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## Ab initio Study of Metal Atoms on SWNT Surface

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### ABSTRACT

Interactions of metal atoms (Al, Ti) with semiconducting single walled carbon nanotube (SWNT) are investigated using first-principles pseudopotential calculations. Six different adsorption configurations for aluminum and titanium atoms are studied. Comparison of the energetics of these metal atoms on (8,0) SWNT surface shows significant differences in binding energy and diffusion barrier. These differences give an insight to explain why most of metal atoms (such as Al) form discrete particles on nanotube while continuous nanowires are obtained by using titanium in the experiment.

### INTRODUCTION

Carbon nanotubes [1] have induced great research interests due to their unusual physical, chemical and mechanical properties [2-5]. These unique properties make them an ideal candidate for the building blocks of molecular scale machines and nanoelectronic devices [6-9]. One of the proposed applications is to use carbon nanotubes as templates to obtain a variety of nanowire materials [10]. Both experimental and theoretical studies of metal-nanotube systems are necessary to achieve metal nanowires using nanotubes [11, 12].

Recently, it has been reported that metal nanowires can be formed by coating various metals on suspended single walled carbon nanotubes (SWNT) using electron beam evaporation [13,14]. Many types of metal atoms (such as Au, Al, Fe) form discrete isolated particles on nanotubes while Ti coating on the suspended tubes are continuous. Other metals can also form continuous nanowires by depositing metal atoms (Au, Al, Fe, etc) on the first coated buffer layer (or adhesion layer) of Ti nanotube nanowire. The experiments show that different metal atoms have different binding characters on the nanotube surface that correspond to different macroscopic coating phenomena. These experimental results suggest that structural and chemical characteristics of metal-tube systems are sensitive to the identity of metal atoms and motivate a detailed theoretical study to investigate the interactions between nanotubes and various metal atoms.

Although the interactions between deposited metal atoms with graphite (or graphene sheet) and  $C_{60}$  have been extensively studied [15,16], a detailed theoretical account for the interactions between various metals and nanotubes is currently lacking. The interactions of metal atoms with SWNTs offer another challenging problem since the characteristics of these interactions would be quite different from graphene sheet and  $C_{60}$ . This is because SWNTs are quasi-one dimensional, and this confined geometry makes the chemistry of SWNTs significantly different from those of two dimensional graphene sheet and finite molecule  $C_{60}$ . Nanotubes are different from graphite or graphene sheet because nanotubes have curved geometry that induces rehybridization of carbon bonding orbitals (non-planar  $sp^2$  bonding configuration) [17,18]. These different bonding character and geometry have lead to significantly different nanotube electronic structure from that of graphite or graphene sheet. On the other hand,  $C_{60}$  is a finite

molecule, and has pentagons in its structure whereas the sidewall of a nanotube normally contains only hexagons. Consequently,  $C_{60}$ 's carbon bonding orbitals have more  $sp^3$  like bonding character which induces much more reactive binding affinity with metal atoms than SWNTs.

Recent tight-binding study of Ni atoms on the armchair SWNTs [19] has addressed an important issue of curvature effect that the interactions of metal atoms with a nanotube is quite different from those with graphene sheet in terms of binding energy, binding character, and charge transfer. Another important issue of why some of metal atoms (Au, Al, Fe, etc) form discrete particles on nanotubes while Ti atoms form continuous nanowire coating is still calling for a detailed theoretical investigation. This paper presents results of first-principle pseudopotential calculations for two representative metal atoms (Al and Ti) interacting with (8,0) semiconducting SWNT. Six different adsorption configurations have been studied. The calculated binding energies, diffusion barriers and diffusion rates shed a light on why Ti atoms form continuous nanowires while Al atoms form isolated discrete particles.

## SIMULATION METHOD

In order to obtain a detailed understanding of the metal nanotube interaction and metal coating behavior, first principles calculations are performed with the DFT++ program [20] using density functional theory (DFT) within the local density approximation (LDA) [21] for two representative systems of Al atom and Ti atom on (8,0) SWNT. Kohn-Sham single-electron wave functions are expanded by efficient plane waves in the supercell  $12 \times 12 \times 4.29 \text{ \AA}^3$  with 40 Rydberg cutoff energy. The Brillouin zone sampling is approximated by six k-points along the tube axis, which is shown to a good approximation for (8,0) and (10,0) nanotubes [22,23]. The structure of an isolated (8,0) SWNT is optimized by fully relaxing the tube structure to the minimum total energy configuration. This relaxed configuration is used for the rest of the simulations. Calculations for the Al-SWNT and Ti-SWNT systems are carried out by relaxing the position of a metal atom on the tube surface with a constraint of maintaining its relative position on a hexagon as shown in figure 1. Carbon atoms near the metal atom are also fully relaxed with the remnant forces of less than  $0.1 \text{ eV/\AA}$ . For these calculations, the error bar of  $\pm 0.05 \text{ eV}$  was estimated for relative energy differences.

