First principles molecular dynamics simulation of graphene growth on Nickel (111) surface

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Abstract. The mechanism of the graphene growth on the nickel (111) surface is studied using first principles molecular dynamics (MD) simulation. To investigate the effects of growth temperature and concentration of carbon atoms on the nickel (111) surface, the systems consisting 50%, 66.7%, and 100% of carbon concentration are annealed from 800 K, 1000 K, 1200 K, and 1500 K until room temperature. It is found from the MD simulation that the optimum temperature for the graphene growth is approximately 1000 K, although the graphene can also be grown at lower temperatures (~800 K) in a high concentration of carbon atoms which is in good agreement with the experiment.

1. Introduction
Graphene has attracted a lot of attentions due to its desirable electronic, optical, and mechanical properties [1][2][3]. Since several years ago, the number of publications and patents on graphene field has been increased significantly [4]. Graphene can be obtained by several ways. One of the most prospective method for large scale production of graphene is known as epitaxial growth on the particular substrate, such as silicon carbide [5][6] or metal substrate [7][8]. Nickel is one of metals that are widely used as the substrate for the graphene growth process via chemical vapor deposition (CVD) method [8]. It has been known that nickel exhibits high carbon solubility [9], which means that carbon atom can easily diffuse into the nickel substrate.

The previous experimental research of carbon behaviour on the nickel (111) surface has reported that specific formations of carbon are observed in particular temperature range. At the temperature more than 1200 K, carbons are diluted in the surface. Carbon atoms segregate to the surface to form monolayer graphene at the temperature between 1100 K and 1200 K. At the temperature below 1100 K, multilayer graphenes are formed by the precipitation of carbon atoms on the nickel surface due to the reduced carbon solubility of nickel bulk at low temperature [10].

So far, many theoretical studies have been performed to investigate the evolution of isolated carbon atoms on the nickel (111) surface. Meng and co-workers have employed the reactive force field (ReaxFF) potential as the interatomic potential within classical molecular dynamics (MD) simulation [11]. Other MD studies of the graphene growth on the nickel (111) surface have been carried out by means of density functional tight binding (DFTB) method. In the initial stage of their simulations, the
carbon atoms are distributed randomly in the interstitial state of the nickel subsurface. During the MD simulation at 1180 K, the carbon atoms nucleate underneath, and then segregate to the nickel surface. They obtained many pentagonal (5-membered) and hexagonal (6-membered) with few heptagonal (7-membered) carbon rings from the MD simulation. Additionally, some species of amorphous carbon cluster are also found in the nickel subsurface [12][13].

A number of theoretical studies of the graphene growth on the nickel (111) surface have been carried out recently. However, so far we are unaware of any MD studies of carbon nucleation on the nickel surface employing pure DFT method. In this study, we aim to reveal the mechanism of graphene growth on the nickel (111) substrate in various concentrations of carbon atoms and growth temperatures using first principles MD simulations. This simulation method has been employed in our previous studies of the hydrocarbon dehydrogenation on the nickel (111) surface [14][15][16].

2. Methods

This research has been conducted by using first principles MD simulation. The electronic states are calculated by the projector-augmented-wave (PAW) [17][18] method. The Perdew-Burke-Ernzerhov (PBE) [19] generalized gradient approximation (GGA) is employed for the nonlocal exchange-correlation effect. The empirical correction of the van der Waals interaction is described by the DFT-D approach [20]. The plane wave cutoff energies are 30 Ry and 250 Ry for the electronic pseudo-wave function and pseudo-charge-density, respectively. The energy functional is minimized iteratively using a preconditioned conjugate-gradient method [21]. The Brillouin zone is sampled using Γ point. Projector functions are generated for the 3d, 4s, and 4p states of nickel and the 2s and 2p states of carbon.

Three simulation systems are generated as the initial configurations. The systems include three layers of the nickel (111) plane, containing 30 nickel atoms in each layer, with (i) 50%, (ii) 66.7%, and (iii) 100% of carbon concentration, i.e. 15, 20, and 30 carbon atoms, respectively. These carbon atoms are distributed randomly on the nickel (111) surface. In order to hinder the carbon diffusion into the nickel subsurface, all carbon atoms on the nickel surface are connected with the bonds. The atoms in the bottommost layer of the nickel substrate are fixed to mimic the infinite thickness of substrate. The dimensions of supercell are 12.94 × 12.95 × 20.0 Å in the x-, y-, and z-directions, respectively. The Nosé-Hoover thermostat [22][23] is employed in the canonical-ensemble at the finite temperatures. The equations of motion are numerically solved via an explicit reversible integrator [24] with a time step of 0.968 fs. In each MD simulation process, the systems are equilibrated for 5 ps at particular growth temperatures, and then annealed until room temperature by the cooling rate 200 K/ps.

3. Results and Discussion

In this section, the results of the MD simulation of graphene growth on the nickel (111) surface are reported. These include the investigation on the effect of the annealing temperatures and the concentrations of isolated carbon atoms on the nickel surface as well.

3.1. Effects of the annealing temperature on the graphene growth on nickel (111) surface.

The growth temperature affects the quality of the product material. It has been known from the experimental report that the carbon atoms on the nickel surface exist in the different forms depending on the temperature, either they dissolve into the nickel subsurface or segregate to the nickel surface to form the nickel carbide or the graphene, respectively [10].

