical reaction of a monocrystalline substrate of Si with gaseous CO [2]–[4]. A key distinction of these reactions from the reactions in the liquid or gaseous phases is the formation of point defects in crystals, in particular, vacancy sites, and their direct involvement in the topochemical transformation. Another aspect of topochemical reactions is the elastic stress that may occur at the interface between the host and the guest solid phases. For example, the interaction of point dilatation defects in the intermediate phase of the reaction between Si and CO [5], first, makes the formation of misfit dislocations of lattices inappropriate [4] and, second, ensures the relaxation of the elastic stress in the film. These two facts make the topochemical conversion of particular relevance for the epitaxy of semiconductor films [6].

II. TOPOCHEMICAL REACTION WITH SiC FORMATION

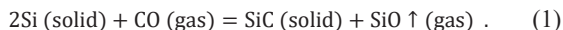
In order to provide the effective usage of a new relaxation mechanism of elastic energy due to the interaction of point defects, we suggest the deposition process of SiC not from the vapor phase but immediately from the matrix of the single crystalline Si substrate due to the chemical reaction between the crystalline Si and gaseous CO [2]–[4]

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We selected this reaction because of the fact that the forming gaseous SiO partially carries the atoms from the Si matrix inducing vacancies in it, while gaseous CO is the source of carbon atoms C arranged in atomic voids of the Si lattice. Both Si vacancies and incorporated C atoms are the dilatation centers in the cubic Si lattice and interact with each other [1]. Fig. 1 illustrates the difference between the regular mechanism of SiC thin film growth and the mechanism of topochemical epitaxy suggested in this work. In the first case, the film grows on the substrate surface by diffusion which results in too large stress energy, whereas, in the last case, the film grows just inside the substrate, and the attraction between C atoms and Si vacancies provide nearly complete relaxation of the stress energy. The merging process of vacancies after film formation results in the pore formation under the SiC film [2].

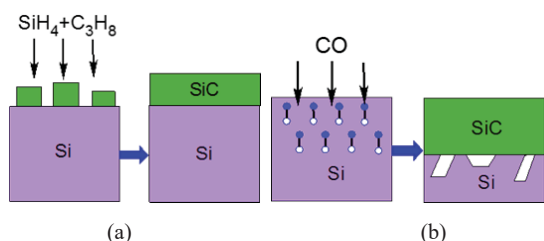


Fig. 1 Schematic pattern of routine SiC thin film growth (a) and the suggested one (b). In the second case dumbbells represent the attraction between different point defects, namely, C atoms and Si vacancies (dilatation dipoles)

The interaction of point defects in cubic and hexagonal crystals has been recently investigated in [7]. In particular, it was proved that, in a cubic crystal like Si, the attraction energy between C atom in the interstitial position and Si vacancy equals to

$$E_{int} = -E_0 \left(\cos^4 \phi_x + \cos^4 \phi_y + \cos^4 \phi_z - \frac{3}{5} \right), \quad (2)$$

where $\cos \phi_i = x_i/r$ are the cosines between the axes x , y , z and a direction of the line connecting the centers of interacting defects. The expression $\cos^4 \phi_x + \cos^4 \phi_y + \cos^4 \phi_z - 3/5$ reaches its minimum, equaled to -0.27, in the direction $\langle 111 \rangle$. Therefore, the direction $\langle 111 \rangle$ is the most energetically favorable for pairs of point defects like C atoms and Si vacancies.

Let us estimate the effect of Si vacancies and dilatation elastic stress on reaction (1). The total energy of point defects in a crystal with cubic symmetry, which is Si, reaches its minimum in the event that vacancies are arranged in pairs in direction $\langle 100 \rangle$ [4]. In this case, the energy of attraction of one pair of defects is

$$E_{int} = -\frac{(c_{11}+2c_{12})\Omega_{Si}}{6\pi} \frac{c_{44}(c_{11}+2c_{12})}{(c_{12}+2c_{44})^2} \frac{c_{12}-c_{11}+2c_{44}}{c_{44}} \quad (3)$$

