

Electronic Structure Tailoring and Selective Adsorption Mechanism of Metal-coated Nanotubes

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Received August 11, 2007; Revised Manuscript Received November 27, 2007

ABSTRACT

Effects of various metal coating (Co, Ti, Pd, W, and Ru) on electronic structures of carbon nanotubes are systematically studied by both *ab initio* calculations and field-emission experiments. The theoretical results indicate that the adsorption of metal atoms leads to substantial changes in the band structures and work functions of nanotubes. In particular, titanium is found to be the most effective coating material for the application of nanotubes to the field emission display, by lowering the work function and increasing the local density of states near the Fermi level. This is confirmed by the field-emission experiments using Ti-coated nanotubes, which shows enhanced emission performances. In addition, it is found that the Ti coating extends the lifetime of the nanotube substantially. Through the thermogravimetric analysis and theoretical modeling, we propose that this is related to the role of metal coating as a protection layer against residual gases such as oxygen, which cause the degradation of nanotubes. The applications of metal-coated nanotubes to other types of electronic devices are also discussed.

Ever since the discovery of carbon nanotubes (CNTs) in 1991,¹ the application of CNT to the mainstream industrial products has been a key issue. Despite several outstanding chemical and physical properties inherent to CNT, there are few reports on the actual devices fabricated with CNT as a base material. This is in part attributed to the fact that bare CNTs alone cannot satisfy all requirements of actual applications. As a result, considerable efforts have been directed toward tailoring electrical and mechanical properties of CNT through various methods. Among them, the doping or coating methods have been known as practically viable approaches to tailor electrical properties of CNTs.^{2–3} In particular, hybrid materials made of metals (or metal oxides) and CNT have been attracting much attention because both tailoring of electrical properties and reinforcement of mechanical properties can be achieved by simple coating processes. The coated metals (or metal oxides) on CNT can modify the electronic structure of CNTs through a charge transfer and orbital hybridization. In addition, metals (or metal oxides) are likely

to passivate defect sites on the CNT surface, thereby stabilizing CNT mechanically as well as chemically.⁴

In this letter, we explain the mechanism of electronic structure tailoring and selective gas adsorption of the metal-coated CNTs. Specifically, we are interested in applying metal-coated CNTs to electron emitters in the field emission display (FED).⁵ Theoretical predictions using density functional calculations provided a useful guideline to select candidate metal species. The actual experiment on the CNT coated with selected metals verified that the field emission properties are enhanced with an increased lifetime. The advantage of using metal-coated CNT in other nanodevice will be also discussed based on our theoretical models.

Calculations on the atomic binding energies and electronic structures of metal-coated CNTs were performed with a spin-polarized *ab initio* pseudopotential calculation within the local density approximation using a plane-wave basis set.^{6,7} The ultrasoft pseudopotentials⁸ were employed with the cutoff energy of 300 eV. The *z*-direction lies along the nanotube axis, and the lateral (*xy*) dimensions of the tetragonal supercell were set to be large enough to avoid the intertube interaction (separated by more than 8 Å). The Brillouin zone of the supercell was sampled by $1 \times 1 \times 8$ Monkhorst–Pack *k*-point generation scheme. The atomic coordinates were relaxed until the Hellmann–Feynman

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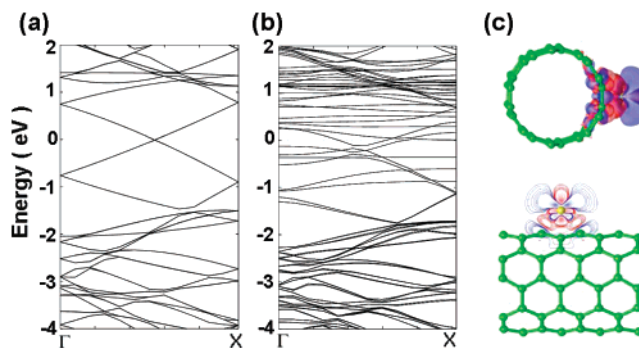
Table 1. Binding Energies and Work Functions for Various Metal-Coated (5,5) Nanotubes

