

**MODELING OF EPITAXIAL GRAPHENE ASSEMBLY FROM
SILICONE CARBIDE WITH THE USE OF SEMI-EMPIRICAL
QUANTUM CHEMISTRY METHODS**

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A new direction of our research – the modeling of the epitaxial graphene assembly from silicon carbide with the use of semi-empirical quantum chemistry methods as well as the modeling of properties of actually imperfect graphene crystals

Objectives of this research are

-preliminary theoretical test of technologies, presumably able to correct the defects of real epitaxial graphene grown on SiC

The problem of epitaxial graphene synthesis on different SiC faces is a **test problem** for the reliability of our approach

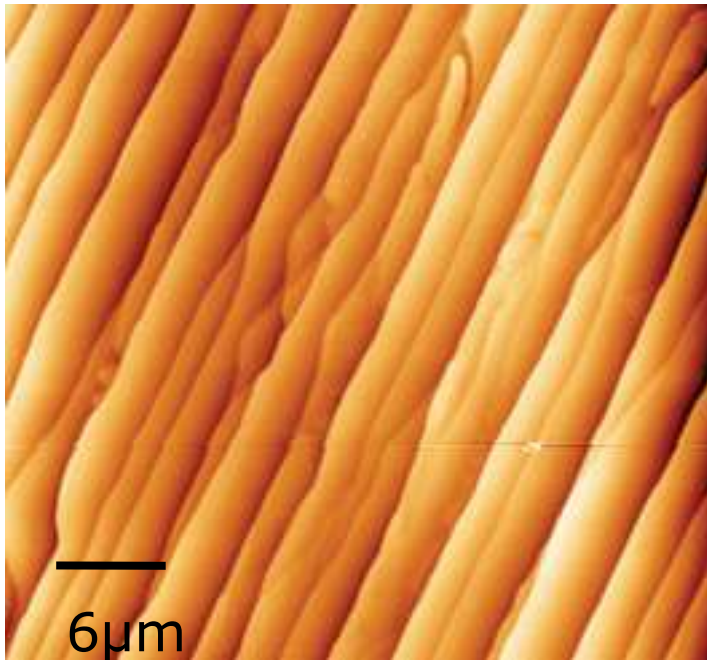
The concept: to reconstruct a real picture of the transition

“epitaxial SiC→Graphene growth” from the most general reasons and experience, not referring to experimental data

For example, we are not specified by a concept whether the graphene plane is connected with the underlying SiC layer via covalent or Wan-der-Waals bonds. We try the both versions

One of the results (see below): No graphene growth can start on Si face until $n\sqrt{3}\cdot n\sqrt{3}$ R30° reconstruction arises with $n=6$. This result is reasoned **without** application to geometrical **commensurability** of SiC- and of graphene cell size

Typical defects of epitaxial graphene - seams on the one-layer graphene structure

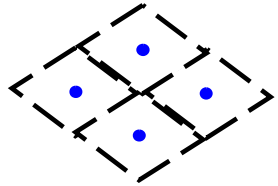


AFM image of graphene on 6H-SiC (0001) with a nominal thickness of 1.2ML formed by annealing in Ar ($p=900$ mbar, $T=1650^{\circ}$ C). *K. V. Emtsev, A. Bostwick et al Nature Materials. V.8. 2009*