where c_{11} , c_{12} , and c_{44} are elastic moduli of Si, and Ω_{Si} is the volume occupied by one atom of Si. It has taken into account that the minimum value of the expression with the directing cosines, achieved at $\langle 100 \rangle$ is $-2/5$, the effective volume of a vacancy (the vacancy power) is $(2/3)\Omega_{Si}$, and the distance between vacancies in a pair is the length of bond in Si, that is, $\approx (2/3)\Omega_{Si}$. Substituting the values of the elastic moduli in (7), we obtain $E_{int} \approx -0.74$ eV. An increase in the dilated elastic energy per atom, by the fact that the volume occupied by one Si atom in SiC is 3.4% larger than in Si, is $E_{dil} = 0.2$ eV [4]. Consequently, the change of the thermodynamic potential of (1), associated with the elastic fields around vacancies, is

$$\Delta\Phi = \left(\frac{1}{2}E_{int} + E_{dil} \right) N_A = 16 \frac{\text{kJ}}{\text{mol}}, \quad (4)$$

where N_A is the Avogadro's number. Adding this value to the thermodynamic potential of (1), calculated from thermodynamic data, it is possible to determine the constant of (1), which is the ratio of the equilibrium pressures of SiO and CO. The temperature dependence of the constant of (1), calculated with the correction (3) and without it, is presented in Fig. 2. It is seen that the elastic fields increase the reaction constant by approximately fourfold.

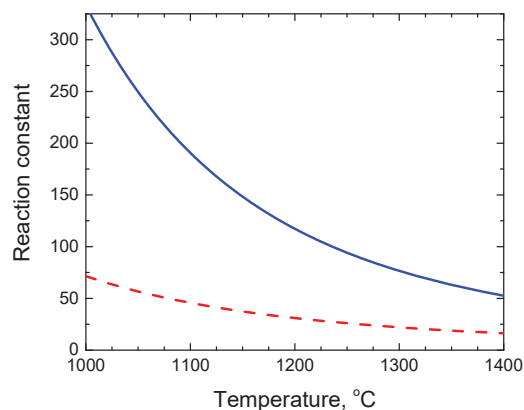


Fig. 2 Temperature dependence of the constants of reaction (1), (solid line) taking into account the anisotropic elastic fields and (dashed line) without them

The pressure-flow phase diagram, describing the composition of the new phase was calculated on the base of previous results. In the actual temperature range of $1000^\circ\text{C} < T < 1400^\circ\text{C}$, only reactions, describing the formation of new phases SiC, SiO₂, and C from the initial phase Si, are taken into account [6]. The boundary of phases SiC and SiC + C + SiO₂ is determined by the equilibrium pressure of CO. The boundary of phases SiC and SiC + SiO₂ is given by the total gas flow in the system, because it determines whether a maximum pressure of SiO obtained by (1) is greater than in the equilibrium pressure [6]. The maximum pressure of SiO was calculated for the case of Si(111) and the conditions of vacuum furnace, in which the experiments on the topochemical transformation of $\text{Si} \rightarrow \text{SiC}$ were carried out [3], [4], by using the kinetic theory of nucleation in this transition

and the constant of (1) (Fig. 3). The results of calculations for two temperature values of 1200 and 1210 °C are presented in Fig. 3. The dependence of the boundary flow on temperature depends on two factors. With increasing temperature, first, the equilibrium value of SiO increases, thereby decreasing the value of flow, and, secondly, the rate of reaction (1) increases since diffusion is accelerated. This factor, on the contrary, increases the value of the boundary flow. In practice, the gas flow through the system is measured in standard cubic centimeters per minute (SCCM), that is, at constant $T = 20$ °C and $p = 1.01$ bar, independent of the temperature and gas pressure in the system. That is why the boundary flow increases nonlinearly with increasing pressure of CO . If the design of furnace, the surface area of Si plates and the direction of their surface, or other parameters change, the value of the boundary flow also changes, as the overall rate of (1), determining the flow of SiO , alters.