Metal	Co	Ti	W	Ru	Pd
binding energy (eV) to (5,5) CNT	2.53	2.76	2.09	3.18	2.32
work function (eV) of metal-coated (5,5) CNT	4.49	4.29	4.51	4.51	4.51

forces were reduced to within 0.05 eV/\AA . To study the field emission properties of metal-coated (5,5) nanotube, we also carried out density functional calculations using the localized basis set,⁹ and an electric field of 0.5 V/\AA was applied along the z -direction. As model systems for theoretical investigation, we chose the (5,5) armchair nanotube with Co, Ti, W, Pd, and Ru as coating materials. These metals were selected on the basis of their melting points, ionization energies, work functions, and Pilling–Bedworth ratios.¹⁰

We first calculated the binding energy to investigate the adhesion properties of metals on CNT. For the adsorption of single atoms, it is found that metals are exothermically adsorbed on metallic (5,5) nanotube with large binding energies as shown in Table 1. It is notable that ruthenium and titanium are strongly bound to the surface of the nanotube. The adsorption on the semiconducting (8,0) nanotube showed similar results. In the case of O_2 adsorption, the molecule binds to the nanotube with a binding energy of 0.25 eV with the equilibrium distance of 2.7 \AA from the nanotube surface. This indicates that selected metals can bind to the nanotube more tightly than oxygen molecules and protect CNT from degradation by oxygen molecules. The most stable adsorption site of metal atoms is the center of the hexagonal ring of the nanotube except for Pd atoms. This is contrasted to the O_2 adsorption where O_2 binds at the C–C bond in nanotube. The difference could be attributed to distinct orbital characters between the bound molecules or atoms.

Next, work functions of metal-coated CNTs were examined. The work function is a critical parameter influencing the field emission efficiency because it is directly related to the tunneling length of emitted electrons. According to the Fowler–Nordheim equation,¹¹ field emission currents exponentially increase as the work function of emitters decreases. In our calculations, the work functions were computed as the energy difference between the Fermi level and vacuum level.¹² The calculated work functions in Table 1 show that the work function is lowered upon metal coating [work function of bare (5,5) CNT is 4.54 eV]. As compared to other metals, Ti affects the work function of the CNT most significantly. Therefore, it is expected that the Ti coating would enhance the emission currents. In addition, we also computed the work function of the nanotube when a Ti_4 cluster in a tetrahedral shape is attached on the nanotube. We found that the work function is 4.25 eV in comparison with 4.29 eV when single Ti atom is adsorbed. (See Table 1.) The small decrease could be attributed to the multiple bonding of Ti atoms to the nanotube. These results demonstrate that the reduction of work function will persist when Ti nanoparticles are attached.

**Figure 1.** Comparison of band structure of (a) bare (5,5), (b) Ti-coated (5,5), and (c) differential charge density before and after Ti coating. The Fermi level is set to 0 eV .

For more detailed analysis, we inspect the band structure and charge density in Figure 1. As the Ti atom adsorbs on CNTs, bands are split around the Fermi level due to the mixing between π -orbitals of CNTs and Ti- d orbitals. The work function of Ti-coated CNTs is lowered compared to the bare CNT because the Fermi level shifts upward from that of the pristine nanotube. In addition, the density of states (DOS) increases near the Fermi level, which is a result of the d -orbital mixing, and therefore further increases of tunneling currents are expected. The differences in the work function of various metal-coated CNTs originate from the degree of orbital mixing between CNTs and metals. When the energy level of the highest occupied molecular orbital (HOMO) of the metal is higher than the Fermi level of the CNT, the energy level of mixed states becomes higher than the original Fermi level of the CNT. In other words, the new Fermi level shifts upward and results in a reduction of the work function. This is consistent with the atomic calculations that show that Ti has the largest HOMO energy among studied metals, which leads to the lowest work function (HOMO level of Ti atom is -3.41 eV while those of W, Pd, Co, and Ru atoms are -4.26 , -4.30 , -4.50 , and -4.11 eV from the vacuum level, respectively). The charge density differences [$= \rho(\text{Metal} + \text{CNT}) - \rho(\text{Metal}) - \rho(\text{CNT})$], are plotted in Figure 1c. It is found that electronic densities are concentrated near the interface between the Ti atom and CNT wall, indicating a covalent-type bonding. The spatial distribution in Figure 1c also confirms significant orbital mixing between Ti states and π -bands of the CNT.

