

Computer Simulation of Epitaxial Graphene Assembly on Silicon Carbide Surface with Using Semi-Empirical Quantum Chemistry Methods

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The described simulation is an initial step in a series of calculation problems in the graphene area. They seek to formulate experimental conditions of SiC Epitaxial Graphene formation under which the probability of joints, "moire" superstructures and similar defects would be reduced to minimum.

As a test for suitability of the approach the variants of reconstruction for Si (0001)- and Carbon (0001) faces, preceding the graphene synthesis, were researched. It was shown that the simulation reproduces principal experimental results such as $[6\sqrt{3}\times 6\sqrt{3}]R30^0$ reconstruction for the Si face as well as specific form of small-scale reconstructions on carbon face.

As we know from experiments, the immediate synthesis of graphene from SiC is preceded by a series of the surface reconstructions. I.g., the $[6\sqrt{3}\times 6\sqrt{3}]R30^0$ reconstruction is authentically observed for Si face $[0001]_{Si}$.

Formally, the origin of this reconstruction is associated with the formation of a matching superstructure, in which 6 centered hexagonal Si cells of "zigzag"-shaped sides of 0.308 nm size, having a period of 0.533 nm along the "zigzag" sides of the cell, correspond with 13 hexagonal graphene cells with an accuracy of ~ 1% [1].

At the same time this reconstruction is not the unique one. Therefore a task was formulated to analyze the possible reconstruction shape in the course of SiC → Graphene transformation with a viewpoint of the matrix energy code.

The research apparatus were semi-empirical quantum chemistry methods CC. Molecular mechanics (MM)- optimized configurations were used as an initial approximation.

For Si $[0001]$ face an immediate object of the research was the reconstruction cells $[6\sqrt{3}\times 6\sqrt{3}]R30^0$ and $[n\times n]$. All the Si atoms within the cell were considered to be evaporated, except the only atom, located at the center of the cell (atom 1 in Fig.1).

The simulation showed that the atom becomes a natural centre of the graphene cell mesh (a nucleus). Building material for the mesh are "sticking" carbon atoms (atoms 4 in Fig.1), remaining on the surface of the upper SiC layer after Si atoms are evaporated.

However, the drift of such atoms drift towards the center of the cell only occurs if $n \geq 6$. Otherwise the activation barrier for the drift is significantly higher than the evaporation energy for Si atoms. So, the character of the $[6\sqrt{3}\times 6\sqrt{3}]R30^0$ reconstruction is reasoned without application to geometrical commensurability of the SiC- and the graphene cell size.

In the case of the graphene formation at the carbon face the process is developed as a sequence of the surface reconstructions with a rather short spatial periods $[2 \times 2]$, $[3 \times 3]$.

CC methods allowed to get clear this sequence as well as to find the intermediate form of the before-graphene superstructures.

The driving force for the transformation on C-face is a large quantity of energy binding carbon atoms one with another. This fact reduces drastically the activation barriers for joining carbon atoms, despite the destruction of highly symmetrical structure of SiC.

Some intermediate configurations with short-period reconstruction along the energy-optimal assembly path are shown in Fig.2.

References

[1] K.V. Emtsev, A.Bostwick, K.Horn, et. al. Nature Materials. 2009. Vol 8 . P.203-210.

Figures

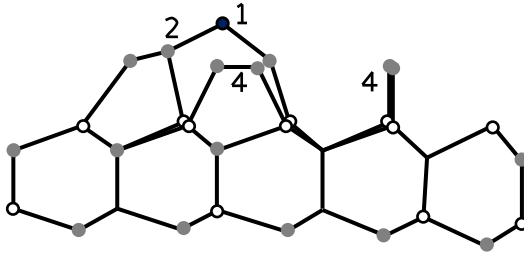


Fig.1.

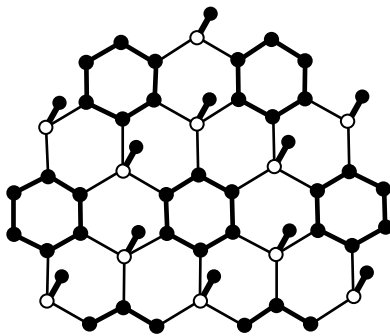


Fig.2. a

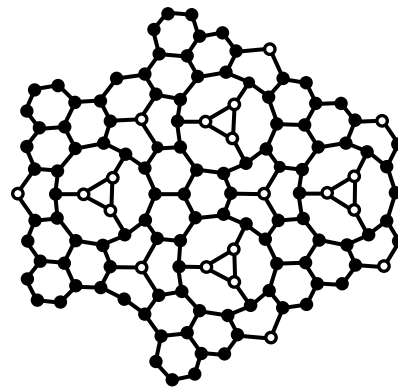


Fig.2. b

Figure captions

Fig.1. A fragment of the reconstructed SiC surface in a vicinity of the central Si atom. Sideway view. PM3 optimization. The Si atom (deep blue) is bonded with 3 carbon atoms (dark black lines of bonds, carbon atoms are grey, Si atoms in the underlayer are white circles).

Fig.2. a) a [2x2] reconstruction with the period of 5.832 Å (mismatch lattice with SiC~4%); C-atoms, sticking from the plane, are shown as tilted lines; carbon atoms are black, Si atoms are white. b) a [3x3] superstructure with the period of 9.096 Å (mismatch is 0.85%).