ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2012, Vol. 86, No. 7, pp. 1091–1095. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.A. Kuzubov, N.S. Eliseeva, P.O. Krasnov, F.N. Tomilin, A.S. Fedorov, A.V. Tolstaya, 2012, published in Zhurnal Fizicheskoi Khimii, 2012, Vol. 86, No. 7, pp. 1207–1211.

STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Calculating the Energy of Vacancies and Adatoms in a Hexagonal SiC Monolayer

A. A. Kuzubov[a,b,c], N. S. Eliseeva[a], P. O. Krasnov[b,c], F. N. Tomilin[a,b], A. S. Fedorov[b], and A. V. Tolstaya[a]

[a] *Siberian Federal University, Krasnoyarsk, 660041 Russia*

[b] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia*

[c] *Siberian State Technological University, Krasnoyarsk, 660049 Russia*

e-mail: alex_xx@rambler.ru; nataxa1.09@mail.ru

Received July 21, 2011

Abstract—It is noted that the development of semiconductor SiC-electronics is prevented by a low quality of grown silicon carbide single crystals. It is found that structural defects of a substrate penetrating into an epitaxial layer upon subsequent homoepitaxial growth can considerably degrade a device's characteristics. We investigate the effect of the deformation of a hexagonal SiC monolayer on vacancy stability and material properties, and study the processes of silicon and carbon adatom migration over a surface of SiC.

Keywords: silicon carbide, defects, adatoms, density functional method.

DOI: 10.1134/S0036024412070138

INTRODUCTION

Silicon carbide is the only binary compound of the fourth group elements that exists in the solid state. This material has found wide application in semiconductor techniques. Electroluminescent devices, detectors of visible and ultraviolet light [1, 2] and nuclear [3] radiation have been produced on its basis.

Two modifications of the compound are known, α and β. Silicon α-carbide has a laminated structure with a hexagonal crystal lattice that forms a great number of polytypes. Silicon β-carbide has a face-centered cubic lattice [4, 5]. This material can also exist in the form of thin films [4, 6]. The formation of silicon carbide films of one modification or another depends directly on the parameters of synthesis [7].

Like carbon, silicon carbide, having a hexagonal crystal lattice, can exist in the form of separated planes that form so-called two-dimensional silicon carbide (2D SiC) [8, 9]. A number of 2D materials based on hexagonal SiC that differ in their conducting properties have been described in the literature. The plane structure of the SiC monolayer, being periodic in two directions, is a semiconductor. However, the electronic structure of a band cut from the monolayer changes in dependence on the arrangement of peripheral hexagons. Silicon carbide bands with a sutural structure are nonmagnetic semiconductors, while zigzag ones are magnetic conductors [10].

Defects of different types can exist in silicon carbide monolayers with vacation defects and adatoms observed most frequently. In the case of high concentrations, vacation defects are able to change material properties considerably. In the investigated structure, vacancies of one type of atoms (carbon or silicon) and bivacancies of carbon and silicon are simultaneously possible. The stability of monovacancies was calculated in [11, 12]. According to those papers, the energies of formation for monovacancies of carbon and silicon are −2.57 and 6.98 eV, respectively. The obtained results are doubtful because the carbon vacancy turned out to be stable. This was perhaps due to the small size of the cell of the SiC monolayer chosen for our calculations.

A monolayer of hexagonal SiC is grown on a substrate, which should lead to the deformation of its crystal lattice. This could change the thermodynamic stability of vacancies and, consequently, the concentration of vacation defects. The concentration of vacancies is also substantially affected by their recombination with carbon or silicon adatoms. In this case, an important factor is the rate of adatom displacements over the monolayer surface. Earlier, we performed similar works in which graphene and h-BN were selected as objects of investigation [13, 14]. The considerable effect of crystal lattice deformations on the stability of vacancies and material properties was demonstrated in those papers.

