Charge properties and stability of 2D silicon carbide

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Abstract. In this paper, low-dimensional silicon carbide (SiC) obtained on the basis of SiC monolayers with a stoichiometric composition of 1:1 and a number of layers from 1 to 3 has been studied based on the quantum-chemical analysis of the structure and charge properties of this material. The redistribution of the electron density registered in a stack of graphene-like SiC layers allowed us to propose a method of identification of low-dimensional silicon carbide structures. The analysis of geometric and energy parameters made it possible to suggest the sustainable existence of two structural types of 2D-SiC, which differ in the way they are positioned within the layers. As a result of the analysis of the effective charge magnitude, the correlation between this parameter and the geometry of the optimized structure was established. It is proved that taking into account the charge properties of low-dimensional silicon carbide makes it possible to trace the structural changes in the system, identify a specific allotrope, and establish the order of the monolayers.

1. Introduction

The experimental obtaining of graphene has stimulated interest in the study of graphene-like atomically thin materials [1]. To date, a wide range of stable low-dimensional structures has been obtained experimentally. Two classes of materials can be distinguished among them: 2D structures based on precursors with the van der Waals type of the interlayer interaction, which include, for example, hexagonal boron nitride, graphene, transition metal dichalcogenides [2], and covalent interlayer bonding such as 2D allotropes of elements of the 4th group and their compounds (silicene, germanene, stanene, etc.) [3].

Among the low-dimensional structures with a covalent type of interlayer interaction, silicon carbide is of particular interest. Its precursor has a number of unique electrophysical properties: a large band gap, a wide temperature range of operation, high mechanical and chemical strength, and hardness to radiation exposure [4]. At the same time, one of the factors hindering the development of traditional electronics based on silicon carbide is polytypism. In the case of structures with reduced dimensionality, this means the presence of structure-dependent properties of low-dimensional allotropes. Therefore, a challenging task is to study the structural stability and properties of various topological forms of 2D phases of silicon carbide. One of the key areas of research performed in this field is the prediction of the structure and properties of atomically thin crystals with different layer stoichiometry, structure of a unit cell, number of layers, and their mutual arrangement [5, 6].

Earlier, we carried out a comparative theoretical and experimental study of the formation of low-dimensional allotropes of layered homoatomic materials with different types of interlayer interaction –
antimony and graphite. This proves that a characteristic feature of layered materials with a covalent type of interlayer interaction is the formation of 2D allotropes with an effective charge on the outer bilayers, which is caused by the electron density redistribution in the bilayer under conditions of a limited number and size of layers [7].

A quantum-chemical study of 2D silicon carbide allotropes (a binary compound with a covalent type of interlayer interaction) shows the possibility of forming a number of stable allotropic modifications with a band gap from 1.3 to 2.5 eV and different band structures depending on the number and mutual arrangement of layers in the structure [8].

The purpose of this work is to study the electron density redistribution in 2D silicon carbide during the structural evolution of its stable allotropic modifications.

2. Research methods

Our objects of study are the multilayer structures based on atomically thin silicon carbide, differing by the mutual arrangement and number of layers, similar to those proposed earlier [8]. Each layer of such a structure is a graphene sublattice composed of successively alternating silicon and carbon atoms. The following modifications are considered (the structure is presented before the geometry optimization):

- \( \text{AAAA} \), with the same configuration of atoms in all layers;
- \( \text{A\bar{A\bar{A}}} \), with “inversion” of atoms in adjacent layers;
- \( \text{A\bar{A\bar{A}}} \), derived by moving the middle layer in \( \text{A\bar{A\bar{A}}} \) along one of the translation vectors by the bond length \( R_{Sl-C} \);
- \( \text{AA'A} \), derived by moving the middle layer in \( \text{AAA} \) along one of the translation vectors by the bond length \( R_{Sl-C} \);
- \( \text{ABA} \), derived by moving the middle layer in \( \text{AAA} \) diagonally to the translation vectors by the bond length \( R_{Sl-C} \);
- \( \text{ABA} \), derived by moving the middle layer in \( \text{AAA} \) diagonally to the translation vectors by the bond length \( R_{Sl-C} \).

The electronic structure of 2D allotropes of silicon carbide was studied by the electron density functional theory (DFT) in the LSDA approximation using a 3-21G valence-split basis and a number of k-points of 80,000. This method is widely used for the simulation of multilayer 2D nanomaterials including multi-layer graphene [9].

In order to study the distribution of charges and their correlation with the structure and properties of 2D SiC, the following characteristics were calculated after optimizing the geometry of the structures (table 1): the intralayer bond lengths between silicon and carbon atoms (\( R_{Sl-C} \)), the interlayer distance (\( R_{sh} \)), the reduced bond energy (\( E_b \)), the interlayer bond energy (\( E_{bsh} \)), the band gap (\( E_g \)), the effective atomic charge (\( Q_b \)), and the effective layer charge (\( Q_{bsh} \)).