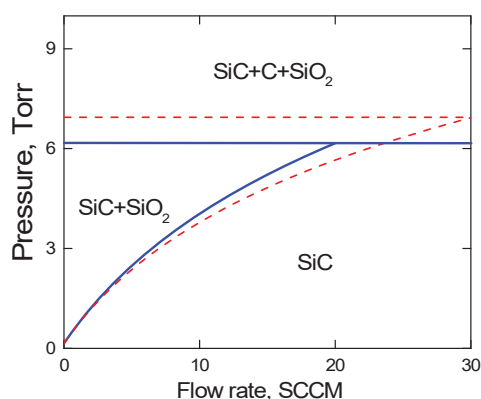


Fig. 3 Pressure–flow phase diagram, describing the composition of the solid phase resulting from the topochemical conversion in a vacuum oven: (solid lines) $T = 1200$ °C, (dashed lines) $T = 1210$ °C

III. EXPERIMENTAL AND RESULTS

To confirm experimentally the suggested relaxation mechanism of elastic energy, Si (111) substrates 35 mm in diameter were held in a vacuum furnace at $T = 1200$ – 1350 °C in the atmosphere of CO at $p = 10$ – 300 Pa for 5–60 min [2]–[4]. A

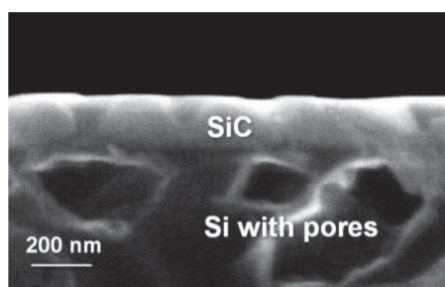


Fig. 4 Microscopic image of the cut of SiC sample grown inside Si by the topochemical reaction with CO . An average thickness of the sample is 180 nm. Si under the layer of SiC contains some amount of pores and voids

SiC film 50–200 nm thick grew inside the Si substrate during this time (Fig. 4). The average value of tensile elastic stresses in SiC films measured by an FLX-2320-S thin film stress measurement system is 0.5 GPa in the absence of lattice misfit and cracks [2]–[4]. Microscopic analysis revealed an almost ideal conjugation of the lattices of Si and SiC [3]. Such a low measured elastic energy with the ideal conjugation of lattices in the absence of misfit dislocations and cracks can be interpreted by the relaxation of elastic stresses due to the ensemble of dilatation dipoles. Monocrystalline nanoscaled layers of SiC of hexagonal polytypes 4H and 6H are obtained on Si for the first time. Best of them has full width at half maximum (FWHM) (ω - θ) in the range 20–40 arcmin at the SiC thickness of 100 nm, and FWHM (ω - 2θ) in the range 5–10 arcmin. At the present time, SiC layers on Si substrates of 6 inch are available [8].

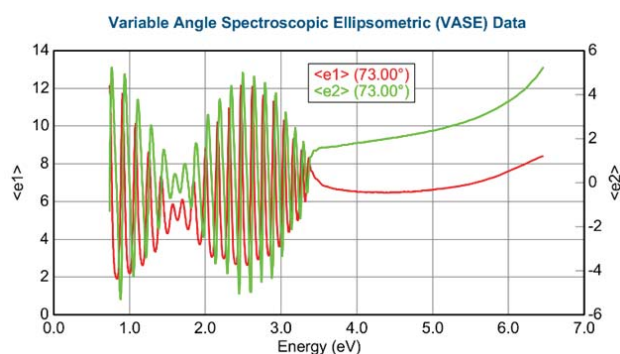


Fig. 5 Ellipsometric spectrum of GaN/SiC/Si (ϵ_1 and ϵ_2 are real and image parts of dielectric function correspondingly). The direct bandgap 3.3 eV of GaN is clear observed. 1 μm epitaxial GaN film is completely transparent up to the bandgap

To find out if it is possible to use SiC/Si samples obtained by the topochemical synthesis as the templates for the further growth of wide-gap semiconductors, we deposited such materials as AlN , GaN , ZnO , CdS , CdSe , Ga_2O_3 by different techniques, mainly, hydride vapour phase epitaxy (HVPE), chemical vapor deposition (CVD), atomic layer epitaxy (ALE), and vacuum evaporation. All of them are epitaxial without polycrystalline phase.

