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Simulation on initial growth stages of graphene on Pt (111) surface

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Epitaxial growth process and morphology evolution in the initial growth stages of graphene on Pt (111) surface have been studied by means of canonical Monte Carlo simulation. It is found that the nucleation, carbon chains, carbon rings, and then graphene domain are formed orderly in the early growth stages during the annealing process. The dynamic processes of the morphology evolution are visualized through the simulation. The formed structures of graphene are investigated quantitatively by pair distribution function, atomic intervals, and the bend angles among the three contiguous carbon atoms. The lattice mismatch between graphene and the Pt (111) surface is accommodated by the main structure of hcp-fcc. These simulation results are consistent with experimental observations and may give further insights to the epitaxial growth of graphene in the atomic scale. © 2012 American Institute of Physics. [doi:10.1063/1.3686609]

I. INTRODUCTION

The Nobel physics prize on graphene has strongly stimulated one's interests on its unique properties and potential applications. The reliable productions of large-area and high-quality graphene sheets are essentially required for developing the relative functional devices.^{1–3} One promising approach to fabricate graphene is the epitaxial growth on metal substrates by thermal decomposition of hydrocarbon or surface segregation of carbon atoms from the bulk metal. Up to now, graphene has been epitaxially grown on various metal surfaces, such as Ru (0001),⁴ Ir (111),⁵ Cu (111),⁶ Ni (111),⁷ Pd (111),⁸ Rh (111),⁹ and Pt (111).^{10–13} The epitaxial growth process has been investigated by low energy electron microscopy, scanning tunneling microscopy (STM), and spectroscopy, as well as Raman and Rayleigh spectroscopy techniques. Even so, little is known about their atomic-scale growth process and thermal stability in those previous studies. On the other hand, the first-principles calculations^{14–16} have demonstrated the energetics and kinetics of graphene nucleation and indicated the epitaxial growth process on metal surfaces; however, further improvement would be facilitated through more completely and deeply understanding the atom behavior in the early growth stages.

The previous reports have demonstrated a surface catalyzed process for graphene growth on metal substrate.^{17,18} The reaction of a carbon source at the metal surfaces can lead to the formation of various condensed carbonaceous phases, carbide or graphene, depending on the interaction strength with the metal catalyst. Understanding the early formation process and development of these characteristics on the surfaces of relevant materials is very important to create graphene in a well-controlled and reproducible manner. The

Pt (111) surface is favorable to grow graphene, because (I) it is a natural catalyst of hydrocarbons, which causes hydrocarbon molecules to dissociate upon contact, and (II) its surface has the minimum effect on the physical properties of graphene, due to very weak graphene-substrate interaction. However, less work was conducted on the epitaxial growth of graphene on the Pt (111) surface in the initial stages.

Monte Carlo (MC) simulations have been employed extensively to study various aspects of deposition, diffusion, and crystal growth process and have provided valuable insight into the atomistic processes.^{19–21} In the present paper, canonical MC (constant number of atoms, constant volume, and constant temperature) simulations were used to probe the epitaxial growth process and surface morphology of graphene in the initial growth stages on the Pt (111) surface. The graphene domain was prepared by segregation of random distributed carbon atoms on the surface. Based on the results of the experimental report, we focused on the annealing process at the temperature of 973 K to show the atomic growth process and the quality of graphene on the Pt (111) surface and then changed the growth temperature in the simulation programs for comparing the different growth processes under the different temperature conditions.

II. COMPUTATIONAL METHODOLOGY

In the present MC simulations, the many-body Tersoff potential was used to describe the carbon-carbon (C-C) interaction, and the cutoff distance was chosen to be 10 Å. The Tersoff potential gives a convenient and relatively accurate description of the structural properties and energetics of carbon, including elastic properties, phonons, polytypes, defects *et al.*^{22,23} and has been proven to be convenient to use in atomistic simulations.²⁴ It is well known that the first-principles calculations provide the most reliable interatomic potentials for atomistic simulation. However, it is not easy to

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implement in the general computers, because it is so time consuming. Recent x-ray absorption measurements have suggested that monolayer graphene on Pt stands out as the system with the weakest graphene-metal interaction among a broader group of 3d, 4d, and 5d transition metals.¹² Previous observation on both diffraction and imaging¹³ of coexisting rotational domains and interfacial moiré structures for graphene on Pt (111) has further demonstrated the weak Pt-C interfacial interaction. This supports that the weak substrate coupling Pt-C can be described by the Lennard-Jones (LJ) potential.^{25,26}