We performed electronic structure calculations under electric fields to investigate field emission properties of metal-coated CNTs. Figure 2 shows DOS of bare and Ti-coated CNTs under an external field of 0.5 V/\AA . When the external field is applied to the Ti-coated CNT, DOS near the Fermi level is increased compared to the bare CNT. The wave function of HOMO in Figure 2c indicates that the increase of DOS near the Fermi level originates from the metal atoms, in line with the above analysis. Therefore, metal atoms may play as additional emission sites under field-emission conditions. For the quantitative analysis, we integrated local density of states from -1 to 0 eV (Fermi level) in Figure 2, which can be related to the emission probability of electrons from the nanotube.^{13–15} Here, we

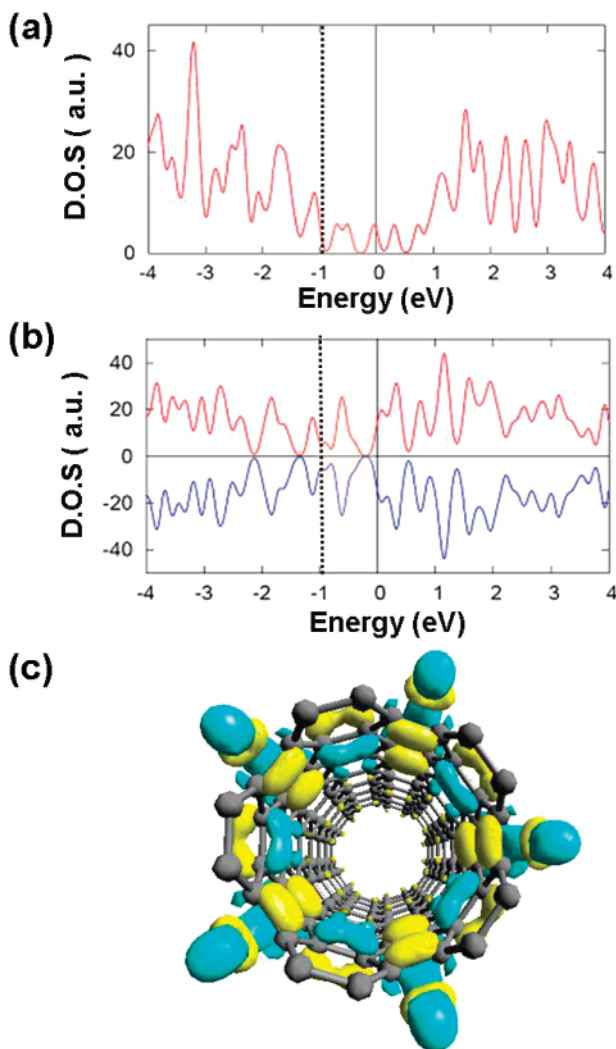


Figure 2. Comparison of DOS for (a) the bare CNT tip and (b) Ti-coated CNT tip under an external field of 0.5 V/\AA . HOMO of Ti-coated CNT tip is shown in (c).

Table 2. The Integrated DOS between -1 and 0 eV (the Fermi Level) for Metal-Coated or Bare Nanotube Tips

coating metals	bare	Ti	Pd	Ru
integrated DOS (arb. unit)	0.044	0.139	0.050	0.105

assume that only electronic states within a narrow energy window near the Fermi level could contribute to the low-temperature field emission. The calculated values are summarized in Table 2. From the results, the Ti coating is found to be most effective in increasing DOS at the Fermi level.

