

Theory on Initial Stage of Epitaxial Graphene Growth on SiC(0001)

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1. Introduction

Epitaxial graphene grown on SiC substrate is expected to provide graphene substrate for industrial electronics [1]. While wafer-scale wide mono- and bi-layer graphene can be already fabricated, graphene with more uniform thickness and crystallinity is expected. To control the uniformity, atomic scale understanding of the growth mechanism is necessary. We have therefore made both experimental and theoretical studies [2-6].

Our experimental observation [2] shows that the $\sqrt{3} \times \sqrt{3}$ -to- $6\sqrt{3} \times 6\sqrt{3}$ transformation causes the surface morphology to roughen severely, even though the initial $\sqrt{3} \times \sqrt{3}$ surface has regular step/terrace array, when the SiC(0001) substrate is annealed at around 1000-1400°C in the ultrahigh vacuum less than 10^{-8} Torr. The monolayer and bilayer graphene islands densely nucleate near the steps almost simultaneously, although the density of the monolayer islands is higher than that of bilayer islands. After bilayer graphene growth, the substrate rather recovers the regular step/terrace structure, and bilayer graphene covers the surface almost homogeneously.

Our theoretical studies [3-6] have revealed that a new graphene layer always grows from the interface between the old graphene sheets and the SiC substrate. The detail of the growth mechanism is however still unknown. To study how and why the roughening proceeds during the growth, in this contribution, we theoretically study the initial stage using the model with a single step trench array.

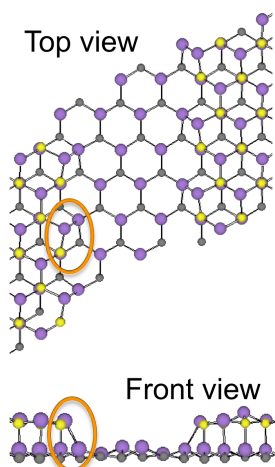


Fig. 1: Calculated model of trench array on SiC(0001) substrate with two single [11-20] steps. Large and small circles are Si and C atoms, respectively.

2. Method

Our calculation method is the first-principles method with pseudopotentials, plane wave bases, and a density functional [3-6]. The model we used in the calculation is a trench array on SiC(0001) substrate with single [11-20] steps as shown in Fig. 1. The lateral unit cell is $\sqrt{3} \times 4\sqrt{3}$, and the lower and the upper terraces with the same width are located repeatedly. We employ the repeated slab geometry. The thickness of the lower terrace part is three SiC layers, and the back-side of the slab is terminated by H atoms. After a Si atom is removed or C atoms are adsorbed by hand from this initial surface, the atomic positions are fully optimized with fixing the back-side surface C atoms, and the total energy is calculated. We here focus on the energetics, and the kinetic or dynamic barrier is not considered.

After the structural optimization, the Si at the step top makes a covalent bond with the Si at the step bottom and suppresses the number of its dangling bonds (Fig. 1). The step is thus stabilized. Such stability of the step affects the growth mechanism in the initial stage as shown in the following sections.

3. Si sublimation

First we study the preferable site for Si sublimation from the initial model surface. Figure 2 (a) shows the site positions, from which the Si atom is removed, and Fig. 2 (b) shows the energies, which is required for the Si sublimation, as the differences from that at site A. The calculation shows that the Si atom at the first neighbor sites of the step top (site B in Fig. 2) is the most preferable and that at the second neighbor sites of the step bottom (site F) is the next, while the Si atom at the step bottom (site D) is the most difficult for the Si atom to sublimate. The energy difference between sites B/F

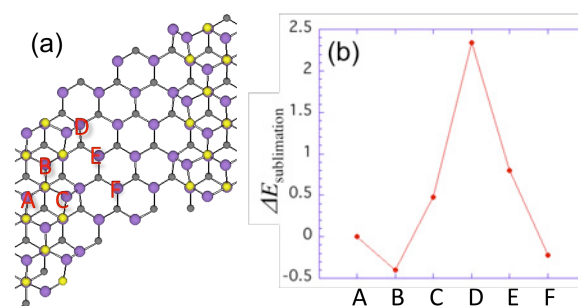


Fig. 2: (a) Site positions, from which Si atom is sublimated. (b) Relative energies for Si sublimation from the corresponding site.