A schematic diagram of the initial configuration is presented in Fig. 1. In the present simulations, 60 carbon atoms are placed directly and randomly on the surface to simulate the initial growth stages in detail. The substrate includes 330 Pt atoms and consists of 3 layers, which have been tested as adequate for simulation.¹⁰ Pt has a face-centered crystal structure and its (111) plane has a hexagonal symmetry. Graphene crystallizes in the honeycomb structure, which also has a hexagonal symmetry. Therefore, the Pt (111) surface has the proper symmetry for the growth of epitaxial graphene layers. The main aim of our paper is to show the epitaxial growth process and morphology evolution in the initial growth stages of graphene on the Pt (111) surface. The movable atoms of the Pt substrate have minimum effect on our main aim, due to the weak Pt-C interfacial interaction. Consequently, the layers of the substrate are kept fixed in the simulation processes, and the fixed substrate model has been used in other related, similar simulation work.²⁷ Accordingly, MC simulations are employed in a canonical ensemble condition. Periodic boundary conditions are applied in the

x and y directions, and an open boundary condition is applied in the direction perpendicular to the surface. MC steps (MCS) are used to represent the simulation time. One MCS is defined as the duration in which all the sample metal atoms have an attempt to migrate, and the standard Metropolis method is then adopted.²⁸ Free relaxation is carried out for enough time to obtain equilibrium, and once the equilibrium has been reached, the annealing procedure is added for the temperature.

III. RESULTS AND DISCUSSION

Graphene synthesis on a metal surface is accomplished usually based on the high-temperature pyrolysis of small hydrocarbons, such as ethylene or propylene. The sample is firstly exposed to the carbon source (e.g., at 300 K) and then subsequently annealed to the desired temperature above 900 K.¹⁸ Summarizing the experimental results from the previous reports,^{10–13,18} as the first example, the nucleation, growth mechanism, and quality of graphene on the Pt (111) surface are firstly simulated at the temperature of 973 K. The representative processes to form a monolayer graphene domain by carbon surface segregation, initiated by annealing at 973 K, are shown in Fig. 2. It can be seen that the carbon atoms are gradually induced by the substrate to form the well-known monolayer graphene domain. Firstly, the carbon atoms nucleate quickly, as shown in Fig. 2(a) and Fig. 2(b). They do not aggregate together to form one carbon cluster directly; only some dispersive small clusters, such as dimer, trimer, multimer, atomic chains, and so on emerge. Secondly, the small clusters are swallowed by the carbon chains and the total number of the nanoclusters decreases. Interestingly, the small clusters do not stack on the carbon chains, but coalesce on the edges or ends of the carbon chains, so the carbon chains become longer and larger as some small clusters disappear (see Fig. 2(b) to Fig. 2(f)). Thirdly, the hexagonal carbon rings are found when the carbon chains continuously twist and incorporate other carbon atoms. A minority of isolated carbon rings is also observed near the maximal carbon cluster, and other carbon chains would incorporate to the isolated rings also, indicating that nucleation is homogeneous and not restricted or entirely governed by specific sites. Finally, all the carbon chains coalesce to form a carbon network with units of hexagonal rings incorporating through each other, and then the monolayer graphene domain is presented on the Pt (111) surface.

The nucleation, epitaxial growth process observed in Fig. 2 can be described by the decrease of small cluster density through diffusion and coalescence of mobile small clusters upon contact, in line with previous conclusions drawn for other transition metal substrates, such as Ru and Ir.^{29,30} During migrating on the surface, the small clusters encounter ends or edges which belong to other clusters and where their attachment is enhanced and their mobility likely decreased, allowing for extended graphene domains to grow by coalescence and incorporation of other small carbon clusters. As mentioned above, the initial epitaxial growth stage of graphene on the Pt (111) surface is fully established in the atomic scale. It can be concluded that the nucleation, carbon

FIG. 1. (Color online) Schematic initial states of the atomic configuration in top view (up) and side view (down).

FIG. 2. (Color online) Some typical time-dependent morphologies at temperature of 973 K. MCS represents the simulation time.

chains, carbon rings, and then graphene domains form orderly in the annealing process. The detailed morphology evolution process can be seen in the movie in Ref. 31.