The above analysis on the binding energies, work functions, and DOS at the Fermi level all indicate that Ti is the optimal coating material to enhance the field emission properties of CNT. Motivated by the theoretical observations, we synthesized Ti-coated CNTs and applied the composite materials to the field emission display. There are several coating methods that can be applied to CNTs, such as electrochemical reduction,¹⁶ e-beam evaporation,¹⁷ and nanoparticles dispersing¹⁸ methods. In this work, we adopted the chemical reduction method¹⁹ because it is a simple procedure

that can be employed for the mass production. We mixed titanium trichloride (TiCl_3) solution and thin multiwall CNT (radius of $\sim 8 \text{ nm}$) powders. Sodium borohydride (NaBH_4) (1 M (mol/l)) solution was dropped as a reducing agent into the dispersed CNT solution with a strong sonication. We then obtained Ti-coated CNT powder after washing and drying.

Figure 3a shows the morphology of the Ti-coated CNTs investigated by transmission electron microscopy (TEM). The image was taken using a Philips F20 Techni and CM20FEG. The image shows uniform Ti-coated CNTs with lengths up to several hundreds of micrometers. High-resolution TEM (HRTEM) image given in the inset reveals more detailed atomic structures of the samples, and it was found that diameters of the coating particles were $5\text{--}10 \text{ nm}$. The elemental analysis of the sample was carried out using energy dispersive X-ray spectroscopy (EDX) with carbon-coated copper (Cu) grid. The results are given in Figure 3b, and it was confirmed that Ti peaks were present. It was noted that no impurity in the samples was observed within the detection limit of the EDX. The presence of O peak in EDX results raises the possibility that Ti nanoparticles were partially oxidized during the drying procedure. In Figure 3c, the crystal structure of products was characterized by X-ray diffraction (XRD, Rigaku D/max-rc) with a graphite monochromator and Cu $K\alpha$ radiation ($\lambda = 0.1541 \text{ nm}$). All diffraction peaks were identified as titanium metals in the hexagonal-closed packed α -phase (JCPDS cards, No. 65–9622) or CNTs. Although the Ti metal comprises a small portion of the sample, its peaks are much stronger and sharper than those of CNTs. Considering both EDX and XRD results, it is plausible that Ti nanoparticles are partially oxidized at the surface region and the inner parts in contact with the nanotube remain as metallic. As demonstrated by the calculations, Ti atoms or clusters are strongly bound to the nanotube, and therefore the interface between the Ti nanoparticle and nanotube might not be easily oxidized.

To form the cathode of the FED, we applied the screen-printing method (using CNT–polymer paste), which was more practical than direct growth techniques such as chemical vapor depositions for the large area display and mass production used in the industry.²⁰ Ti-coated CNT powders were mixed with general organic vehicles and inorganic binders. A three-roll mill process was carried out for mixing and dispersion of CNT powder in the organic vehicles. The paste was patterned on indium–tin–oxide-coated glass by the screen-printing method. It was then thermally treated in nitrogen (N_2) atmospheres at temperatures ranging from 400 to $450 \text{ }^\circ\text{C}$ to decompose the vehicles.²¹ The measurements of field emission currents and lifetime were carried out using a diode structure ($1/500$ duty) in a vacuum chamber.

In Figure 4, the measured I – V and lifetime characteristics of Ti-coated field emitters are shown. Figure 4a shows that the turn-on field of Ti-coated CNT films ($3.7 \text{ V}/\mu\text{m}$) is substantially smaller than that of bare CNT films ($5.5 \text{ V}/\mu\text{m}$). In addition, the threshold electric field to reach a current density of $100 \mu\text{m}/\text{cm}^2$ is decreased from 7.65 to $6.19 \text{ V}/\mu\text{m}$ after Ti coating. The decrease in turn-on voltages and

