Surface energy anisotropy of iron surfaces by carbon adsorption

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Received 14 May 2003; received in revised form 30 June 2003; accepted 2 July 2003

Abstract

To investigate the surface energy anisotropy of carbon-adsorbed iron surfaces related to carbon nanotube growth we have performed self-consistent pseudopotential density-functional calculations. The iron particle’s equilibrium shape is obtained from the Wulff construction using the calculated surface energies. We investigate the adsorption and diffusion of carbon atoms on the iron surfaces. It is found that the desorption energy of the carbon atoms and the activation energy for carbon diffusion are very different on different facets. Using the energetics of carbon-adsorbed iron surfaces, we evaluate the formation energies of the surfaces as a function of carbon chemical potential. Since the surface energies of the low-index iron facets are affected differently by the presence of carbon, the crystal shape is changed correspondingly.

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PACS: 68.10.Cr; 68.35.Fx; 68.35.Bs; 71.15.Hx; 71.15.Nc
Keywords: Ab initio density-functional calculations; Surface energy; Surface diffusion; Carbon; Iron; Crystal shape; Growth

Since the first discovery of the carbon nanotubes (CNTs) [1], a lot of efforts have been made to synthesize CNTs for technological applications. For the nanotubes to be used for practical devices such as field emission display, it is important to control size (diameter and length), vertical alignment, low temperature growth, etc. A large-scale synthesis of well-aligned CNTs has been achieved by various chemical vapor deposition (CVD) methods [2–4]. In the CVD process, transition metal catalysts such as Fe and Ni play an essential role in the nucleation and growth of aligned CNTs. Catalysts can be prepared in the form of particles by the etching process. The size of the catalytic particles is known to determine the size of CNTs. The acetylene on iron is a prototype of the catalytic growth of CNTs, which shows a large yield of CNTs and the homogeneous distribution of the tube diameter [5]. The hydrocarbons such as acetylene are known to easily decompose into carbon and hydrogen on transition-metal surfaces [6]. Then hydrogen usually desorbs in the form of H₂ under the CNT growth condition, and carbon atoms will cover the iron surfaces. Therefore, it is worthwhile to study the adsorption and diffusion behaviors of carbon atoms on the iron surfaces in the initial stage of CNT growth.

In this study we mainly focus on energetics of the carbon-adsorbed iron surfaces that can be obtained after hydrogen desorption. First, we obtain the equilibrium crystal shape of the bare iron particle from the Wulff construction using the calculated surface energies of low-index iron surfaces. Then, we investigate the adsorption and diffusion of carbon atoms on the iron surfaces. The surface formation energies of carbon-adsorbed iron are evaluated as a function of the carbon chemical potential. Upon carbon adsorption, the crystal shape due to changes in the surface energy anisotropy is investigated.

To evaluate the formation energies of low-index surfaces of bare and carbon-adsorbed iron, we have performed ab initio calculations within generalized gradient approximation (GGA) using a spin polarized version of the Vienna ab initio simulation package (VASP) [7]. The atoms are represented by ultrasoft potentials as provided with VASP [8]. We use a kinetic energy cutoff of 287 eV. In order to simulate the bare iron surfaces we use a symmetric slab model with (1 × 1) surface supercell consisting of seven layers of iron, and a vacuum region equivalent to at least 10 Å. In the surface
In order to compare surfaces with different carbon adsorption (coverage), we consider the formation energy of each surface as a function of the carbon chemical potential, \( \mu_C \). Then the equilibrium shape of the iron particle is studied using the Wulff construction \([9]\). The formation energy \( \Omega \) is defined \([10]\) as

\[
\Omega = E - n_{Fe}\mu_{Fe} - n_C\mu_C,
\]

where \( E \) is the total energy of a surface at zero temperature, and \( n_{Fe} \) and \( n_C \) are the numbers of Fe and C atoms, respectively. We use the bulk energy for \( \mu_C \). The surface energy \( \gamma \) is then taken as the formation energy divided by the surface area. Temperature dependence of the surface energy is mainly incorporated through the chemical potential of carbon. Although the CNT growth is a highly nonequilibrium process, the study of equilibrium systems would be the first step in understanding the initial growth behaviors.