In this work, we calculate the energies of vacancies and bivacancies in a monolayer of hexagonal SiC upon uniaxial deformations of the structure (by 1 and 2% along each of the translation vectors) and investigate

Table 1. Value of the magnetic moment, in dependence on the relative strain value (σ) and the type of vacancy (Si, C, SiC)

σ	μ, μ_B
Si	
0.98	1.16
0.99	1.16
1.00	1.18
1.01	1.50
1.02	1.50
C	
0.98	0.00
0.99	0.00
1.00	0.00
1.01	0.00
1.02	0.00
SiC	
0.98	0.00
0.99	0.00
1.00	0.00
1.01	0.00
1.02	1.99

the parameters of the migration of carbon and silicon adatoms over the monolayer's surface.

CALCULATION METHODS

Calculations were performed using the VASP (Vienna ab Initio Simulation Package) program [15–17] within the density functional theory (DFT) formalism [18, 19] on a plane-wave basis and employing Vanderbilt ultrasoft pseudopotentials [20]. Electron–electron interaction was considered within the generalized gradient approximation (GGA) using the exchange-correlation potential PW91. The nudged elastic band method was employed to find the transition state and potential barriers for the hopping of a carbon (silicon) adatom over the surface.

A supercell containing 7 × 7 × 1 silicon carbide unit cells was initially simulated. A vacuum space of 15 Å was inserted along the normal to the planes in order to separate the planes of neighboring cells. This value was fitted based on the assumption that the neighboring planes do not interact at this distance. The reciprocal lattice space in the first Brillouin zone was automatically divided into a network according to the Monkhorst–Pack scheme [21], the number of $\boldsymbol{k}$ points along each of the directions was 2 × 2 × 1. The cutting energy of plane waves used in the calculations was 287 eV. In simulating the investigated structures, we optimized the geometry with a maximum force value of 0.01 eV/atom.

To estimate the stability of a single vacancy, the energies of formation for vacancies $E(V_x)$ were calculated in this work according to the formula

$$E(\mathrm{V_x}) = E_{\mathrm{total}}(\mathrm{Si_{49}C_{49}} + \mathrm{V_x}) - E_{\mathrm{total}}(\mathrm{Si_{49}C_{49}}) + \mu_{\mathrm{x}},$$

where x = Si or C, $E_{\mathrm{total}}(\mathrm{Si_{49}C_{49}} + \mathrm{V_x})$ is the total energy of SiC monolayer with a vacancy, $E_{\mathrm{total}}(\mathrm{Si_{49}C_{49}})$ is the total energy of the monolayer, and μ_{x} is the chemical potential of carbon (silicon).

The chemical potential was calculated using the formula

$$\mu_{\mathrm{Si}} = E_{\mathrm{total}}(\mathrm{SiC}) - {}_{\mathrm{C}},$$

$$\mu_{\mathrm{C}} = E_{\mathrm{total}}(\mathrm{SiC}) - {}_{\mathrm{Si}},$$

where $E_{\mathrm{total}}(\mathrm{SiC})$ is the total energy of the silicon carbide unit cell of the 2H polytype, ${}_{\mathrm{C}}$ is carbon atom energy in the lattice of graphite, ${}_{\mathrm{Si}}$ is the silicon atom energy in the crystal lattice.

The energy of formation for a bivacancy was calculated using the formula

$$(\mathrm{V_{SiC}}) = E_{\mathrm{total}}(\mathrm{Si_{48}C_{48}}) - E_{\mathrm{total}}(\mathrm{Si_{49}C_{49}}) + E_{\mathrm{total}}(\mathrm{SiC}),$$

where $E_{\mathrm{total}}(\mathrm{Si_{48}C_{48}})$ is the total energy of SiC monolayer with a bivacancy, and $E_{\mathrm{total}}(\mathrm{SiC})$ is the total energy of the SiC unit cell.

RESULTS AND DISUSSION

In this work, we studied the influence of defects and deformations on the properties of a SiC monolayer and the stability of defects subjected to deformations. The structures of a SiC monolayer without defects, with a carbon (silicon) vacancy, and with a bivacancy of carbon and silicon were therefore considered. Deformations were simulated by reducing or enlarging the translation vector along one of the axes by 1 and 2%.