## RESULTS AND DISCUSSION

To investigate and carefully study the interactions of single metal atoms (Al and Ti) with (8,0) SWNT, six distinct sites are considered for a single metal atom adsorption on the nanotube surface. Figure 1 shows schematic diagrams of six different adsorption sites for a metal atom (Al or Ti) on the (8,0) SWNT. These six sites in figure 1 are described as follows. (1) A metal atom directly above a C atom is called as Direct Top Site (DT). (2) A metal atom over a C-C bond at a distance of one quarter of C-C bond length is called Bond Quarter Site (BQ). (3) A metal atom over a C-C bond at the middle of C-C bond length is called Bond Middle Site (BM). (4) A metal atom above the long diagonal of a hexagon (Path 2 in Fig. 2) at one quarter of the diagonal length (which is twice of C-C bond length) is called Hexagon Quarter 1 Site (HQ1). (5) A metal atom above the short diagonal of a C-C hexagon (Path 3) at one quarter of the diagonal length

(which is  $\sqrt{3}$  of C-C bond length) is called Hexagon Quarter 2 Site (HQ2). (6) A metal atom directly above the center of a hexagon is called Hexagon Center Site (HC).

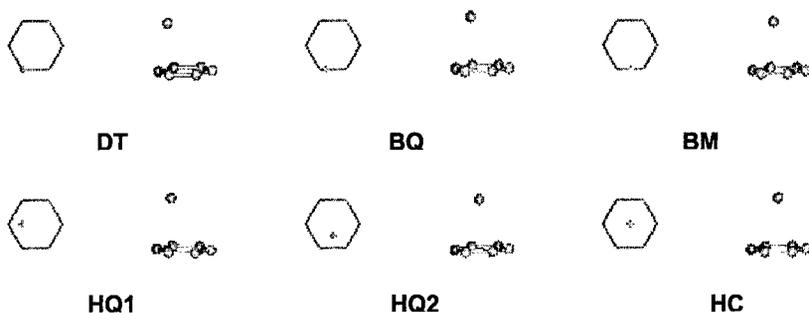


Fig. 1. Schematic diagram of six different configurations of a single metal atom on the (8,0) SWNT surface.

These six distinct sites of a metal atom on the nanotube surface described in figure 1 give three possible diffusion paths for a metal atom to follow on the surface. A schematic diagram of these three diffusion paths is shown in figure 2. Path 1 describes a metal atom diffusion along the C-C bond. Path 2 shows that a metal atom jumps from the top of a carbon atom into the center of hexagon and jumps on top of another carbon atom. Finally, path 3 shows a metal atom diffusion from the center of a C-C bond into the center of hexagon and to another BM site. Six distinct bonding sites combined with three different diffusion paths also describe the rest of the hexagon through symmetry and consequently provide a clear picture of how a single metal atom (Al or Ti) interacts with nanotube not only from the energy point of view but also from kinetics point of view.

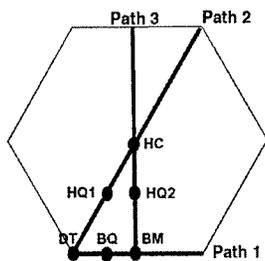


Fig. 2. Schematic diagram of three different diffusion paths representing possible paths for a metal atom to follow on the surface of a nanotube.

The calculated binding energies and binding distances for these six different binding sites are summarized in the Table 1. Table 1 shows that the metal atom over the center of a hexagon ring is the most stable binding site for both Al atom and Ti atom. The quantitative results of the binding energy and binding distance between these two metal atoms (Al and Ti) and (8,0) SWNT clearly show that the binding energy for Ti atom ( $2.27 \pm 0.05$  eV) is significantly larger than that of Al atom ( $1.25 \pm 0.05$  eV). This result is consistent with the experiment [13] where Ti atoms deposited on nanotubes exhibit the higher condensation and sticking coefficient than other metal atoms including Al atom.

Table 1. Summary of the binding energy and binding distance for Al or Ti single atom on (8,0) nanotube surface at six different locations.

Bonding Location		Binding Energy (eV) ( $\pm 0.05$ eV)	Binding Distance (Å)
Al-SWNT (8,0)	Direct Top Site (DT)	-1.13	2.21
	Bond Quarter Site (BQ)	-1.17	2.17
	Bond Middle Site (BM)	-1.20	2.14
	Hexagon Quarter 1 Site (HQ1)	-1.12	2.01
	Hexagon Quarter 2 Site (HQ2)	-1.20	1.93
	Hexagon Center Site (HC)	-1.25	1.82
Ti-SWNT (8,0)	Direct Top Site (DT)	-1.63	1.97
	Bond Quarter Site (BQ)	-1.81	2.00
	Bond Middle Site (BM)	-1.87	1.98
	Hexagon Quarter 1 Site (HQ1)	-1.93	1.83
	Hexagon Quarter 2 Site (HQ2)	-1.97	2.15
	Hexagon Center Site (HC)	-2.27	1.63