First we investigate the equilibrium shape of the bare iron particle by evaluating the surface energies of low-index surfaces such as \((100)\), \((110)\), and \((111)\), which are obtained by setting \( n_C = 0 \) in Eq. (1). The calculated surface energies of iron are shown in Table 1. The theoretical values are larger than the experimental value (2.15 J/m\(^2\)) at 1400 °C \([6]\), which is expected because of the dependence of surface energy on temperature is usually given by the relation: \( \gamma(T) = \gamma(0)(1 - T/T_c)^n \) with \( n \sim 1 \), where \( T_c \) is the critical temperature at which the condensed phase vanishes.

The anisotropy of the surface energy \( \gamma(\theta) \) determines the equilibrium crystal shape of the crystals \([9]\). The procedure to find the crystal shape is given in Ref. \([11]\). To construct the crystal shape from the surface energy results, we mark the energy points corresponding to the \((100)\), \((111)\) and \((110)\) facets along the respective directions. We then assume the Wulff plot makes concave contact with those points, in order to obtain the crystal shapes related to these points of the surface energy function. The crystal shape viewed from \([011]\) direction is shown in Fig. 1(a). For another view of the crystal shape we plot it in \(xz\) plane, which is shown in Fig. 1(b).

From these plots, it is found that the surface areas of these low-index facets are comparable since the surface energies of three low-index iron surfaces are very close each other.

In many experiments of CNT growth, the iron can be prepared in the form of particles by etching the iron thin films. Since the iron particles consist of several facets, it will be important to consider the role of facets to understand the CNT growth mechanism by investigating the diffusion and reaction of carbon atoms on iron facets. Since, from the results of the crystal shape, the areas of the low-index facets are comparable each other, we need to consider the diffusion and reaction of carbons on all the low-index facets considered here, which will be an important issue in relation to the CNT growth when the iron particles are used as catalysts.

In order to understand the adsorption behavior of carbons in the initial stage of CNT growth, we investigate the adsorption of carbon atoms on the iron surfaces. The desorption (adsorption) energy \( E_{\text{des}} \) \((E_{\text{ads}}) \) per carbon atom from the surface is defined as the energy difference per surface site between the carbon-adsorbed surface and the bare surface plus a free carbon atom. To find a stable configuration of carbon atoms (monomer or dimer) on each surface, we calculate the total energies
energy D cell, from which we obtain the (approximate) activation potential energies of some points on each surface unit the diffusion behavior of carbon atoms, we calculate the energies of the strongest binding site on each surface are 0.78 and 0.16 eV per carbon atom, respectively. The desorption energies on the (100) and (110) surfaces, the strongest binding site of a carbon atom is the center site of the (1×1) surface unit cell of each surface where the adsorbed carbon is located atop the second-layer iron atom as shown in Fig. 2(a) and (b). On the (111) surface, the strongest binding site is also shown in Fig. 2(c), while the sites on the top of the second-layer and third-layer iron atoms are higher in energy by 0.78 and 0.16 eV per carbon atom, respectively. The desorption energies of the strongest binding site on each surface are given in Table 1. On the other hand, for investigation of the diffusion behavior of carbon atoms, we calculate the potential energies of some points on each surface unit cell, from which we obtain the (approximate) activation energy $\Delta E^\text{act}$ for diffusion of a carbon atom on each surface (see Table 1). The diffusion of carbon over the bridge centers on the (100) and (110) surfaces has the barrier of about 1.3 and 1.0 eV, respectively. On the (111) surface, the carbon located on the most stable site shown in Fig. 2(c) will diffuse to any closest equivalent site over the top of the nearest second-layer or third-layer iron atom with the barrier of about 0.8 and 0.2 eV, respectively. Thus, the diffusion barrier for the overall carbon diffusion is about 0.8 eV on the (111) surface.

For the carbon monomer, the binding energy is strongest and the activation energy is largest on the (100) surface, thus the carbon atoms are likely to be strongly adhesive on the (100) surface. Therefore, the (100) surface will be quickly covered up by carbon atoms. On the other hand, the (111) surface shows the weakest binding and smallest activation energies. Thus, the {111} facet of the iron particle is likely to be the most reactive in diffusion and reaction of carbon atoms while the {100} facet is least reactive. Thus the desorption and activation energies are different on each facet, so the diffusion behaviors of carbon atoms are also different.