The optimum temperature for the graphene growth on the nickel (111) surface is investigated in our study. For this purpose, the MD simulations at four different annealing temperatures, i.e. 800 K, 1000 K, 1200 K, and 1500 K, are performed for the system with 66.7% of carbon concentration in which the initial configuration is shown in figure 1(a).
Several new carbon rings are formed at the growth temperatures of 800 K and 1000 K. In this study, the carbon ring is defined as the pentagonal, hexagonal and heptagonal ring which is observed in the grain boundaries of graphene. Figure 1(b) shows that one new hexagonal carbon ring is formed at 800 K of growth temperature. A new hexagonal and a new heptagonal carbon rings are found at 1000 K of growth temperature in addition to two pentagonal carbon rings which are not broken during growth process. Since the hexagonal carbon ring is the main component of graphene, its formation indicates the existence of graphene on the system. At the growth temperatures of 1200 K and 1500 K, one and two pentagonal rings are deformed from three pentagonal rings found in the initial configuration. At the growth temperature 1500 K, some carbon atoms are dissociated from carbon chains and buried in the nickel subsurface arising from the disorder of nickel atoms at the surface. This result is in agreement with the experimental fact that carbon atoms are diluted in the surface at the temperature higher than 1200 K [10].
Figure 2 shows the population of carbon rings and other forms of carbon atoms at various growth temperatures. Carbon rings are formed by only 40% and 25% of the total carbon atoms on the nickel (111) surface at 1200 K and 1500 K, respectively. It is found that the carbon atoms as much as 55% are in the form of carbon ring at growth temperature of 800 K. The highest population of carbon chains are obtained at the growth temperature of 1000 K thus considered as the optimum temperature for the graphene growth. This is in reasonable agreement with the recent experimental finding that the monolayer graphene is grown within the temperature range between 753 K and 923 K [25].

3.2. Effect of the carbon concentration on the graphene growth on nickel (111) surface

In this subsection, the effect of different carbon concentration on the graphene growth on the nickel (111) surface is discussed. For this purpose, three different systems containing 50%, 66.7%, and 100% of carbon concentration are annealed from 1000 K to the room temperature.

![Figure 3](image)

**Figure 3.** Initial and final configurations of the systems with (a) 50%, (b) 66.7%, and (c) 100% of carbon concentration on the nickel (111) surface. All the systems are annealed from 1000 K to the room temperature. Red, cyan, and black spheres represent nickel atoms, carbon atoms, and carbon chains, respectively.

In the system with 50% of carbon concentration, the carbon chain in the initial configuration makes a bond with another carbon on the surface to form a pentagonal carbon ring as shown in figure 3(a). When the concentration of the carbon atoms on the nickel (111) surface is increased to 66.7%, one new hexagonal and one new heptagonal carbon rings are formed from carbon chains and a broken pentagonal carbon rings that exist in the initial configuration as it is seen in figure 3(b). For the system with 100% of carbon concentration on the nickel (111) surface, the carbon atoms form one new pentagonal, two new hexagonal, and one new heptagonal carbon rings in addition to one pentagonal and one hexagonal carbon rings found in the initial configuration (figure 3(c)). These results are similar with the graphene growth process in the experiment that the number of hexagonal carbon rings is increased when more carbon atoms are supplied to the nickel (111) surface from the dehydrogenation reactions of carbon precursor molecules.
Figure 4. Populations of carbon rings and other forms of carbon as the function of carbon concentration on the nickel (111) surface after the annealing process from 1000 K until room temperature.

It can be seen from figure 4 that only 35% of carbon population forms the carbon rings in the system with 50% of carbon concentration on the nickel (111) surface. On the other hand, the populations of carbon atoms which form carbon rings increase to 75% for the system with higher concentration of carbon atoms on the nickel (111) surface.

3.3. Graphene growth on nickel (111) surface in the high concentration of carbon atoms

In this subsection, we demonstrate the graphitization process of the system with 100% of carbon concentration on the nickel (111) surface at growth temperatures of 800 K and 1000 K.

Figure 5. Initial, equilibrated, and final configurations of the graphene growth processes at (a) 800 K and (b) 1000 K using the system with 100% of carbon concentration. Red, cyan, and black spheres represent nickel atoms, carbon atoms, and carbon chains, respectively.
In the initial configuration shown in figure 5, the carbon structures on the nickel (111) surface consist of one pentagonal and one hexagonal carbon rings and the other structures. The new formations of two pentagonal, two hexagonal, and one heptagonal carbon rings are observed after the system are equilibrated at 800 K for 5 ps as shown in figure 5(a). The number of carbon rings does not change when the temperature of the system is decreased until room temperature.

It can be seen from figure 5 (b) that the carbon atoms form one new pentagonal, two new hexagonal, and one new heptagonal carbon rings after the equilibration at 1000 K. When the temperature is lowered to 300 K, the new carbon ring is not formed. The same mechanism is also observed in the graphene growth process at 800 K of annealing temperature.

This simulation result supports the experimental finding that the monolayer graphene can be grown on the nickel (111) surface at low temperature (~800 K) using high concentration of carbon atoms [25][26]. It is also confirmed from this result that the graphitization processes occur during the equilibration.

4. Conclusion
We have investigated the graphene growth mechanism on the nickel (111) surface using first principles MD simulations. The MD simulations have been carried out for various concentrations of carbon atoms and for different annealing temperatures. The optimum temperature for the graphene growth process on the nickel (111) surface is estimated as 1000 K. It has also been confirmed that the higher concentration of carbon atoms on the nickel (111) substrate provides the better graphene formation, as well as the capability of the graphene growth at low temperature (~800 K). Furthermore, the graphitization process occurs during the equilibration of the system.

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