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Atomic layer coating of hafnium oxide on carbon nanotubes for high-performance field emitters

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Carbon nanotubes coated with hafnium oxide exhibit excellent electron emission characteristics, including a low turn-on voltage, a high field enhancement factor, and exceptional current stability. Their enhanced emission performance was attributed to a decrease in the work function and an increase in the electron density of states at the carbon nanotube Fermi level closest to the conduction band minimum of hafnium oxide. In addition, the enhanced current stability was attributed to the ability of hafnium oxide to protect the carbon nanotubes against ions and free radicals created in the electron field emission process. © *2011 American Institute of Physics*. [doi:10.1063/1.3650471]

Carbon nanotubes (CNTs) are excellent candidates for high-performance electron field emitters because of their nanoscale structure as well as their unique mechanical and electronic properties.[1–3] Electrons are emitted from the tip of CNTs at several volts per micrometer, whereas the field emission threshold from a metal is about 10^4 V/μm.[4,5] However, CNT emitters show time-dependent structural degradation during electron emission, which shortens the lifetime of the device. When the CNT emitter is subjected to an electric voltage, joule heating at the CNT tips shortens the tubes, which causes a reduction in the local field and the electron emission current. In addition, the field emitted electrons induce the excitation and ionization of gases trapped in the vacuum. The ions and free radicals thus generated are accelerated towards the CNT emitter by the negative bias, leading to device failure.[6,7] This problem has been tackled by coating the tips of the CNTs with wide band gap materials that have a small electron affinity, such as magnesium oxide, nickel oxide, and silicon dioxide.[8–11]

Hafnium(IV) oxide (HfO_2) was selected as the coating material for the CNTs in this study because of its chemical stability at high temperature, excellent electrical conductivity, high melting point (3056 K), high dielectric constant ($\varepsilon_\infty = 4$), low electron affinity (EA = 2), and large band gap (6 eV).[12] Atomic layer chemical vapor deposition was employed for coating the CNT emitter with hafnium oxide, rather than other methods such as magnetron sputtering, plasma-assisted chemical vapor deposition, electroless plating, or other routine chemical methods.[13–15] Atomic layer deposition produces uniform films of a controlled thickness with excellent step coverage. The morphology of the hafnium oxide coating and the chemical bonding between the

coating and CNTs were then investigated by various methods. Finally, the field electron emission properties of the hafnium oxide-coated CNTs, namely, the turn-on field, the field enhancement factor, the current densities, and the current stability, were compared with those of the pristine CNTs using an illustration of the electron emission mechanism at the interface between the hafnium oxide and the CNTs [see the supplementary material for details of the preparation of the CNT emitters and characterization tools[20]].

The morphology of the pristine and hafnium oxide-coated nanotubes was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The nanotubes were tightly bundled [Fig. 1(a)], and an individual tube with diameter of 6-9 nm [Fig. 1(b)] was found to consist of seven concentric tubules [Fig. 1(b), inset]. A relatively homogenous film of hafnium oxide, 4 nm ($\pm$1 nm) thick, was deposited on the surface of the nanotubes by three cycles of atomic layer deposition [Figs. 1(c) and 1(d)]. The atomic concentrations of oxygen (2.67%) and hafnium (1.17%) obtained by energy dispersive spectroscopy [Fig. S1][20] indicated that the chemical formula of the hafnium oxide layer is HfO_2. Moreover, the thickness of the hafnium oxide layer could be controlled by carrying out 3, 6, and 9 deposition cycles, resulting in layers of 4-12 nm.

The chemical bonding of the hafnium oxide layer was studied by x-ray photoelectron spectroscopy (XPS). The wide-scan XPS spectrum showed peaks at 17.65 eV (Hf 4f), 213 and 224 eV (Hf 4d), 284.4 eV (C 1s), and 532.2 eV (O 1s) [Fig. 2(a)]. The single peak at 17.65 eV was assigned to Hf 4f [Fig. 2(b)]. The two peaks at 213 and 224 eV [Fig. 2(b)] originated from Hf 4d3/2 and Hf 4d5/2, indicating the formation of Hf-O chemical bonds.[16] Therefore, the Hf precursor initially coated the surface of the tubes and then formed Hf-O bonds. In addition, the structural changes in the carbon nanotubes caused by atomic layer deposition were evaluated using Raman spectroscopy. The strong G-band (E_{2g2} mode) at 1592 cm^{-1} and the relatively weak D-band (the defect-induced

