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Tight-binding calculation of growth mechanism of graphene on Ni(111) surface

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Abstract. The nucleation of graphene on Ni surface, as well as on the step, is studied using a tight binding method of SCC-DFTB. The result demonstrates that the fcc configuration has the lowest total energy and thus is the most stable one compared to the other two structures when benzene ring is absorbed on the Ni(111) surface. The activity of marginal growth graphene's carbon atoms decreases from the boundary to the center, when they are absorbed on the substrate. Graphene layer can grow continuously on step surface formed by intersection of Ni(111) and Ni($1\bar{1}1$) surface. Meanwhile, a mismatch will occur between the graphene layer and Ni surface and thus leads to flaws when the layer grows larger. Reducing the mismatch between the graphene and the step surface will benefit the growth of graphene of large area and high quality.

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Key words: graphene, metallic substrate, surface structure, growth on step, tight binding approximation

1 Introduction

Since its discovery in 2004 [1], graphene has quickly become a hot topic of physical, chemical and material research and has a huge application potential in a variety of areas [2,3]. The controllable preparation of graphene of high quality and large size is extremely valuable in researches of its intrinsic physical properties and practical application. There are several methods to prepare graphene nowadays such as micromechanical cleavage [4], redox method [5], crystal epitaxial growth [6], transition metal catalyzed chemical vapor deposition [7] and so on. Among those above, chemical vapor deposition fairly controls

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*Corresponding author. *Email address:* `zhouchen0331@gmail.com` (C. Chen) the growth of graphene on metallic substrate by deciding the growth parameters such as proper substrate, temperature [8].

A good match of crystal lattice between graphene and metallic substrate will guarantee a large size of graphene of high quality and strong adhesive attraction. In 2008, Yu *et al.* [9] prepared graphene of high quality on Ni and controlled the thickness and defect of graphene. In 2009, Kim *et al.* [10] achieved epitaxial growth in the scale of centimeter on polycrystalline Ni films. With the development of this method, graphene or double-layer graphene can now cover 87 percent of the Ni surface [11]. Wang *et al.* [12] calculated and explored the properties of epitaxial growth of graphene on metal surface. Xu *et al.* [13] calculated the structural stability of graphene absorbed on Cu(111) and Ni(111) by first-principle calculations.

It is of great importance to explore the growth mechanism of graphene on metallic substrate in order to instruct the preparation of graphene with large size and high quality. The C atoms of graphene's growth mainly result from the catalytic decomposition of methane. On the surface of active metal like Pd [14] and Ru [15], methane can break down to carbon atoms directly. Because of the high solubility of carbon atoms, it is easy for methane to decompose on Ni surface [16]. While on Cu and other relatively inert metal surface, it is difficult for methane to dehydrogenate completely. Actually it tends to nucleate from the structure of CH_x [17].

Because substrate's surface activity on the step is higher than that on flat surface, the growth of graphene is easier on the step surface. Coraux *et al.* [18], found step-like structure on the surface and obtained graphene of very few impurity when prepared graphene on Ir(111) surface by low pressure chemical vapor deposition. Loginova *et al.* [19], released that the growth mainly occurs near the metallic step in a low density of carbon atmosphere, while occurs on both step and flat surface in a high density of carbon atmosphere. In 2010, Sprinkle *et al.* [20], found that graphene nanoribbon of high quality can grow on $(1\bar{1}\,0n)$ step surface of SiC crystal after pretreatment. Günther *et al.* [21], released more ordered monocrystal graphene film when researching epitaxial graphene on Ru(0001) surface by experiment method. Density functional theory calculation verified that the single step growth mode is the result of interaction between graphene and metal.

There are many experiment results in preparation of graphene on substrate before, but the growth mechanism is not completely clear. The researches in growth on step surface are fewer. By geometry optimizing and calculating the absorption energy with tight-binding theory method, this article explores the interaction between graphene and Ni substrate, marginal activity when growing on Ni substrate and then growth situation on Ni step substrate.