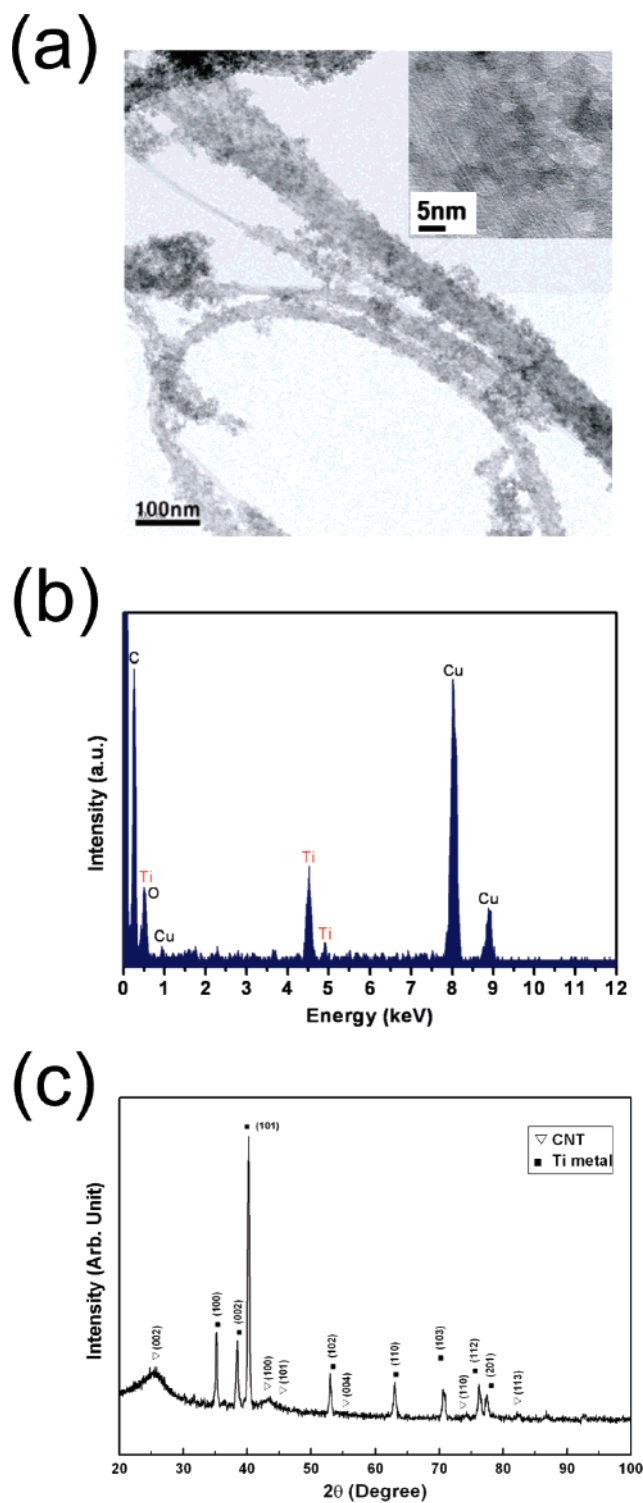


Figure 3. (a) TEM image of Ti/TiO_x-coated nanotube bundles. (b) Results of EDX analysis. (c) XRD pattern of the metal-coated CNTs. Miller indices corresponding to α -Ti and CNTs are indicated.

increase in emission currents after Ti coating are in accord with the foregoing theoretical predictions. As mentioned in the above, there is a possibility that Ti metals on the CNTs were oxidized during the fabrication process and the titanium oxide could be formed on the surface. However, it is believed that the interfaces between CNTs and coated materials are

