

STRUCTURE OF MATTER
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Possibility of a 2D SiC Monolayer Formation on Mg(0001) and MgO(111) Substrates

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Abstract—The geometrical characteristics of a 2D SiC monolayer on Mg(0001) and MgO(111) plates regarded as potential materials for growing two-dimensional silicon carbide were studied. The most favorable positions of the atoms of 2D SiC on the substrates were determined. In the 2D SiC/Mg(0001) system, unlike in 2D SiC/MgO(111), the deviation of the carbon atom from the silicon carbide monolayer was insignificant (0.08 Å). Consequently, magnesium can be used as a substrate for growing two-dimensional silicon carbide. The use of MgO(111) is not recommended because of a significant distortion of the 2D SiC surface.

Keywords: silicon carbide monolayer, density functional theory.

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INTRODUCTION

Silicon carbide has two modifications: α , which has a layered structure with a hexagonal crystal lattice and forms a large number of polytypes, and β , which has a face-centered cubic lattice [1, 2]. This material can also be synthesized in the form of thin films [1, 3]. Like carbon, silicon carbide with a hexagonal crystal lattice can exist as individual planes, forming so-called two-dimensional silicon carbide (2D SiC) [4, 5]. In view of its unique properties, SiC is widely used in nanoelectronics. Two-dimensional silicon carbide has the advantage of being direct-band conductor compared to other polytypes. Consequently, this is a promising optoelectronic material which is competitive with GaAs and GaN semiconductors.

2D SiC was predicted in theoretical studies of single-walled SiC nanotubes obtained by rolling a monolayer [6–8]; it has not yet been synthesized. Nevertheless, the phonon frequencies were calculated in a the-

oretical study reported in [9], and the results indicated that the SiC monolayer is stable. Therefore, two-dimensional silicon carbide can be obtained experimentally.

Epitaxy seems to be the most attractive technique for its preparation. It is readily performed if the difference between the lattice constants of the substrate and the synthesized material does not exceed 10%. Otherwise, the build-up material will have many defects; in the case of silicon carbide, this can lead to growth of a film of another polytype. Since the difference between the lattice constants of a Mg(0001) metallic plate and those of 2D SiC is less than 0.03% (Fig. 1), we can assume that this material can be used as substrate for growing a two-dimensional silicon carbide monolayer with a minimum number of defects.

Using magnesium as a substrate for growing a 2D SiC monolayer, however, involves some difficulties. The most widespread technique for obtaining thin

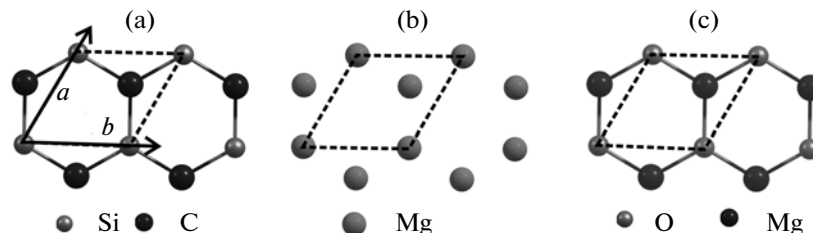


Fig. 1. 2D SiC, Mg, and Mg(111) unit cells; the subindices t and e denote the theoretical and experimental values [22, 23]; $a_t = b_t =$ (a) 3.0472, (b) 3.1286, and (c) 2.9267 Å; $a_e = b_e =$ (b) 3.2093 and (c) 2.9819 Å.

films of silicon carbide of other polytypes is CVD from gas mixtures of silane and hydrocarbons and from various organosilicon compounds (e.g., methyltrichlorosilane or hexamethyldisilazane) in a flow of hydrogen or argon [10]. The disadvantages of this method are the use of toxic volatile organosilicon compounds and high temperatures comparable to the melting temperature of magnesium. Growth of the production of silicon carbide-based devices has stimulated the search for more economical and ecologically safe technologies for the fabrication of SiC layers. One of such methods can be the preparation of films by laser sputtering.

Thin silicon carbide films of other hexagonal polytypes are obtained by vacuum laser ablation; the substrate temperature then is 250–500°C [11]. The melting point of magnesium is 650°C, which makes it possible to use it as a substrate for preparing hexagonal silicon carbide monolayers.