It can be seen from our results (Table 1) that a SiC monolayer acquires a magnetic moment in the presence of silicon vacancies. This is due to the presence of cut bonds on carbon atoms surrounding a rather large silicon vacancy. An analogous situation is observed in the presence of a bivacancy, if strong stretching is applied. Upon the formation of a carbon vacancy, the distance between the neighboring silicon atoms is relatively short, giving rise to the appearance of multiple bonds between them. Correspondingly, no magnetic moment is observed in this case, nor in the presence of a bivacancy.

Below, we calculate the formation energies of defects. Their dependences on the relative strain are presented in Fig. 1. According to the plots, the carbon vacancy with the lowest energy of formation is the one

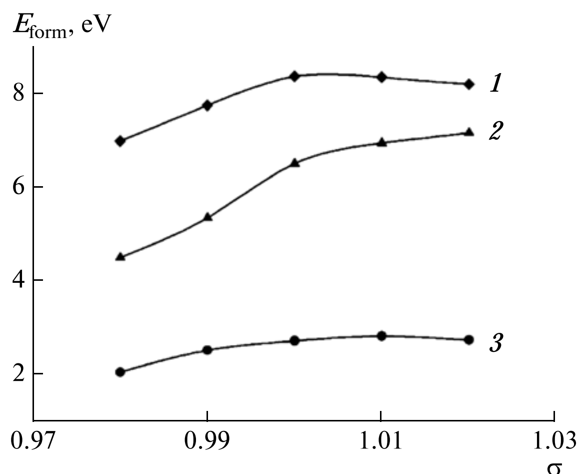

Fig. 1. Dependence of the energies of formation for defects on the relative strain value (σ): (*1*) Si vacancy, (*2*) bivacancy, (*3*) C vacancy.

most stable. The one most unstable is the silicon vacancy stabilized under strong stretching or compression, like the carbon vacancy. In contrast to the silicon vacancy, the bivacancy is stabilized only at high compression. We can explain the high stabilization of a silicon vacancy and a bivacancy upon high compression by the formation of a bond between the carbon atoms, contributing to the reduction of the defect structure energy (Fig. 2).

The concentration of vacancies can be estimated using the formula

$$N(V_x) = \exp(-E(V_x)/kT).$$

The concentration of carbon vacancies with minimal energy of formation is 6.74×10^{-47} at the standard temperature of 298 K. The concentrations of silicon vacancies and bivacancies are considerably lower because they have higher formation energies.

The number of vacancies is affected by the mobility of carbon and silicon adatoms on the monolayer surface and, consequently, by the possibility of their recombination with vacancies. To estimate the probability of these processes, adatom motions were simulated and the energy barriers to their hopping over the surface of the SiC monolayer were calculated.

Their most favorable positions on the surface of SiC monolayer were localized during our studies of the processes of carbon silicon adatom migrations (Fig. 3). The energy of the most favorable position was taken as the reference point, and the adsorption energies at other positions were calculated with respect to it (Table 2).

CONCLUSIONS

We simulated the transition of an adatom between the most favorable equivalent positions, 1-1 for carbon and 5-5 for silicon, respectively. The calculated energy barrier values for an adatom transition were 0.16 eV for