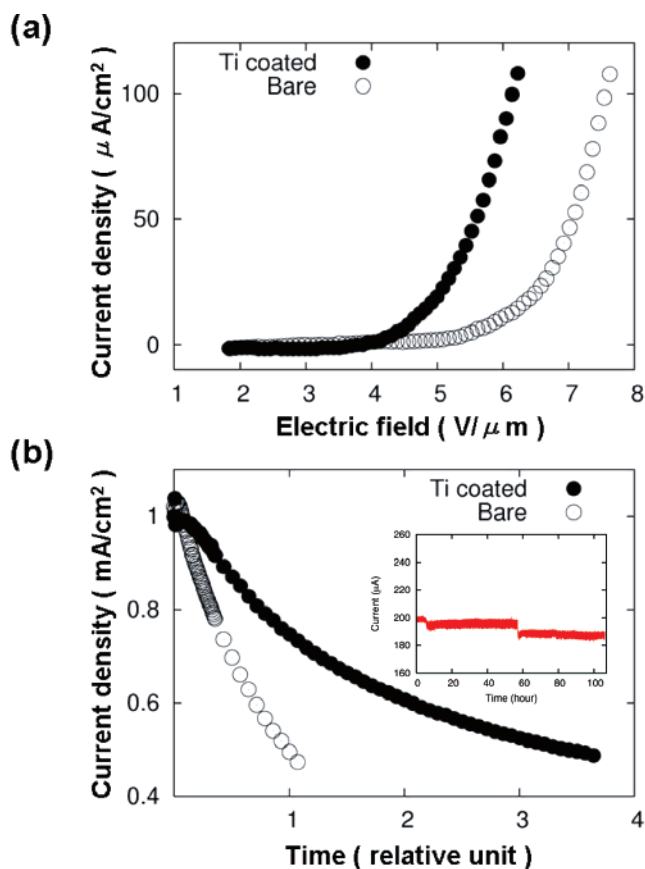


Figure 4. Experimental result of (a) I - V characteristics and (b) lifetime for Ti-coated CNT as compared with bare CNT. The inset shows the fluctuation of currents for 100 h when Ti-coated CNTs are used.

still mainly pure titanium due to a much higher binding energy of Ti compared to that of the oxygen. Therefore, field emission properties would be well represented by the Ti-coated models.

Figure 4b shows the current degradation as a function of time. With the lifetime defined as a time span to reach the half of the initial current density, the lifetime of Ti-coated CNT samples is about 3.5 times longer than that of the pristine CNT. The inset figure shows the stability of the emission current within 100 h. The current fluctuations are found to be less than 10%, demonstrating the device stability. To investigate the microscopic origin of the extended lifetime, we performed a thermal gravity analysis (TGA) under an oxygen environment. This is based on the idea that oxygen molecules are most crucial in degrading the current stability.^{22,23} The derivative TGA graph and burning temperature data are displayed in Figure 5. The burning temperature of Ti-coated CNTs increases by 20 °C in comparison with bare CNTs. This result strongly indicates that Ti effectively protect CNTs from the oxygen attacks.

We performed additional calculations to understand the protection mechanism by coated metals in the presence of oxygen. To this end, we studied the chemisorption of oxygen atoms, which represent an active species to degrade CNTs on Ti surface. (See Figure 6.) We chose Ti(0001) surface because it is known to be the most stable.²⁴ Figure 6 shows

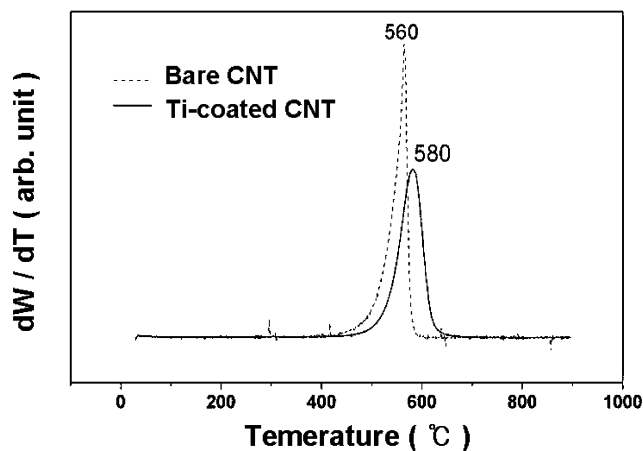


Figure 5. Derivative TGA for bare (dotted line) and Ti-coated CNTs (solid line).