The possibility of magnesium silicides and carbides forming during monolayer growth should be taken into account. Magnesium carbides MgC_2 and Mg_2C_3 , however, cannot be obtained by the reaction of carbon and metal because these compounds decompose above 500°C (MgC_2) and 700°C (Mg_2C_3) [12]. Magnesium silicide films with epitaxially orientated grains and low relief (Mg_2Si) are obtained by solid phase epitaxy ($T = 550^\circ\text{C}$) from a magnesium–silicon mixture on magnesium silicide seed islands [13, 14]. Thick polycrystalline Mg_2Si films with a stoichiometric composition and a forbidden gap of 0.76 eV were formed on a silicon substrate by molecular-beam epitaxy at 200°C [15]. The substrate temperature could not be increased during film growth because the coefficient of accommodation of magnesium to silicon decreased to zero.

Consequently, it may be conjectured that growth of 2D SiC on a magnesium substrate will not be complicated by the formation of magnesium silicides and carbides if definite temperature conditions of growth were selected. The substrate temperature during vacuum laser ablation for growing silicon carbide is 250–500°C [11] and satisfies the temperature conditions under which the formation of magnesium silicides and carbides is unlikely.

The main idea of this study was theoretical investigation of the 2D SiC system on a Mg(0001) plate, which is potential material for a substrate used to grow a monolayer. For comparison, we considered the 2D SiC/MgO(111) system because magnesium oxide is already used as a substrate for growing other polytypes of hexagonal silicon carbide.

CALCULATION PROCEDURE

The objects were modeled using the VASP (Vienna Ab-initio Simulation Package) quantum-chemical package [16–18] within the density functional theory (DFT) formalism [19, 20] based on the local density approximation (LDA). The calculations used the

plane wave basis set and Vanderbilt ultrasoft pseudo-potentials [21].

The plane wave trimming energy in the calculations was 287 eV. All the structures were modeled with geometry optimization with the maximum forces 0.01 eV/Å.

The hexagonal unit cells were modeled at the first stage for 2D SiC and magnesium (Fig. 1). The cubic unit cell was calculated at the first stage for the MgO(111) plate. In these calculations,

the reciprocal space in the first Brillouin zone was automatically partitioned into a Monkhorst–Pack grid [24], the k -point mesh being of $12 \times 12 \times 12$ along each direction.

Then the geometry optimization of the plates was performed. A three-dimensional unit cell was translated along the (0001) direction of a regular crystal to obtain a Mg plate and along the (111) direction to obtain a MgO plate. A vacuum space was set along the normal to the surface. Its length was 15 Å; this value was chosen based on the assumption that the neighboring surfaces will not interact with each other. The number of layers was 8 in the Mg(0001) plate (the plate thickness was 17.7120 Å) and 10 in the MgO(111) plate (10.47281 Å). This choice was dictated by the fact that the properties of the plates change insignificantly when every next layer is added to the system.

When the theoretical ($\rho_{\text{Mg}} = 1.86 \text{ g/cm}^3$, $\rho_{\text{MgO}} = 3.73 \text{ g/cm}^3$) and experimental ($\rho_{\text{Mg}} = 1.74 \text{ g/cm}^3$, $\rho_{\text{MgO}} = 3.58 \text{ g/cm}^3$) densities of Mg and MgO were compared, the error was 7 and 4%, respectively. In addition, we calculated the surface energies and compared the results with the experimental data. For the Mg(0001) plate, the calculated surface energy was 0.037 eV/Å, while the experimental surface energy was 0.047 eV/Å [25]. The reciprocal space in the first Brillouin zone was automatically divided into the Monkhorst–Pack grid, the number of k -points being $12 \times 12 \times 1$ along each direction.

To determine the most favorable position of 2D SiC on the Mg and MgO metal plates, we considered the structures with different configurations of the silicon carbide monolayer (Fig. 2, Tables 1 and 2). For MgO, the oxygen and magnesium surfaces were considered. The energy of binding between the substrate and SiC monolayer surfaces was calculated from the total energies of the systems:

$$E = E_{\text{total}} - E_{\text{plate}} - E_{\text{SiC}}, \quad (1)$$

where E_{total} is the total energy of the system, E_{plate} is the energy of the substrate (Mg(0001), or Zr(0001), or MgO(111) metal plate), and E_{SiC} is the energy of 2D SiC. The calculated data are presented in Tables 1 and 2.