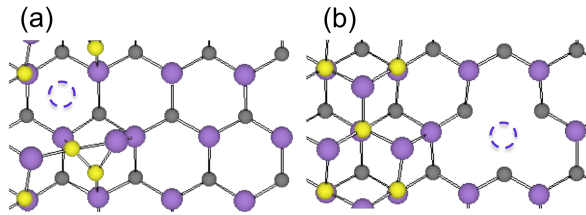


Fig. 3: Close-up top views of the atomic structures after Si sublimation (a) from site B and (b) from site F. Dotted circles indicate the Si sublimation sites.

and D is more than 2 eV.

As shown in Fig. 3 (a), when a Si atom is removed from site B, the atomic structure around the step is reconstructed, and a stable C-C bond is formed. When a Si atom is removed from site F, the stable atomic structure of the step remains, while the atomic structure around site F is reconstructed (Fig. 3 (b)). On the other hand, when a Si atom is removed from site D, the atomic structure of the step is significantly disturbed, and the stable Si-Si covalent bond is disappeared from the step top Si atom. Similarly, the Si atoms around the step edge are difficult to sublimate.

These results indicate that the roughening mode is preferable rather than the smoothing mode by the step flow, being consistent with the experimental observation. To activate the smoothing mode by the step flow, therefore, the step should be unstabilized by some technique.

4. C nucleation

Next we study interaction of a C atom with the step. We put one extra C atom on the initial model surface and study the interaction with the step. We put the C atom in various sites as shown in Fig. 4 (a). The energies, which is required for the C adsorption, is shown in Fig. 4 (b) as the difference from that at site a. The results show that the C atom preferably leaves from the step edge (site a, b, c, or f) and stays at the center of the upper or the lower terrace (site e or h). This is consistent with the stability of the step.

We also put one more extra C atom and study the interactions between the adsorbed C atoms and with the step. The results indicate that the C atoms form a dimer as well as form separated monomers on different terraces. However, they also indicate that the C atoms nucleate at

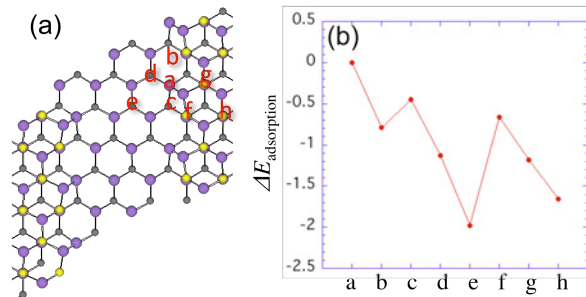


Fig. 4: (a) Site positions, where the remaining C atom is located. (b) Calculated relative energy for the C adsorption.

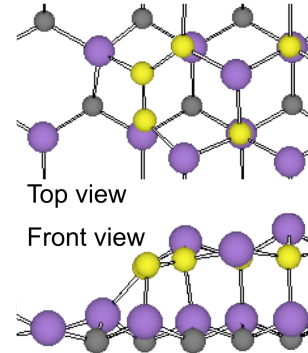


Fig. 5: Close-up views of the atomic structure, where 2 C atoms nucleate at the lower step edge.

the lower step edge more preferably by about 0.2 eV. The nucleated C atoms have covalent bonds with the Si and C atoms at the edge, and form planar Si-C-C-C bond network (Fig. 5). Since the nucleated C atoms have sp^2 -like bond configuration, they must be the seed for the graphene growth from the lower step edge.

These results indicate that C atoms preferably distribute on the center of the terraces in the initial stage, and that they begin to nucleate around the lower step edge when the C coverage increases. Since the Si sublimation supplies excess C atoms as well as roughens the surface, the number of step edges is thought to increase and multilayer graphene grows from the step edges.

5. Conclusion

The first-principles study reveals preferable Si sublimation site and preferable C nucleation site on SiC(0001) surface with the [11-20] trench. It is indicated that the Si sublimation preferably roughens the surface. On the other hand, the C adsorption preferably occurs at the lower step edge, when the C coverage increases. These results consistently explain the experimental observation.

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