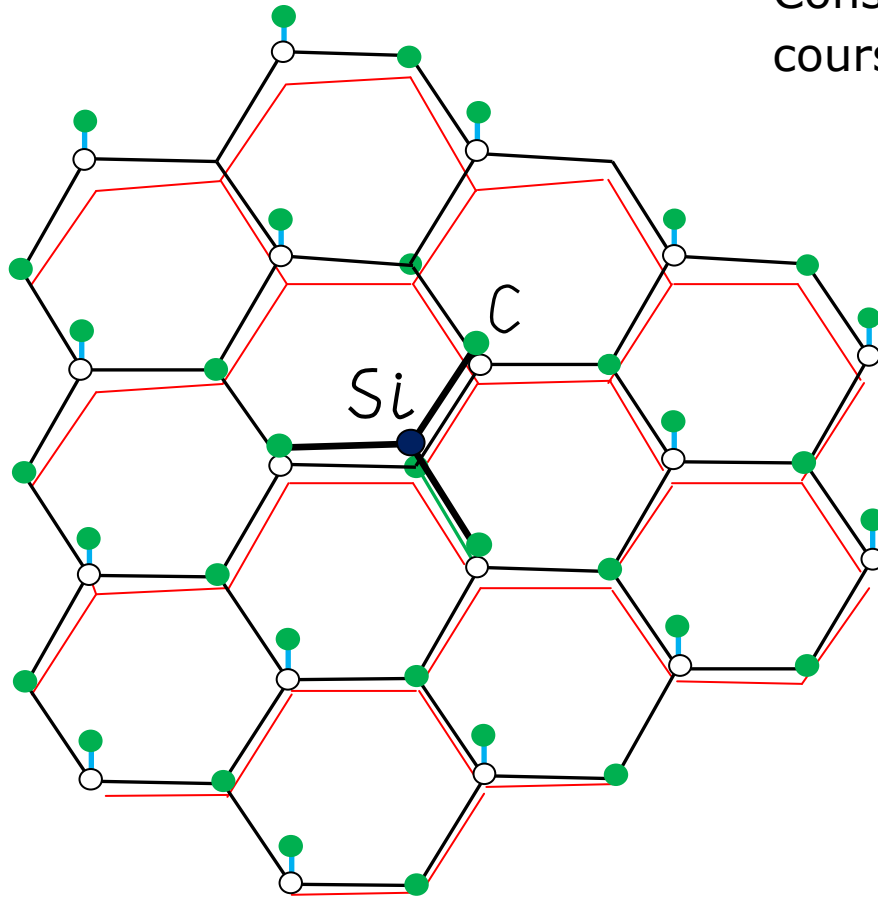
Close-up AFM image of the same surface

OUR MODELING



Place Si atoms (dark blue) at the center of the elementary reconstruction cell $(n\sqrt{3} \times n\sqrt{3}) R30$ or $n \times n$

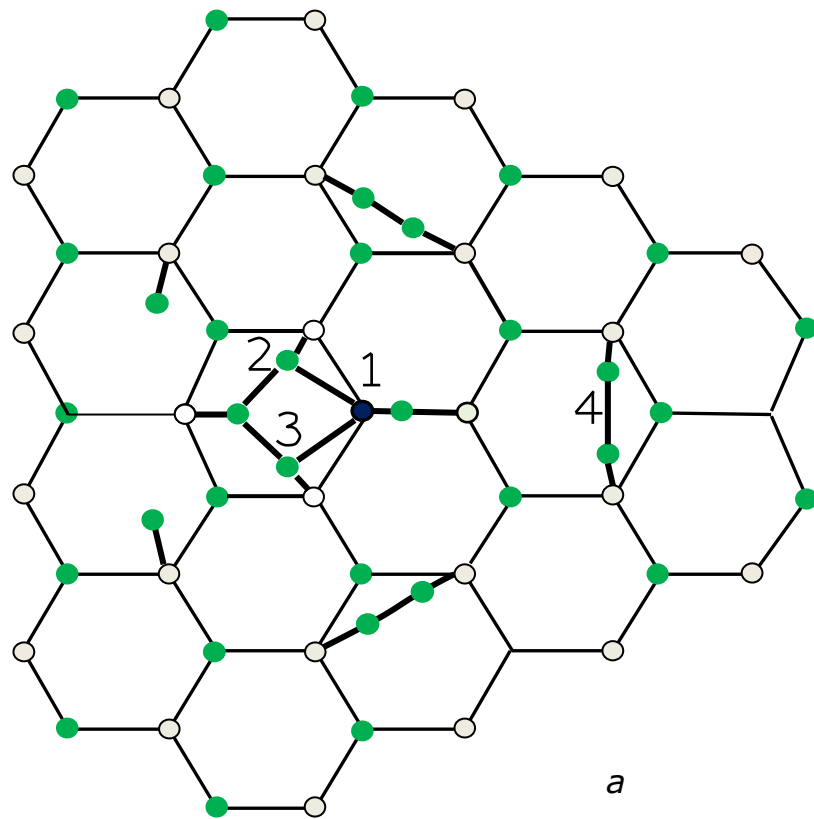
Consider that no other Si atoms survive in the course of evaporation