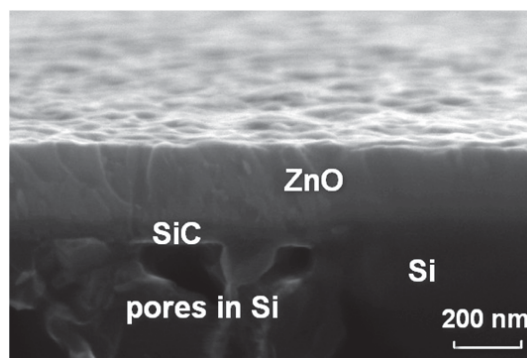


Fig. 6 Microscopic image of the cut of epitaxial ZnO/SiC/Si sample grown by ALE method. An average thickness of ZnO is 250 nm

We have performed a comprehensive analysis of structural, crystallographic, physicochemical, electro-optical, and spectroscopic studies of AlN, GaN and ZnO films growth on the SiC/Si substrates. Figs. 5-7 represents some results of this analysis. A lot of experimental results are also given in reviews [3], [4].

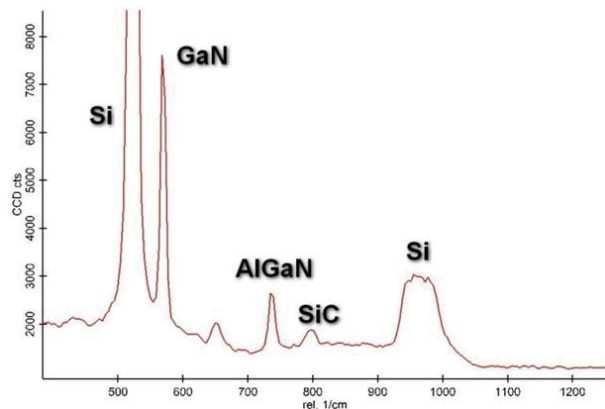


Fig. 7 Raman spectrum of HEMT structure on the base of $n\text{-Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}/\text{AlN}/\text{SiC}/\text{Si}$

IV. CONCLUSION

Thus, a new relaxation mechanism of elastic energy due to the formation of dilatation dipoles is put forward. Usage of this mechanism allowed us to originally grow epitaxial SiC on the Si substrate by the topochemical reaction of the substrate with CO. This relaxation mechanism also permits us to deposit heteroepitaxial films of wide-gap semiconductors (such as SiC, GaN, AlN, AlGaN, ZnO, CdS, CdTe) on Si nearly without misfit dislocations and cracks and having sufficient quality to fabricate many devices for microelectronics and optoelectronics.

REFERENCES

- [1] G. Kaupp, "Prediction of reactivity in solid-state chemistry," in *Making Crystal by Design*, D. Braga and F. Greponi Eds, Wiley, 2007, pp. 87-147.
- [2] S. A. Kukushkin and A. V. Osipov, "A new method for the synthesis of epitaxial layers of silicon carbide on silicon owing to formation of dilatation dipoles," *J. Appl. Phys.*, vol. 113, pp. 024909 1-7, 2013.
- [3] S. A. Kukushkin, A. V. Osipov, and N. A. Feoktistov, "Synthesis of Epitaxial Silicon Carbide Films through the Substitution of Atoms in the Silicon Crystal Lattice: A Review," *Phys. Solid State*, vol. 56, pp.1507-1535, 2014.
- [4] S. A. Kukushkin and A. V. Osipov, "Theory and practice of SiC growth on Si and its applications to wide-gap semiconductor films," *J. Phys. D: Appl. Phys.* 47, 313001 (41p.) (2014).
- [5] S. A. Kukushkin and A. V. Osipov, "First-Order Phase Transition through an Intermediate State," *Phys. Solid State*, vol. 56, pp. 792-799, 2014.
- [6] S. A. Kukushkin and A. V. Osipov, "Phase Equilibrium in the Formation of Silicon Carbide by Topochemical Conversion of Silicon," *Phys. Solid State*, vol. 56, pp. 747-751, 2016.
- [7] S. A. Kukushkin, A. V. Osipov, R. S. Telyatnik, "Elastic Interaction of Point Defects in Cubic and Hexagonal Crystals," *Phys. Solid State*, vol. 57, pp. 971-980, 2016.
- [8] S. A. Kukushkin, A. V. Lukyanov, A. V. Osipov, and N. A. Feoktistov, "Epitaxial Silicon Carbide on a 6 inch Silicon Wafer," *Technical Physics Letters*, vol. 40, No. 1, pp. 36-39, 2014.