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Also, we find the most stable site for the carbon dimer on each surface among the several possible configurations. The most stable sites are shown in Fig. 3, where the carbon dimer is found to be parallel to each surface. On the (100) surface, the configuration shown in Fig. 3(a) is the most stable with the binding energy of 7.63 eV/carbon, while the configuration with a carbon dimer located on the center of (1×1) unit cell lying along the [001] direction is higher in energy by 0.13 eV/C. On the (110) surface, a carbon dimer of which each atom is located on the bridge center along the [001] direction is higher in energy by 0.44 eV/C than the most stable dimer with the binding energy of 7.45 eV/C shown in Fig. 3(b), while a carbon dimer on the bridge center along the [111] direction is higher in energy by 0.48 eV/C than the most stable dimer. On the other hand, a configuration with a carbon dimer along the [TT2] direction on the top of a third-layer iron atom on the (111) surface is slightly higher in energy by about 0.03 eV/C than the most stable configuration with the binding energy of 7.95 eV/C shown in Fig. 3(c).

Finally, using the above results of energetics of adsorption of carbon atoms, we investigate the surface energy anisotropy of the iron surfaces by considering the surface energies as a function of the carbon chemical potential $\mu_C$ (Eq. (1)). The results for surface energies are plotted in Fig. 4. If the carbon chemical potential is too low, carbon adsorption is not energetically favorable and the bare surface has the lowest formation energy. This is represented by the horizontal lines toward the left of the figure, which give the surface energies of bare surfaces. With increasing carbon chemical potential, the curves enter the surface phase with adsorbed monomers after a slope change. This happens on the (100) and (110) surfaces at the $\mu_C$ values of $-9.48$ and $-9.20$ eV, respectively. The (100) and (110) surfaces further changes its slope with increasing $\mu_C$ going into the phase with adsorbed dimers at $-8.41$ and $-8.33$ eV, respectively. However, the (111) surface goes from the bare surface phase to the phase with adsorbed dimers at the $\mu_C$ values of $-9.27$ eV, without having the intermediate phase with monomers adsorbed on the surface.

As seen in Fig. 4, the differences in surface energy between the carbon-adsorbed iron surfaces are not the same as those in surface energy between the bare iron.
surfaces at a given \( \mu_C \). The adsorption of carbon completely change the relation between the surface energies. If we again use the Wulff construction to make the crystal shape of an carbon-adsorbed iron from the calculated surface energies for a given \( \mu_C \), we will find a crystal shape different from that of the bare iron shown in Fig. 1: the crystal shape of the carbon-adsorbed iron including the relative area of each iron facet changes with carbon chemical potential. Since the surface energy of the low-index iron facets are affected differently by the presence of carbon, the iron particle can change its shape due to adsorption of carbon atoms (in the carbon-related growth using the iron catalyst), i.e., thus the surface energy anisotropy changes the crystal shape of the iron catalyst particle. Also, the surface energy anisotropy induced by carbon adsorption will change adsorption properties of incoming carbons and their diffusion behaviors. Therefore, the surface energy anisotropy of the carbon-adsorbed iron surfaces will play an important role in the CNT growth using iron as catalyst.

In summary, we investigated the adsorption and diffusion of the carbon atoms on the low-index (100), (111) and (110) surfaces of iron. The binding energy of the carbon atoms and the activation energy for carbon diffusion were found to be very different on different low-index facets, thus diffusion behaviors will also differ. The surface formation energies of the iron surfaces were evaluated as a function of the carbon chemical potential. Upon carbon adsorption, the crystal shape due to changes in the surface energy anisotropy was investigated. Finally, it is worth noting that this study of role of facets will be closely related to a base growth model proposed for the CNT growth [12].

Acknowledgements

This work was supported from KOSEF and Center for Nanotubes and Nanostructured Composites (CNNC). The author would like to acknowledge the support from the KISTI under Grand Challenge Support Program with Dr. Sang Min Lee as the technical supporter. The use of the computing system of the Supercomputing Center is also greatly appreciated.

References