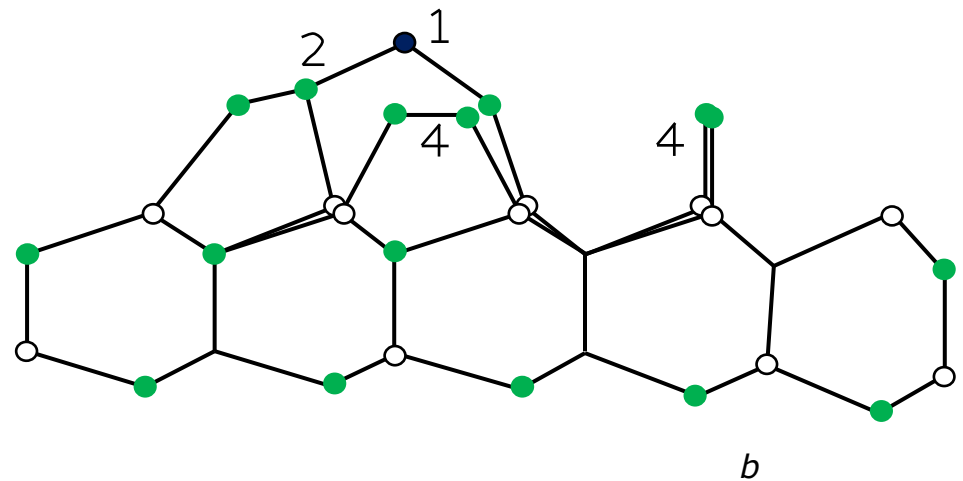
Then the **mental arrangement** of the central Si atom and the carbon atoms surrounding it (MM optimization) is as the follows

Atom Si (dark blue color) is connected to three atoms of carbon (fat black lines of bonds, C atoms are designated as green circles, Si atoms are the white circles)

Consider now the **actual arrangement of carbon and silicon atoms** in a vicinity of this Si atom

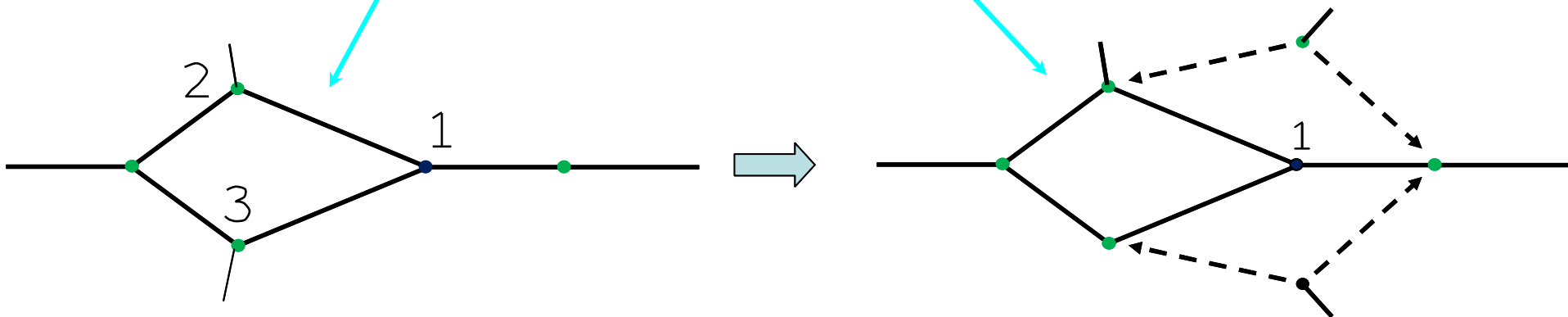


Semi-empirical quantum chemistry optimization of atom arrangements in two upper layers at fixed positions of deeper layers by PM3 method of HyperChem media



