J. At. Mol. Sci.
doi: 10.4208/jams.101411.111611a

Vol. **3**, No. 3, pp. 270-278
August 2012

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

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Received 14 October 2011; Accepted (in revised version) 16 November 2011
Published Online 18 February 2012

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.

PACS: 31.15.-p

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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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 orig-