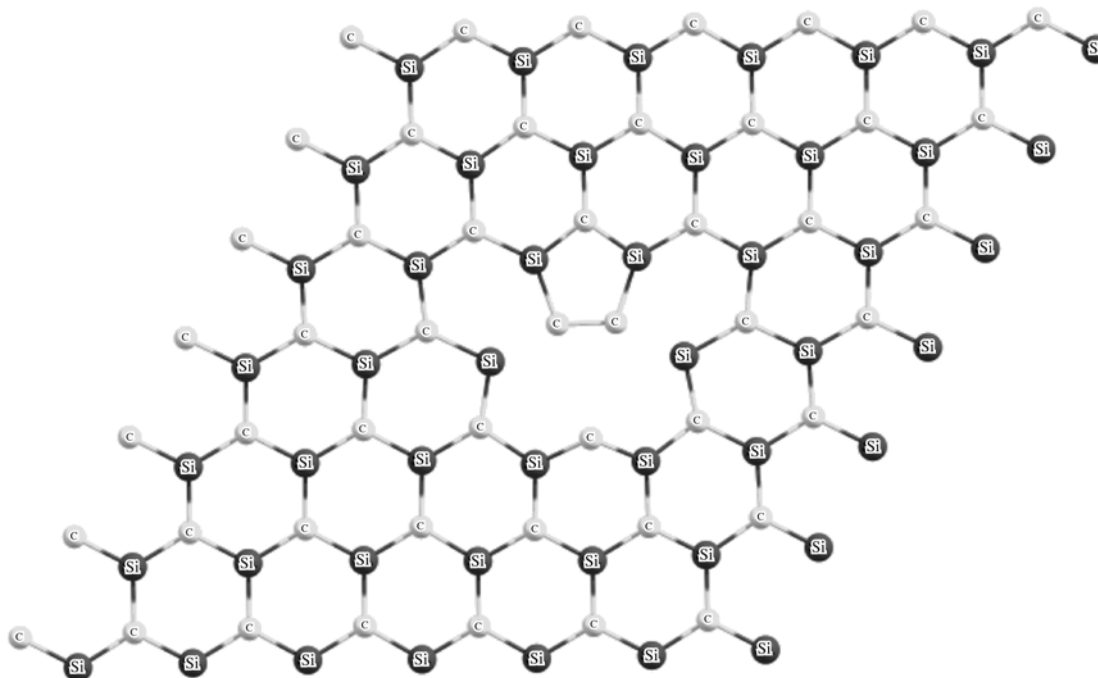

Fig. 2. Structure of a SiC monolayer containing a silicon vacancy.