2 Calculating method

The calculation is based on self-consistent charge density functional tight-binding (SCC-DFTB) method DFTB+ package [22,23]. SCC-DFTB is a density functional theory originated in the tight-binding method. It approximates and parameterizes the exchange integral [24]. The Hamiltonian matrix elements after tight-binding approximation simplification are determined by the self-consistent charge [25]. The potential functions of ZnOrg-0-1 and pbc-0-3 [26] are adopted in the calculation. Structural relaxation optimizes all atomic positions by using the conjugate gradient algorithm. The convergence accuracy of atomic force is 0.05 eV / nm. The energy convergence criterion of electronic self-consistent calculation is 2.72×10^{-4} eV.

Compared to the molecular dynamics method, tight-binding method takes the charge transfer into consideration and has a broader scope and higher accuracy. Thus it is more suitable to structure model in this article. Compared to the first-principle calculation which is based on density functional theory [27], tight-binding method is fast and can calculate relatively large system. On the conditions of mature parameter, relatively accurate quantitative can be obtained [28–30].

3 Results and discussion

In this paper, the benzene ring is used to simulate graphene. The growth of a benzene ring on Ni substrate is explored. As the way of the growth is outward growth from the edge continuously, the method of increasing the number of C atoms in the edge is adopted to study the growth characteristics.

When studying the growth in step, the Ni($1\bar{1}1$) surface which is similar to Ni(111) surface is used to form the step with Ni(111) surface.

3.1 Benzene ring absorbed on Ni(111) surface

The growth method of graphene on a substrate surface is growing outward from the edge of small nuclear unit. Considering that carbon six-membered ring structure is the smallest repeating unit for the two-dimensional graphene, benzene is selected as the initial nucleation unit to explore the law of adsorption of graphene on Ni(111) surface. Ni crystal is a face-centered cubic crystal structure whose cycle period on (111) surface is three layers. Since the appearance of the substrate influences the graphene mostly, 4-layer Ni substrate structure is established. According to the difference of the relative position, there are three distinguished position of stable absorption: hollow, fcc and hcp. The benzene ring center is facing the Ni atoms from the first, second or third layer of the substrate surface [31]. For example, Fig. 1 shows the fcc structure model: benzene ring is placed parallel to the substrate. Here are calculations of three different relative position to obtain the most stable structure.

During the structural optimization, C atoms of benzene ring and the Ni atoms of the top layer can move freely. Meanwhile, the Ni atoms from the following three layers are fixed. There is little change in the atomic structure of Ni substrate and the benzene ring during optimization. The only change lies in the distance between the graphene and Ni substrate. The distance of three kinds of adsorption sites are all about 0.30 nm, little smaller than 0.34 nm, the distance between graphene layers caused by the effect of van der Waals force. This shows that the benzene structure has weak interaction with the substrate surface atoms.

To quantify the strength of adsorption, further calculation of system's adsorption energy ($E = E_0 - E_1 - E_2$) is conducted. In the formula, E_0 stands for the total energy of the system, E_1 stands for the energy of the benzene, E_2 stands for the energy of the Ni substrate. The adsorption energy of three kinds of adsorption sites is -1.0 eV for hollow, -1.3 eV for fcc, -1.2 eV for hcp. As the system stability is proportional to the adsorption energy, so the stability's size relation of the three structures is that: fcc > hcp > hollow. The adsorption energy of fcc structure is highest, so fcc structure is the most stable structure. Thus on the surface of Ni(111) substrate, the graphene structure most likely begins to grow in this way. Following discussion is based on the fcc structure.