The calculation of energy characteristics is based on the results of quantum-chemical modeling of the electronic structure of 2D SiC allotropes. The obtained data correlate with experimental data (for polytype \( \text{A\bar{A}\bar{A}} \), \( R_{Sl-C} = 1.78 \div 1.89 \text{ Å}, R_{sh} \approx 3.09 \text{ Å}, E_g \approx 2.58 \text{ eV} \) [10] and theoretical works (monolayer SiC: \( R_{Sl-C} \approx 1.8 \text{ Å}, E_g \approx 2 \text{ eV}, E_{bsh} \approx 8.4 \text{ eV/atom} \) [11, 12]. This confirms the validity of the methods and approaches used. To estimate the charge characteristics of the structures, we used the Mulliken population analysis [13]. This method allows evaluating the qualitative difference in the charge distribution in the material. At the same time, to analyze quantitative characteristics, it is necessary to use more accurate methods for calculating the population of orbitals.

Silicon carbide allotropes, graphene, and multigraphene were chosen as model structures for quantitative analysis of the energy characteristics of 2D structures, as they are the most studied low-dimensional materials.
3. Results and discussion

According to the simulation results for a silicon carbide monolayer, it was found that the length of the chemical bond \( R_{Si-C} \) is 1.80 Å, which is by 0.38 Å longer than the carbon-carbon bond length in graphene. This is due to the presence of a heavier electron core in the shielded core of the silicon, which ultimately results in a weaker bond than C–C.

This feature of the electronic structure is also observed when, along with a strong covalent bond, a weak ionic one is formed, due to the predominant localization of the valence electrons at the carbon nucleus and the formation of an unlikely atomic charge of 1.315 \( \epsilon \) (\( \epsilon \) is the elementary charge). In this case, the charge is a statistical quantity and is determined by the probability of finding an electron in the vicinity of an atom. Such an approach is often used in quantum-chemical calculations for the analysis of kinetic phenomena in complex organic systems, where the formation of charged states can be interpreted as a local electron density redistribution and an increased reactivity of a section of a molecule [14–16].

Stratified A\( \overline{A} \)\( \overline{A} \): polytype growth is accompanied by a non-symmetric redistribution of the electron density. In this case, a monotonous increase in the specific and interlayer bond energy is observed. The analysis of charge properties of a three-layer structure showed the formation of an effective positive charge \( Q_{bsb-ABA} = + 0.077 \epsilon \) at the outer edges. Thus, the formation of a two-layer configuration is accompanied by a partial hybridization of \( p_z \)-orbitals of monolayer atoms and the formation of an additional covalent bond. Considering that the interlayer bond length in such a structure is less characteristic of \( sp^2 \) condition of 3D-SiC, it can be assumed that the degree of hybridization of the structure is intermediate between \( sp^2 \) and \( sp^3 \) conditions. The symmetrical arrangement of atoms in a two-layer structure explains the neutral charge of the layers. Adding the third layer in such a topology leads to localization of \( p_z \)-orbitals of the middle layer, localization of distributed coupling in the center of the structure and the formation of a positive effective charge.

For the structures of ABA type, the formation of an effective positive charge on the outer faces of the three-layer phase is also characteristic, and the charge in this case is \( Q_{bsb-ABA} = + 0.03 \epsilon \). The electron density distribution for a two-layer configuration ABA is similar to A\( \overline{A} \)\( \overline{A} \) and is characterized by an almost neutral effective charge on the surface \( Q_{bsb-AB} \sim 0.001 \epsilon \). The formation of an interlayer bond in ABA occurs at the expense of half of the atoms (a carbon atom of the middle layer and a silicon atom of the external one), while the other half is localized in the center of hexagons formed by atoms of the neighboring layers and plays an indirect role in the formation of interlayer bonding. Therefore, the ABA allotrope is characterized by almost half of the interlayer energy \( E_{bsb} = 0.156 \) eV and large interlayer distances comparable to the long bond in 3D-SiC. A further growth of the structure leads to localization of partially hybridized \( p_z \)-orbitals of the middle layer, localization of valence \( p_z \)-electrons in the center of the structure and the formation of a positive effective charge on the surface. The surface charge ratio in the structures \( Q_{bsb-ABA}/Q_{bsb-ABA} > 2 \), which is related to the contribution of delocalized \( p_z \)-orbitals of atoms located in the centers of hexagons formed by atoms of adjacent layers.

A consistent increase in the number of layers \( n \) up to 2 and 3 in the A\( \overline{A} \) configuration is accompanied by the transformation of the original structure geometry to the topological ABA type and non-identical evolution of charge properties. Therefore, the two-layer A\( \overline{A} \) configuration characterized by the opposite effective charge of monolayers \( Q_{bsb-ABA} = \pm 0.0125 \epsilon \) and the formation of a three-layer A\( \overline{A} \) phase is accompanied by the formation of the negative effective charge \( Q_{bsb-AAA} = - 0.014 \epsilon \). The negative charge is observed due to the inversion of A\( \overline{A} \) polytype atoms in relation to ABA. As a result, the formation of covalent interlayer bonds in the allotrope occurs at the expense of the silicon atoms of the inner layer. Therefore, the outer layers acquire the negative effective charge as a result of the greater electronegativity of carbon atoms. Since the other characteristics of these two types are identical, we can conclude that taking into account the charge properties allows us to determine the order of monolayers.
Table 1. Electrophysical properties of 2D allotropes of silicon carbide depending on the number and configuration of layers in comparison with 2D allotropes of antimony (R is the bond length between adjacent atoms within the layer; where $R_{sh}$ is the interlayer distance, $E_b$ is the reduced bond energy; $E_{bsh}$ is the reduced interplanar bond energy; $Q_{bsh1}$, $Q_{bsh2}$, $Q_{bsh3}$ are the effective charges per atom in the corresponding layer).