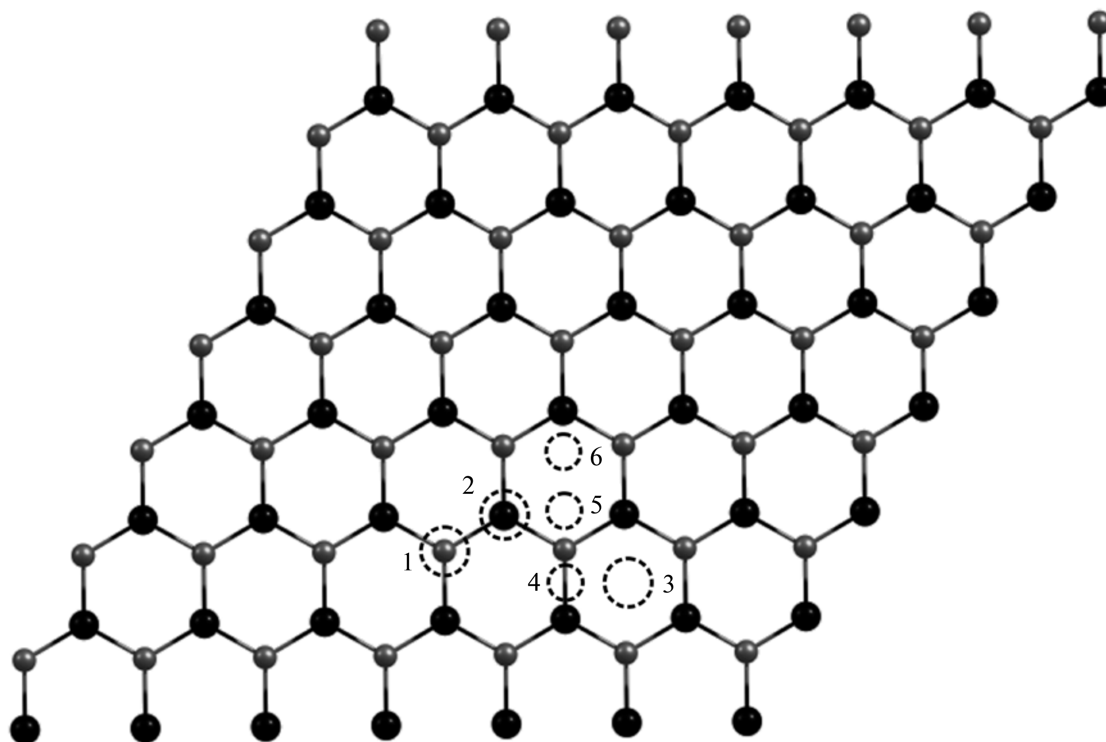

Fig. 3. Adatom positions on the surface of the SiC monolayer (grey atoms are C; black, Si).

silicon and 2.34 eV for carbon. The considerable mobility of the silicon adatom is demonstrated by the rather low value of the energy barrier. Consequently, the probability of the process of its recombination with a vacancy is quite high. The opposite situation is observed for carbon.

Table 2. Dependence of relative adsorption energy (E) on the adatom position (n)

n	E, eV	
	C	Si
1	0.00	0.05
2	0.70[1]	–[4]
3	2.51	1.07
4	0.93[2]	0.03[3]
5	0.04	0.00
6	1.39	0.17

[1] Shifts to position 4.
[2] Displaces from the bond center to carbon.
[3] Shifts to position 1.
[4] Deviates considerably from the initial arrangement.

It can seen on the basis of our results that carbon vacancies are the ones most thermodynamically stable, while a silicon adatom would recombine with a vacancy so far as is possible, due to its high mobility. So, the studied material contains mainly carbon vacancies with concentration of 6.74×10^{-47} as estimated in this work.

ACKNOWLEDGMENTS

The authors are grateful to the Institute of Computer Simulation (Krasnoyarsk), the Joint Supercomputer Center (Moscow), and the computer center of Siberian Federal University (Krasnoyarsk) for allowing us to use the computer clusters on which all our calculations were performed.

REFERENCES

1. S. L. Shi, S. J. Xu, X. J. Wang, and G. H. Chen, Thin Solid Films **495**, 404 (2006).
2. J. Y. Fan, X. L. Wu, and P. K. Chu, Progress Mater. Sci. **51**, 983 (2006).
3. E. V. Kalinina, Semiconductors **41**, 745 (2007).
4. V. Yu. Aristov, Phys. Usp. **44**, 761 (2001).
5. C. H. Park, Byoung-Ho Cheong, Keun-Ho Lee, and K. J. Chang, Phys. Rev. B **49**, 4485 (1994).
6. V. I. Ivashchenko, G. V. Rusakova, V. I. Shevchenko, and A. S. Klymenko, Appl. Surf. Sci. **184**, 214 (2001).

7. V. Yu. Kulikovskii, V. Vorlichek, and P. Bogach, Nanostrukt. Materialoved., No. 1, 42 (2008).
8. B. Baumeier, P. Kruger, and J. Pollmann, Phys. Rev. B **76**, 085407 (2007).
9. H. Sahin, S. Cahangirov, M. Topsakal, et al., Phys. Rev. B **80**, 155453 (2009).
10. Lian Sun, Yafei Li, Zhenyu Li, et al., J. Chem. Phys. **129**, 174114 (2008).
11. Xiujie He, Tao He, Zhenhai Wang, and Mingwen Zhao, Physica E **42**, 2451 (2010).
12. E. Bekaroglu, M. Topsakal, S. Cahangirov, and S. Ciraci, Phys. Rev. B **81**, 075433 (2010).
13. A. S. Fedorov, Yu. E. Anan'eva, A. A. Kuzubov, et al., J. Exp. Theor. Phys. **112**, 820 (2011).
14. A. A. Kuzubov, M. V. Serzhantova, and A. S. Fedorov, JETP Lett. **93**, 335 (2011).
15. G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
16. G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
17. G. Kresse and J. Hafner, Phys. Rev. B **54**, 11169 (1996).
18. P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).
19. W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133 (1965).
20. D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
21. H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).