RESULTS AND DISCUSSION

According to Tables 1 and 2, the most favorable configurations for system with Mg(0001) are (C-top,

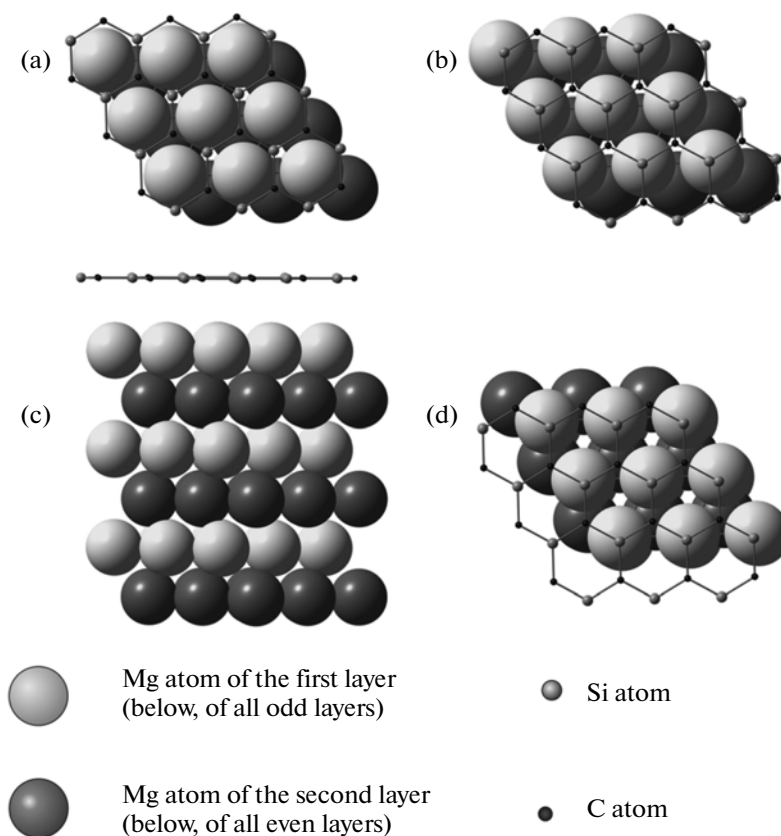


Fig. 2. Different configurations of the SiC monolayer on the Mg(0001) metallic substrate: (a) Si-fcc, C-hcp; (b) Si-top; (c) Si-fcc, C-hcp, D-fcc, side view; and (d) Si-top.

Si-hcp), (Si-top, C-fcc), and (C-top, Si-fcc). The difference in energy between the most and least favorable configurations of the monolayer on the magnesium substrate was >0.3 eV, which corresponds to the temperature ~ 3000 K. Less favorable configurations thus cannot form during the synthesis of a monolayer on a

magnesium substrate by vacuum laser ablation at the characteristic temperature of synthesis $250\text{--}500^\circ\text{C}$.

The geometry of the 2D SiC/Mg(0001) system does not differ considerably from that of individual components (monolayer, plate). Therefore, the difference between the vibration energies of the system and its components in the given temperature range will be insignificant. Since this difference determines the temperature contribution to the binding energy, we can conclude that for the most favorable states, the contributions will be relatively small compared with the electron contributions to the binding energy.

Note that the deviation of the carbon atom from the plane of the silicon carbide monolayer was insignificant for the 2D SiC/Mg(0001) system (0.08 Å). Consequently, magnesium can be recommended as a substrate material for growing a silicon carbide monolayer because a planar monolayer (exactly 2D SiC) is formed.

According to Table 2, magnesium oxide is not recommended as a substrate material for growing 2D SiC because of strong interaction of the monolayer with the surface (especially oxygen surface), leading to its substantial distortion and preparation of another hexagonal polytype.

Table 1. Structural parameters of the 2D SiC/Mg(0001) system and binding energies for different positions of the SiC monolayer on the substrate

Configuration	$R_{\text{Mg}(0001)}$, Å	$R_{\text{Si-C}}$, Å	l_{C} , Å	$-E$, eV
C-top, Si-hcp	2.3106	1.8082	0.0810	0.4749
Si-top, C-hcp	3.3541	1.8066	0.0290	0.0399
C-fcc, Si-hcp	2.4060	1.8079	0.0770	0.1528
Si-fcc, C-hcp	2.4490	1.8081	0.0820	0.1185
C-top, Si-fcc	2.3189	1.8080	0.0800	0.4606
Si-top, C-fcc	2.3189	1.8081	0.0810	0.4749
Si-C monolayer	—	1.7593	0.004	—

Note: $R_{\text{Mg}(0001)}$ is the distance from the surface of Mg(0001) to the nearest atom in the monolayer, Å; $R_{\text{Si-C}}$ is the Si-C distance; and l_{C} is the deviation of the carbon atom from the plane.