| Structure | $R$   | $R_{sh}$ | $Q_{bsh1}$ | $Q_{bsh2}$ | $Q_{bsh3}$ | $E_b$   | $E_{bsh}$ |
|-----------|-------|----------|------------|------------|------------|---------|----------|
| $A$       | 1.805 | -        | 0          | -          | -          | 8.322   | -        |
| $AA$      | 1.804 | 3.380    | 0.012      | -0.012     | -          | 8.399   | 0.154    |
| $AAA$     | 1.804 | 3.190    | -0.014     | 0.028      | -0.014     | 8.434   | 0.224    |
| $A\overline{A}$ | 1.846 | 2.200    | 0          | 0          | -          | 8.444   | 0.242    |
| $A\overline{AA}$ | 1.837 | 2.334    | 0.077      | -0.154     | 0.077      | 8.524   | 0.403    |
| $AB$      | 1.805 | 3.243    | 0.001      | -0.001     | -          | 8.401   | 0.156    |
| $ABA$     | 1.804 | 3.174    | 0.03       | -0.06      | 0.3        | 8.433   | 0.223    |
| $A\overline{A}$ | 1.805 | 2.673    | 0          | 0          | -          | 8.280   | -0.084   |
| $A\overline{AA}$ | 1.804 | 3.156    | 0.001      | -0.002     | 0.001      | 8.316   | -0.014   |
| $AA'$     | 1.843 | 2.214    | 0.021      | -0.021     | -          | 8.324   | 0.004    |
| $AA'$     | 1.836 | 2.428    | -0.014     | 0.028      | -0.014     | 8.408   | 0.171    |
| $A\overline{B}$ | 1.806 | 3.520    | 0          | 0          | -          | 8.377   | 0.120    |
| $A\overline{BA}$ | 1.837 | 2.335    | 0.0775     | -0.155     | 0.0775     | 8.408   | 0.171    |

| Sb        |       |          |            |            |            |         |          |
|-----------|-------|----------|------------|------------|------------|---------|----------|
| 2         | 2.978 | 3.590    | 0.210      | -0.210     | -          | -       |          |
| 3         | 2.977 | 3.590    | -0.210     | 0.210      | -          | 0.147   | 0.009    |

The layer-by-layer growth of an $\overline{A}A'A$-type structure is accompanied by its destabilization with respect to the single-layer SiC. An energy of 84 and 14 meV/atom is required to stabilize the packing of the structure for the two-layer and three-layer phases, respectively. The surface is almost neutral (table 1).

In the case of layered $A\overline{BA}$ growth, a change in chemical bond parameters ($R_{Si-C} = 1.805 \to 1.843 \to 1.836$ Å, $E_b = 8.322 \to 8.322 \to 8.408$ eV/atom) is observed, along with transformation to the most energetically beneficial geometrical configuration corresponding to the $A\overline{AA}$ polytype with a similar evolution of charge properties (table 1). The $AA'A$ geometry optimization is accompanied by a shift of the middle layer in the structure relative to the original geometry and transformation into a topologically invariant $AAA$ type. This process is characterized by a similar electron density distribution of the three-layer phase (table 1).

Comparison of the charge redistribution in 2D SiC with a homoatomic graphene-like system (antimonene) [17] made it possible to establish a number of features of the charge properties of silicon carbide. In antimonene, each layer is a corrugated bilayer with the number of layers $n = 3$, where the middle layer has a slight excess of positive charge. The most stable allotropic modifications of silicon carbide have an excess of negative charge in the middle layer, the value of which is twice the charge of the outer layers (table 1). This indicates the possibility of creating heterostructures based on silicon carbide without significant changes in its properties, such as the width of the band gap.
4. Conclusions
The study of structural changes in multilayer systems based on silicon carbide monolayers revealed the presence of a fractional effective charge. It was found that the magnitude of the effective charge makes it possible to identify allotropes of 2D silicon carbide. The sign of the charge determines the order in which the layers are laid in the structure.

Taking into account the redistribution of charge during the layer-by-layer growth from one to two- and three-layer structures of various allotropic modifications of silicon carbide presumes the electrophysical method of separation of multilayer 2D allotropes of silicon carbide. In addition, the features of the charge redistribution in multilayer structures are the basis for the development of functional devices of nanoelectronics. The electrostatic activity determines the possibility of the formation of composite materials based on 2D SiC.

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