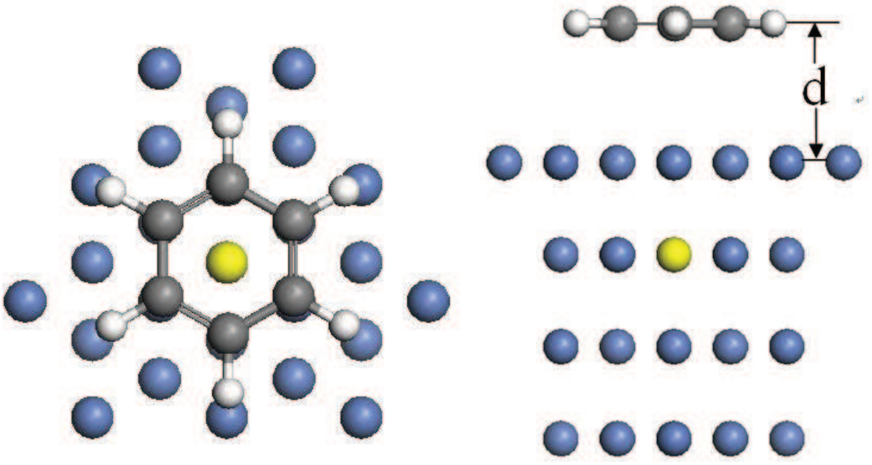

Figure 1: fcc structure of benzene ring absorbed on Ni(111) surface, top view(left) and side view(right)

3.2 Growth on conditions of different edge activity

In growth and expansion process of graphene, the activity of edge atoms plays a key role. In this article, the growth of graphene on conditions of different atomic activity at the edge is explored. Single C atom is added to the benzene ring in the three symmetric directions to explore the law of the interaction between newly added edge C atoms and the Ni substrate atoms. In the actual process of growth in large area, activity of the C atoms in center of a large graphene is similar to the six C atoms in the center in the model. Different numbers of H atoms are added to the edge to saturate the C edge atoms to different degrees. To be specific, in order to explore the growth of graphene edge, no H atom is added for C_9H_3, one H atom in each direction for C_9H_6, and two H atoms in each direction for C_9H_9.

Showed in Fig. 2, after structural optimization, large difference in bonding situation occurs among the three different model of C_9H_n. Table 1 shows the C-Ni bonding length and adsorption energy of each structure. It can be seen that the edge C atoms which are not passivated by additional H atoms are the most active due to the smallest saturation degree. They have the strongest interaction with the top substrate Ni atoms and form three C-Ni chemical bond. Meanwhile, because of the strong edge interaction and relatively short C-Ni bond (0.159 nm), C atoms and top Ni atoms are arranged in deformation to a certain degree. The previous calculation shows that the distance between the simple benzene ring and the first layer of Ni is 0.316 nm, is almost twice of 0.159 nm. So edge C atoms of C_9H_3 bond strongly with Ni atoms.

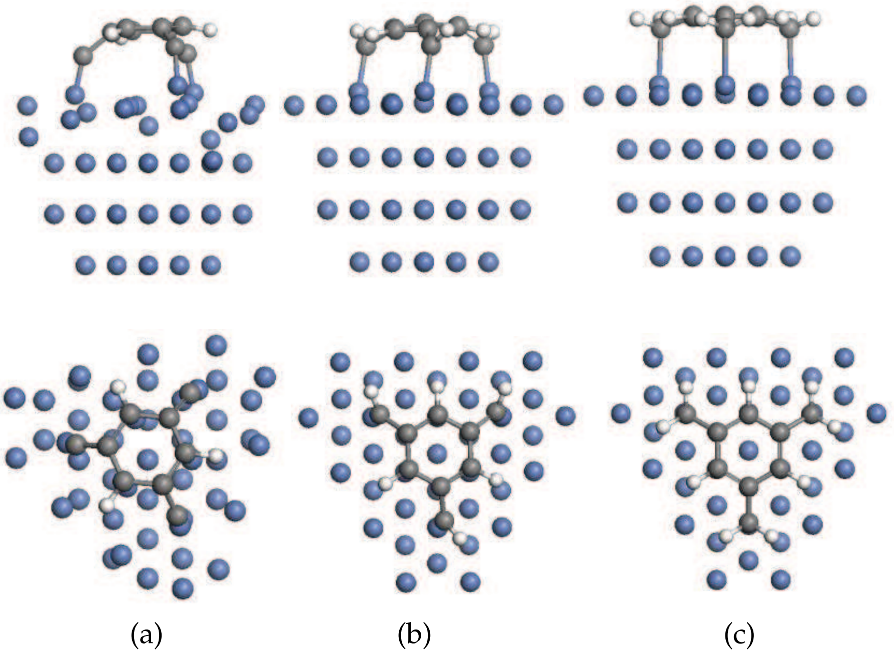
(a) (b) (c)