Based on the quantitative result of the binding energies between metal atoms and the nanotubes, the metal atom diffusion barriers on the nanotube surface along three different paths are shown in figure 3. The result clearly indicates that path 3 in which metal atoms jump from one center of the carbon hexagon ring to a nearby hexagon center gives the lowest diffusion barrier as well as short diffusion length both for Al atom and Ti atom. It is worth to notice that Al atom shows very small energy diffusion barrier ( $\sim 0.05$  eV comparable to error bar) while Ti atom has a significant diffusion barrier ( $\sim 0.4$  eV). These different diffusion barriers allow Al atoms move around the nanotube surface much more rapidly than Ti atom since  $0.05$  eV is comparable to the thermal kinetic energy at room temperature. Using the transition state theory for a simple diffusion model, the kinetics of these metal diffusions on the nanotube surface can be quantitatively described. Since the diffusion frequency ( $\Gamma_{diff}$ ) can be described by the equation  $\Gamma_{diff} = \nu \exp(-\Delta E_d / k_B T)$ , where  $\nu$  is the attempt frequency that is  $1.55 \times 10^{12} \text{ sec}^{-1}$  for Al and  $2.84 \times 10^{12} \text{ sec}^{-1}$  for Ti respectively estimated from the energy curves in figure 3.  $\Delta E_d$  is the diffusion energy barrier, and at  $T=300\text{K}$ , the calculated diffusion frequency for Al atom is

$2.25 \times 10^{11} \text{ sec}^{-1}$  and that of Ti atom is only  $5.57 \times 10^5 \text{ sec}^{-1}$  which is 6 orders of magnitude smaller than Al atom case. These low activation barrier for diffusion and the corresponding high diffusion rate of Al atoms on (8,0) SWNT surface lead to rapid hopping of Al atoms. On the other hand, higher diffusion energy barrier and lower diffusion rate make Ti atoms stay in the middle of the hexagon ring much longer ( $\sim 1 \mu \text{ sec}$ ) before jumping to a neighboring site.

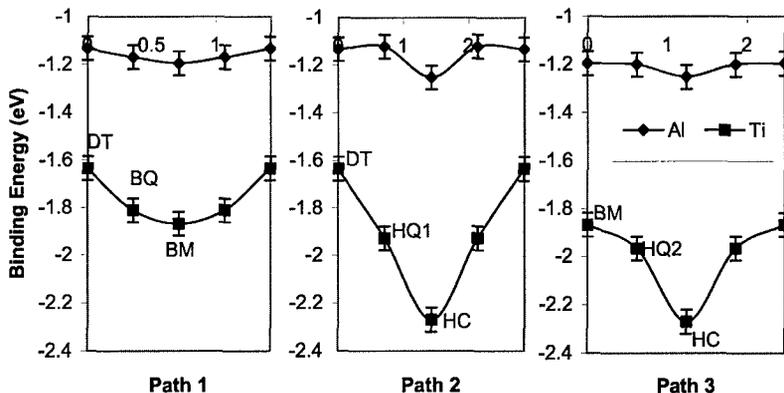


Fig. 3. Binding energy plots for Al and Ti metal atoms on the SWNT sidewall along three different diffusion paths. Error bars of  $\pm 0.05 \text{ eV}$  are also shown in the plots.

Combined with binding energy investigation and diffusion kinetics, the first step explanation of why Ti atoms form continuous coating while Al atoms form discrete isolated particles on the nanotube walls can be provided as follows. The weak Al-SWNT interaction due to small binding energy points to low cluster nucleation barrier. The low nucleation barrier and high diffusion rate for Al atoms cause them to easily form clusters through thermal activation processes. Since the cohesive energy of Al atom in bulk phase is  $3.39 \text{ eV}$  [24] (much higher than the Al-SWNT binding energy of  $1.25 \pm 0.05 \text{ eV}$ ), these Al atoms tend to form small cluster in a short time as they rapidly move on the nanotube walls and collide with each other. This mechanism qualitatively explains discrete isolated particles observed in the experiment [14]. On the contrary, Ti atoms tend to form much stronger binding with nanotubes leading to high nucleation barrier and high sticking coefficient than other metals. When Ti atoms come onto the nanotube surface through electron beam evaporation, these Ti atoms will find the most favorable binding site (over the center of carbon hexagon ring). The chance of these Ti metal atoms to jump out of one site and diffuse into other location to collide with other metal atoms and to merge into a small cluster is very small (by factor of million) compared to other metal atoms. These Ti atoms stay long time at the centers of the carbon hexagon rings and uniformly cover the

nanotube surface. This qualitative argument explains why Ti coating on nanotubes is very uniform and continuous.

It is important to note the current analysis considers only single metal atom on the nanotube surface, and gives only the first step physical explanation of different coating phenomena appeared on the suspended nanotubes. The questions of what will happen when two metal atoms collide with each other and how small cluster will form for most of the metal atoms are still left for future theoretical investigations. The problem of cluster formation or continuous coating formation is under investigation now, and the results will be published later.

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