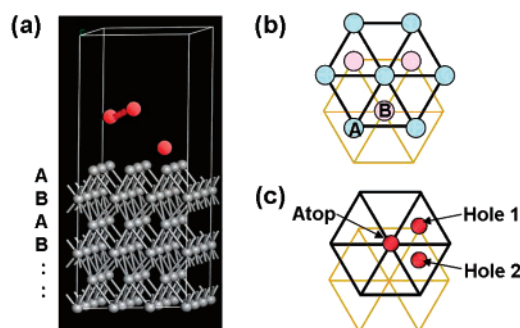


Figure 6. (a) Atomic geometry of Ti(0001) surface. The stacking sequence is represented by A and B. (b) Top view of the Ti(0001) surface. (c) Various adsorption sites for an atomic oxygen.

three representative sites on Ti(0001) surface for the oxygen adsorption. It is found that the oxygen atom binds exothermically to all three sites with a binding energy of 3.91 ~ 6.21 eV (“Hole2” site is found to be the most stable). In contrast, an oxygen atom adsorbs on (5,5) CNT with a binding energy of 0.68 eV. Therefore, the oxygen atoms or molecules will adsorb on the coated metal surface preferentially, and the degradation of the CNT tip by oxygen attacks can be suppressed. We also investigated the stability of coated metals after the oxygen adsorption by examining a local strain on the metal surface. The calculated strains in the local bonding were only 1.9~2.2% for all adsorption sites. Therefore, the coated Ti metals could play a protecting role stably.

As noted in the above, the existence of O peak in the experiment indicates that a part of Ti particles was oxidized. It is worth investigating how the work function is affected when TiO_x , instead of Ti particles, is bound at the nanotube. Because it is very complicated to model the interface between oxide particles and the nanotube, we calculated on TiO_2 molecule adsorbed on the nanotube, as a simplest modeling. It was found that the work function in this case increases by ~0.6 eV even if the molecule is weakly bound at the nanotube. This is mainly because the positive ion (Ti^{+4}) is pointing toward the nanotube and thereby lowering potential

energies of electrons. Even though this kind of polar interface would be rather unrealistic for the TiO_x nanoparticles, the results imply that the work function reduction through the charge transfer is not likely to occur for oxide clusters. In general, the insulating nanoparticles do not interact with the nanotube as strongly as the metal nanoparticles. The observation that the enhancement of field emission persisted over the extended time scale indicates that metal–nanotube bonding should play a role.

The protection mechanism by selective adsorption found in this work may open a new way to reduce electrical noise of nanotube devices that originated from ambient gases. The current fluctuation of single-wall carbon nanotube devices has been reported, and it was found that such noise levels result from the adsorption/desorption of ambient gas molecules in the electrode–nanotube interface region.²⁵ If the metal-coated CNTs are used instead of the bare CNT, one may decrease contact resistances of the electrode as well as the noise of the device, based on the fact that ambient gases are selectively adsorbed on the metal rather than on the CNT. On the other hand, the positive Ti ions in a chemical reduction process favors the defect sites because electrons are localized at those sites. (In fact, Li et al. reported that TiO_2 nanoparticles were selectively adsorbed on the defect sites of the CNT and were used as a detector of defects distribution.⁴) Therefore, metals or metal oxides could passivate the defect sites such as Stone–Wales defects or dangling bonds of CNTs and reduce the resistive heating, which will lead to the increased lifetime of the CNT-based electronic devices in general.

In conclusion, from a successful combination of theoretical predictions and experimental verifications, the Ti-coated carbon nanotubes were found to provide several merits over the bare nanotubes when they were applied to field emission displays. The charge transfer between the metallic nanoparticles and the nanotube lowers the work function of the nanotube, which leads to the enhancement of field emission currents. In addition, oxygen atoms selectively adsorb on the metallic nanoparticles and thereby the nanotube can be protected from the oxygen attacks. This leads to the prolonged lifetime under the field emission conditions, as confirmed by the experiment.