Figure 2: The optimized structures of (a) C_9H_3, (b) C_9H_6 and (c) C_9H_9, side view (up) and top view (down)

Table 1: The C-Ni bonding length of L_{C-Ni} (nm) and adsorption energy E_b (eV) of the structure of C_9H_n.

Structure	C_9H_3	C_9H_6	C_9H_9
LC-Ni	0.159	0.182	0.218
Eb	1.45	0.78	0.64

C_9H_6 structure is formed by adding a hydrogen atom to the edge C atoms, which can be regarded as a transitional structure for further growth. The outermost edge C atoms gradually become the internal C atoms. At this point the edge C atoms are still obviously bonding with the Ni substrate, and the average bonding length of C_9H_6 structure is 0.182

nm. What's more, the flatness degree of the Ni surface is higher than that of C_9H_3. Therefore, it can be concluded that the activity of the edge C atoms of C_9H_6 is less than those of C_9H_3. As for the structure which is added two hydrogen atoms to in each direction, it is to say C_9H_9, the saturation situation of the three C atoms is similar to the internal C atoms. Showed in Fig. 2, the flatness degree of graphene layer and the top Ni atoms were significantly higher than C_9H_3 and C_9H_6, more similar to former simple fcc structure.

According to Table 1, the size relation of the edge C-Ni bonding length among the three structures is that: $L\text{-}C_9H_3 < L\text{-}C_9H_6 < L\text{-}C_9H_9$. Meanwhile, the middle part of graphene also gradually rises up and forms a flat graphene sheet. It is obvious that with the growth of graphene, the original edge C atoms gradually transform into the middle C atoms. Meanwhile, their activity gradually reduces, which also reflects in the surface absorption energy. The size relation in adsorption energy among the three structure is that: $E_b\text{-}C_9H_3 > E_b\text{-}C_9H_6 > E_b\text{-}C_9H_9$. The higher the adsorption energy is, the more active the edge C atoms are. It is consistent with the law of the bond strength.

3.3 Growth of graphene on step surface

The activity of metal atoms on step is generally higher than that of atoms on plane. Therefore, it will be easier for graphene to grow on step. Exploring the growth law of graphene on step plays a significant role in preparation of graphene devices and graphene with specific shape. Taking this in consideration, growth situation of graphene on step is explored.

Because of the crystal symmetry, three other surface called Ni($\bar{1}11$), Ni($1\bar{1}1$) and Ni ($\bar{1}\bar{1}1$) are the same with Ni(111). In order to explore the growth situation of graphene on step, in other words, the possibility that bent graphene layer grows on the step and is still absorbed on the substrate, structure model is built, showed in Fig. 3. Two parts of graphene layers which is based on the fcc structure are separately added on Ni(111) surface and Ni($1\bar{1}1$) surface. H atoms are added to edge C atoms.

After structural optimization, the graphene layers on the two crystal faces grow up