Table 2. Structural parameters of the 2D SiC/MgO(111) system and binding energies for different positions of the SiC monolayer (magnesium/oxygen surfaces) on the substrate

Configuration	$R_{\text{Mg}(0001)}$, Å	$R_{\text{Si-C}}$, Å	l_{Si} , Å	$-E$, eV
C-top, Si-hcp	2.2831/1.5810	1.6897/1.7589	0.0390/0.6870	1.2819/5.8292
Si-top, C-hcp	1.4130/1.6900	1.8426/1.7568	1.0170/0.4870	2.6796/11.8932
C-fcc, Si-hcp	2.2960/1.6280	1.6897/1.7558	0.0260/0.1600	1.2819/5.8234
Si-fcc, C-hcp	2.4160/1.6870	1.7376/1.7545	0.3020/0.4740	1.5549/11.9835
C-top, Si-fcc	2.3000/1.8717	1.6912/1.7380	0.0140/0.4130	0.3840/4.2384
Si-top, C-fcc	2.7169/1.9060	1.6964/1.7371	0.1550/0.3700	0.5176/3.9428

Note: $R_{\text{MgO}(111)}$ is the distance from the surface of MgO(111) to the nearest atom in the monolayer, Å; $R_{\text{Si-C}}$ is the Si–C distance; and l_{Si} is the deviation of the silicon atom from the plane.

Thus the results of this study showed that the most favorable configurations in the 2D SiC/Mg(0001) system were (C-top, Si-hcp) and (Si-top, C-fcc). The deviation of the carbon atom from the plane of the silicon carbide monolayer in this system was insignificant. The formation of magnesium silicides and carbides is unlikely, due to which 2D SiC can be grown on a magnesium substrate.

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REFERENCES

- V. Yu. Aristov, Usp. Fiz. Nauk, No. 5, 801 (2001) [Phys. Usp. **44**, 761 (2001)].
- C. H. Park, Byoung-Ho Cheong, Keun-Ho Lee, et al., Phys. Rev. B **49**, 4485 (1994).
- V. I. Ivashchenko, G. V. Rusakova, V. I. Shevchenko, et al., Appl. Surf. Sci. **184**, 214 (2001).
- B. Baumeier, P. Krüger, and J. Pollmann, Phys. Rev. B **76**, 085407 (2007).
- H. Sahin, S. Cahangirov, M. Topsakal, et al., Phys. Rev. B **80**, 155453 (2009).
- A. Mavrandonakis, G. E. Froudakis, M. Schnell, et al., Nano Lett. **3**, 1481 (2003).
- M. Menon, E. Richter, A. Mavrandonakis, et al., Phys. Rev. B **69**, 115322 (2004).
- M. W. Zhao, Y. Y. Xia, F. Li, et al., Phys. Rev. B **71**, 085312 (2005).
- E. Bekaroglu, M. Topsakal, S. Cahangirov, et al., Phys. Rev. B **81**, 075433 (2010).
- A. A. Zelenin, M. L. Korogodskii, and A. A. Lebedev, Fiz. Tekh. Poluprovodn., No. 10, 1169 (2001) [Semiconductors **35**, 1117 (2012)].
- A. S. Gusev, C. M. Ryndya, N. I. Kargin, et al., Poverkhnost', No. 5, 18 (2010) [J. Surf. Invest. **4**, 374 (2010)].
- K. Pigon, Helv. Chim. Acta **44**, 30 (1961).
- N. G. Galkin, S. V. Vavanova, A. M. Maslov, et al., Thin Solid Films **515**, 8230 (2007).
- S. V. Vavanova, N. G. Galkin, K. N. Galkin, et al., Vestn. DVO RAN, No. 6, 85 (2005).
- J. E. Mahan, A. Vantomme, G. Lagouche, et al., Phys. Rev. B **54**, 16965 (1996).
- G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
- G. Kresse and J. Hafner, Phys. Rev. B **54**, 11169 (1996).
- P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).
- W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133 (1965).
- D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- S. Sasaki, K. Fujino, and Y. Takeuchi, Proc. Jpn. Acad. **55**, 43 (1979).
- E. R. Jette and F. Foote, J. Chem. Phys. **3**, 605 (1935).
- H. Sung, G. Erkens, and J. Funken, Surf. Coat. Technol. **54–55**, 541 (1992).
- H. J. Gotsis, M. J. Mehl, and D. A. Papaconstantopoulos, Phys. Rev. B **65**, 134101 (2002).

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