References

- (1) Iijima, S. *Nature* **1991**, 354, 56.
- (2) Fischer, J. E. *Acc. Chem. Res.* **2002**, 35, 1079.
- (3) Charlier, J. C.; Terrones, M.; Baxendale, M.; Meunier, V.; Zacharia, T.; Rupasinghe, N. L.; Hsu, W. K.; Grobert, N.; Terrones, H.; Amarutunga, G. A. *J. Nano. Lett.* **2002**, 2, 1191.
- (4) Li, X.; Niu, J.; Zhang, J.; Li, H.; Liu, Z. *J. Phys. Chem. B* **2003**, 107, 2453.
- (5) Han, S.; Ihm, J. *Phys. Rev. B* **2002**, 66, 241402.
- (6) Ihm, J.; Zunger, A.; Cohen, M. L. *J. Phys. C: Solid State Phys.* **1979**, 12, 4409.
- (7) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, 23, 5048.
- (8) Vanderbilt, D. *Phys. Rev. B* **1990**, 41, 7892.
- (9) (a) We performed calculations using DMol³, which is a registered software product of Molecular Simulations, Inc. (b) Delley, B. *J. Chem. Phys.* **1990**, 92, 508. (c) Delley, B. *J. Phys. Chem.* **1996**, 100, 6107.
- (10) Shackelford, J. F. *Introduction to Materials Science for Engineers*, 5th ed.; Prentice Hall, Inc.: Upper Saddle River, NJ, 2000.

- (11) Gomer, R. *Field Emission and Field Ionization*; Harvard University Press: Cambridge, MA, 1961.
- (12) Shan, B.; Cho, K. *Phys. Rev. Lett.* **2005**, *94*, 236602.
- (13) Zhou, G.; Duan, W.; Gu, B. *Phys. Rev. Lett.* **2001**, *87*, 95504.
- (14) Zhou, G.; Duan, W.; Gu, B.; Kawazoe, Y. *Appl. Phys. Lett.* **2002**, *80*, 1999.
- (15) Han, S.; Ihm, J. *Phys. Rev. B* **2000**, *61*, 9986.
- (16) Ang, L.; Hor, T. S. A.; Xu, G.; Tung, C.; Zhao, S.; Wang, J. L. S. *Chem. Mater.* **1999**, *11*, 2115.
- (17) Zhang, Y.; Franklin, N. W.; Chen, R. J.; Dai, H. *Chem. Phys. Lett.* **2000**, *331*, 35.
- (18) Oh, S.; So, B.; Choi, S.; Gopalan, A.; Lee, K.; Yoon, K. R.; Choi, I. S. *Mater. Lett.* **2005**, *59*, 1121.
- (19) Xue, B.; Chen, P.; Hong, Q.; Lin, J.; Tan, K. L. *J. Mater. Chem.* **2001**, *11*, 2378.
- (20) Kang, S. K.; Choi, J. H.; Park, J. H.; Han, J. H.; Yoo, J. B.; Nam, J. W.; Lee, C. K.; Kim, J. M. *J. Vac. Sci. Technol., B* **2004**, *22*, 1345.
- (21) Park, J.; Moon, J.; Han, J.; Berdinsky, A. S.; Yoo, J.; Park, C.; Nam, J.; Park, J.; Lee, C. G.; Choe, D. H. *J. Vac. Sci. Technol., B* **2005**, *23*, 702.
- (22) Dean, K.; Chalamala, B. R. *Appl. Phys. Lett.* **1999**, *75*, 3017.
- (23) Lim, S. C.; Choi, Y. C.; Jeong, H. J.; Shin, Y. M.; An, K. H.; Bae, D. J.; Lee, Y. H.; Lee, N. S.; Kim, J. M. *Adv. Mat.* **2001**, *13*, 1563.
- (24) Shih, H. D.; Jona, F.; Jepsen, D. W.; Marcus, P. M. *J. Phys. C: Solid State Phys.* **1976**, *9*, 1495.
- (25) Vijayaraghavan, A.; Kara, S.; Rumyantsev, S.; Khanna, A.; Soldano, C.; Pala, N.; Vajtai, R.; Kanzaki, K.; Kobayashi, Y.; Nalamasu, O.; Shur, M. S.; Ajayan, P. M. *J. Appl. Phys.* **2006**, *100*, 24315.

NL0720051