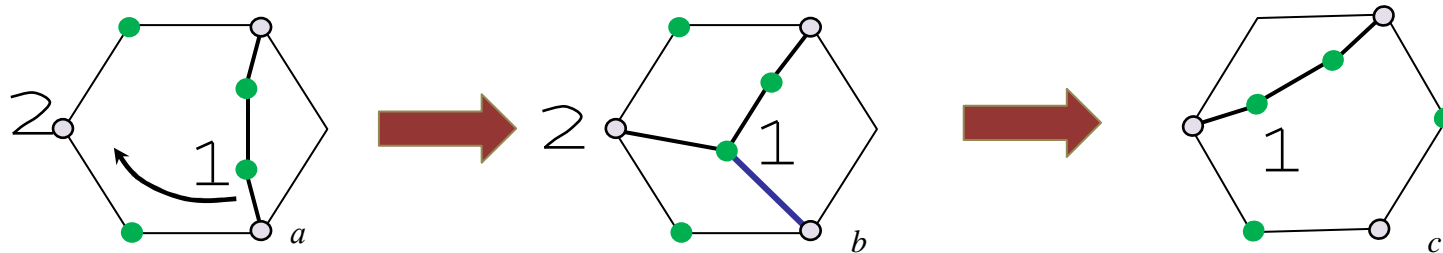
Fragment of the reconstructed Si-face in a vicinity of the central Si atom. The configuration shown in the previous slide transforms in such a way that the central **Si atom** accumulates four carbon atoms around itself **to become the seed of a graphene surface growth**. A break of a part of chemical bonds between this surface and the SiC underlayer occurs

In the course of high temperature anneal the configuration in the previous slide (the closest vicinity of the central Si atom (atom 1)) is transformed into a graphene plane seed. The Si atom is extracted then out of the graphene surface and does not prevent from the formation of newer graphene cells



Subsequent graphene cells are formed on the basis of this seed

During the further evolution the seed is covalently connected with the substrate chemically via some number of atoms at its edge and partially the atoms of its central part.

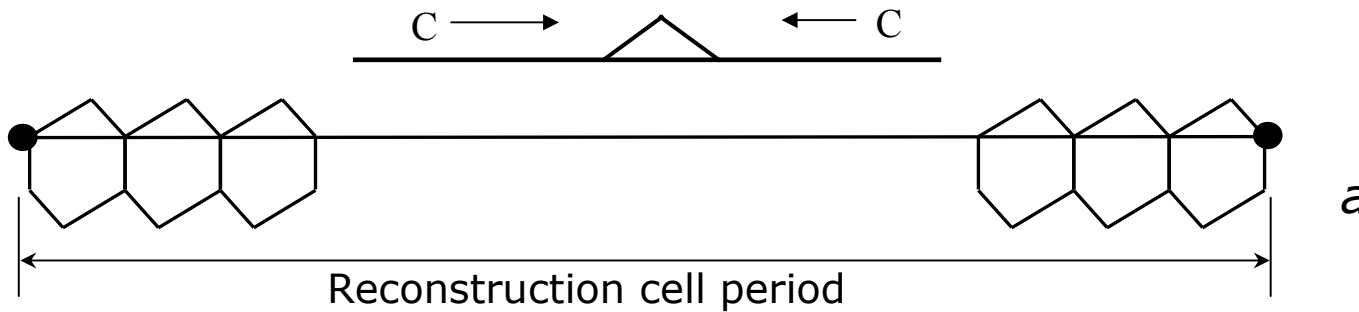


Carbon atoms able to build up the graphene surface, are incorporated in bridges 4 (slide 5), perpendicularly placed as to the planes $\{0001\}$. Atoms of the bridges are bonded between themselves and with underlying SiC faces via covalent bonds.