The inset in Fig. 3(a) depicts the simulated interval of about 3.03 Å between the graphene domain and Pt (111) surface. The separation matches with the experimental value of 3.30 Å^{10,12} and is close to the interlayer spacing of 3.40 Å for graphite, as shown in Fig. 3(c). This indicates that the coupling between graphene and metal is approximately available for LJ potential. Some atomic intervals and bend angles in the graphene domain are presented in Fig. 3(b). It is well known that graphene is one layer of the graphite. Accordingly, the similar intervals and angles of the supercell of graphite are shown in Fig. 3(c). The shortest interval of 1.47 Å is also obtained by calculation using the pair distribution function, as shown in Fig. 3(a). The ideal value of the shortest interval is 1.42 Å. The average distance between the second-nearest neighbors is 2.54 Å, and the ideal value is 2.56 Å. The average angle among the three contiguous carbon atoms is 121.15°, and the ideal value is 120°. The simulated three groups of data agree well with the experimental values. It also demonstrates that the many-body Tersoff potential is accurate enough to describe the C-C interaction in the structure of graphene.

The structure of graphene/metal interface is very important to control the growth process and to understand its properties. To get a better observation of the structure between graphene domain and the Pt (111) surface, the first and the

second layers of the Pt substrate are taken away one by one, as shown in Fig. 4. From the top view, the carbon atoms of the graphene domain are basically distributed above the Pt atoms of the second and the third layer sites. The different distributed structures are generated from the lattice mismatch between graphene and the metal substrate. According to Ref. 16, the first layer of the Pt (111) substrate can be called top sites, the second layer can be called hcp sites, and the third layer is called fcc sites. It can be concluded that the graphene domain in the simulation is a main structure of hcp-fcc. Other structures, such as top-fcc (carbon atoms are distributed above the first and the third layer), top-hcp (carbon atoms are distributed above the first and the second layer) *et al.* should also exist on the metal surface. Only hcp-fcc structure has been observed here that may be ascribed to the few carbon atoms and the fix and complete Pt substrate in the simulation model.

Besides the above process at 973 K, the growth characteristics of monolayer graphene on Pt (111) have also been simulated at several other temperatures, such as 273 K, 573 K, 773 K, 1273 K, and 1473 K. Figure 5 presents the last configuration of the simulation results. The low temperature cannot drive the carbon atoms to grow a continuous monolayer graphene domain, but to form the isolated carbon chains and rings. A longer carbon chain can be observed at 773 K. The results of the carbon atoms that disperse in the larger area and refuse to aggregate can be explained by two reasons. One is that the carbon atoms cannot absorb enough energy to

(c)

FIG. 3. (Color online) (a) The pair distribution function (PDF) of the simulated graphene domain at the 973 K, inserted with its side-view morphology with the distance of 3.03 Å between graphene domain and the Pt (111). (b) The top-view of the simulated graphene domain at the temperature of 973 K and the corresponding atomic intervals and bend angles. (c) Some normal parameters of atomic intervals and bend angles of the graphite superstructure. All length units are Å.

FIG. 4. (Color online) The structure of the interface between graphene domain and Pt (111) substrate in top view (up) and side view (down) for (a) three layers, (b) two layers, and (c) single bottom layer of the substrate.

escape from the surface at the relatively lower temperature. The other reason is that the carbon atoms are slightly soluble in the platinum.¹¹ The lower temperature there is, there will be lower solubility for the carbon in the platinum. With the rising of temperature, such as 1273 K and 1473 K, carbon atoms still stay in a monolayer graphene domain, but the

wrinkle appears in some parts because of the high kinetic energy of the carbon atoms at a higher temperature. Whether low temperature or high temperature, the defective rings (octagons or heptagons) exist. It may be ascribed to the energy of the atoms. As a whole, the quality of graphene should be improved by achieving proper growth temperature.

FIG. 5. (Color online) The simulated atomic configurations at the different temperatures in top view (up) and side view (down).

IV. CONCLUSIONS

In summary, using the Monte Carlo simulation, we have shown the nucleation, epitaxial growth process, and surface morphology of the initial growth stages of graphene on the Pt (111) surface. Details of the growth process can be concluded as follows: carbon atoms nucleate to form small clusters firstly on the Pt (111) surface, and then the small clusters form the carbon chains and carbon rings orderly. Just at the appropriate temperature, the carbon chains and carbon rings would form the smooth monolayer graphene domain. Surface morphology and the structure of graphene are consistent with experimental observations. These theoretical studies can shed light on the epitaxial growth of graphene in the atomic scale and raise the possibility of completely understanding the growth mechanism. We would be very interested to further investigate the growth process in a configuration with the step edges, defects on the surface, movable substrate, and other thermodynamic ensembles.

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