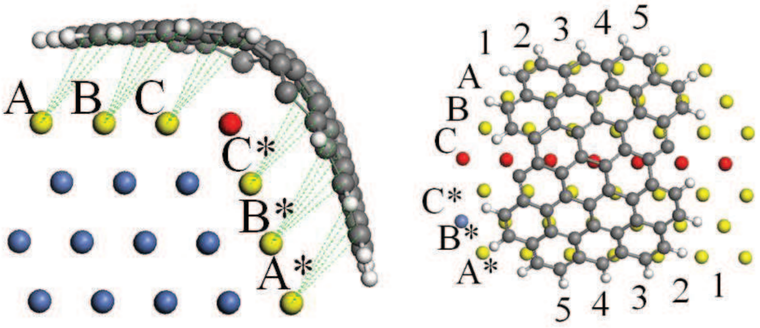

Figure 3: The growth condition of graphene on step

together and are still absorbed flat on the Ni surface. Contrary to fine match between C atoms and Ni atoms on single Ni(111) substrate, there is an obvious deflection dislocation between graphene layer and Ni substrate layer. As showed in the left one in Fig. 3, dotted lines are the lines between C atoms and the corresponding Ni atoms. From the side view, the lines are like an umbrella because the deflection dislocation between graphene layer and substrate layer leads to a dislocation in the lines. Showed in the right part of the Fig. 3, the Ni atoms at the intersection of two planes are marked in red. There is an obvious angle deflection between zigzag chain of C atoms and red chain of Ni atoms.

The variation tendency of distance between C atoms and corresponding Ni atoms is offered in Fig. 4. On the flat plane, the distance declined from left to right and is bigger than 0.316 nm basically. While on the slope plane, the law is opposed. It is because that the relative deflection between graphene and Ni substrate is second rotational symmetry related to carved lines of the surface angle. From the value of the data, conclusion can be draw that the growth situations on flat plane and slope plane are similar. The distance between C atoms and their corresponding Ni atoms also basically exceed 0.316 nm. Meanwhile, on both the flat plane and the slope plane, the angle deviations are both 11°. This result means that two graphene layers can link to each other after rotate with an equal degree on two symmetry planes which have a certain included angle.

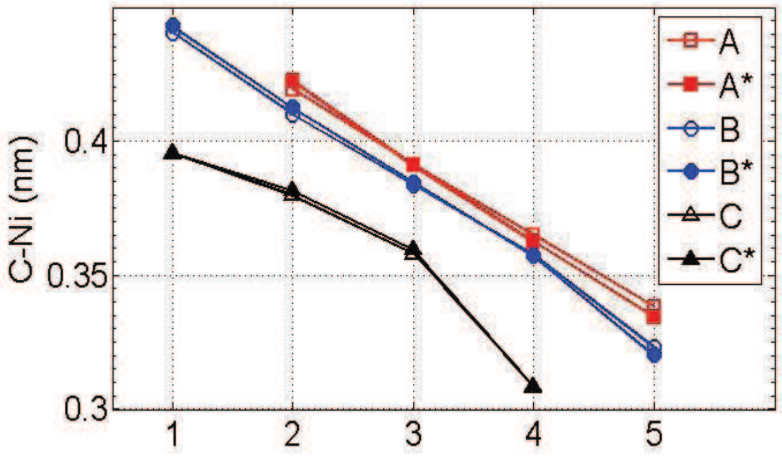

Figure 4: The distance between C atom and the corresponding Ni atom

At the same time, no matter on the flat plane or the slope plane, the distance between C atoms and their corresponding Ni atoms increases when the C atoms become remoter to the intersection of the surfaces. It shows that the mismatch degree between graphene and the substrate increases when the C atoms stand off the intersection. It can be predicted that the mismatch degree will be so big that lots of defects form on condition of a large area of graphene. Thus, the stability of graphene growth on Ni substrate decreases. Improving the match degree between graphene and the step surface will be a necessary precondition to prepare large areas of high quality graphene.

4 Conclusion

This article explores the growth mechanism of graphene on Ni substrate by SCC-DFTB method, and then the situation of growth on step area. Through structural optimization of three different absorption position named hollow, fcc and hcp, the fcc structure is found to be the most stable one with the biggest absorption energy. Benzene ring on the Ni(111) can absorb C atoms around it and then expand itself to a large area of graphene. The activity of C atoms declines from edge to the center. When the crystal structure of the flat plane and the slope plane is similar, graphene show a property of continuous growth but a deflection disposition at the same time. It can be predicted that relatively large number of defects will be formed when graphene grows in the step surface to a large area. According to what have been demonstrated, as for metal polycrystalline substrate, improving the match degree between graphene and step-like metal substrate will be an effective way to reduce flaws and improve stability.

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