The "drift" of the bridges towards the growing graphene surface is a stepped-wise process. Each step of the drift is a carbon bridge turn (arrow $1 \rightarrow 2$ in configuration "a") which includes, in turn, two steps

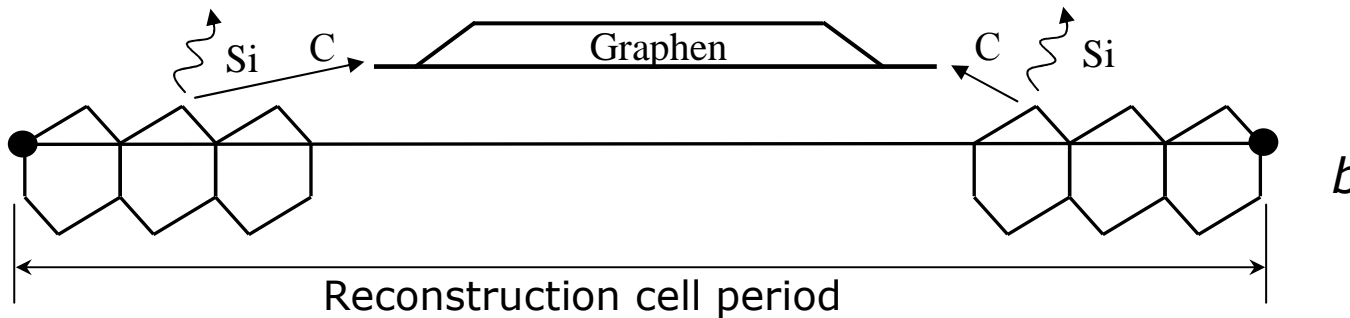
- additional bonding of one of the C-atoms of the bridge (atom 1) with originally vacant Si atom (atom 2) ($a \rightarrow b$ transfer)
- disruption of the old C-Si bonding (indigo) with this carbon atom ($b \rightarrow c$ transfer)

But C atoms in the bridges can make up only a small part of C atoms necessary to fill the graphene surface (stage "a"). At least two further stages "b" and "c" are necessary to complete the process



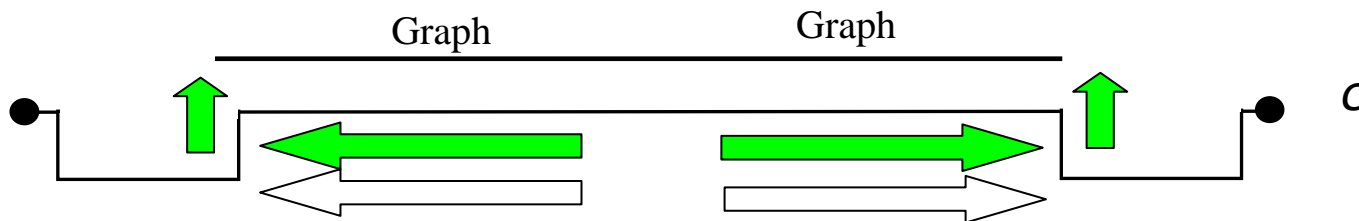
a

b: Underlying SiC face **around** the graphene is gradually released from the most of Si atoms (wave-shaped arrow). Released C atoms drift towards the graphene



b

c: graphene plane grows at the expense of under-laying SiC destruction **under** graphene. Green and white arrows - under laying drift of C- and Si- atoms



c

So, **two processes** determine the rate of initial graphene surface growth at the stages "a" and "b"

- carbon bridge "drift" (mainly at the stage "a")
- evaporation of Si atoms from a released surface of the second silicon layer

Activation energies for these two processes behave differently depending on the reconstruction $n \cdot 3^{1/2}$ cell size

Herewith

$E_a^{(\text{evap})}(n)$ for the Si atom evaporation slightly depends on n (next slide)

$E_a^{(\text{drift})}(n)$ for carbon bridge drift decreases noticeably (next slide)

As soon as the reconstruction cell size becomes large enough ($n=6$ as $n=4$ it is not great enough, whilst the evident lower size reconstructions $n=2$ and 3 born $n=6$ in natural way), the graphene growth starts. Since this moment this growth can only be stopped by insufficient temperature. No bottleneck of the assembly exists further on.

So, the reconstruction cell size does not follow literally from the commensurability requirement for the Graphene- and for the SiC cells.