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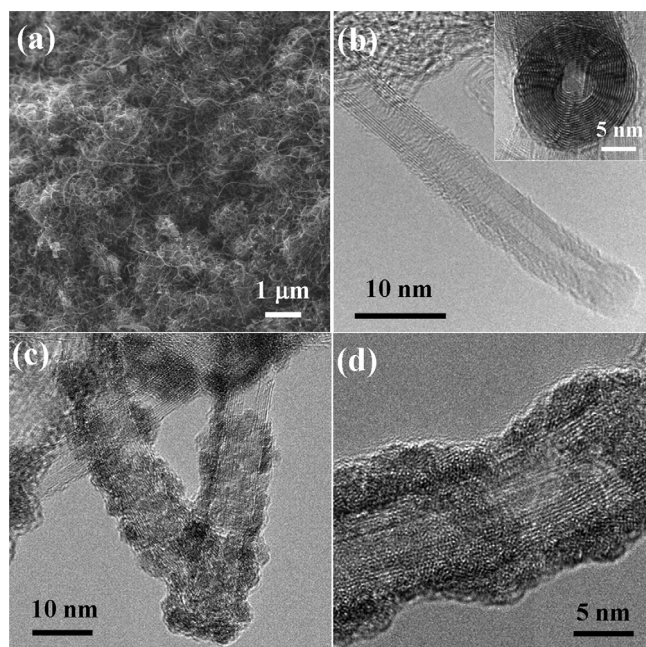
FIG. 1. (a) SEM and (b) TEM images of multi-walled carbon nanotubes. Inset shows a cross section of the TEM image in (b) which indicates that the nanotube consists of several concentric tubules. (c) and (d) Typical TEM images of the hafnium oxide coated carbon nanotubes.

mode) at 1341 cm^{-1} were observed for all samples [Fig. 2(d)]. The R value (I_D/I_G) was calculated by dividing the integrated intensity of the D band by the integrated intensity of the G band; this value is used as an indicator for the presence of defects in carbon materials. The low R value (0.3891) in the pristine tubes reflects a low density of defects. The oxygen high vacuum annealing method induced a large increase in the R value of the pristine tubes (0.8562), indicating the generation of defects on the sidewalls of tubes via the chemical attack of chemically active oxygen species. In contrast, the large decrease in the R value for the hafnium oxide coated

nanotubes suggests that the defects on the surface of the tubes are removed through the formation of covalent bonds between the hafnium oxide coating and oxygen.

Before evaluating the emission current stability as a function of time, the I-V field emission curves of the CNT emitters were recorded before and after the hafnium oxide coating. A low current density of 0.04 mA/cm^2 at 5 V/μm and a high turn-on field of 3 V/μm were observed for the oxygen high vacuum annealed CNT emitter [Fig. 3(a) and Fig. 3(a) inset]. In contrast, the hafnium oxide coated nanotube emitter showed a high current density of 0.12 mA/cm^2 at 5 V/μm and a low turn-on field of 2 V/μm [Fig. 3(b) and inset in Fig. 3(b)]. From their corresponding Fowler-Nordheim (F-N) plots [Figs. 3(c) and 3(d)],[17] the large increase in the field enhancement factor (which is defined as the maximum electric field divided by the average electric field) and substantial decrease in the turn-on field indicate that the field emission performance of the hafnium oxide coated CNT emitter is significantly enhanced [see Fig. S2].[20] The CNT emitter with a 12 nm coating exhibited the highest field enhancement factor and the lowest turn-on field.

An illustration of the field emission from hafnium oxide coated nanotube [Fig. S3(a)][20] and its geometry was used [Fig. S3(b)][20] to understand the enhanced properties of the hafnium oxide coated CNT emitter. A simplified band diagram for the field emission mechanism of the hafnium oxide-coated CNT emitter at a low applied field was also constructed [Fig. S3(c)].[20] The important parameters in the band diagram are the electron affinity (χ), the barrier height (Φ_B), the work function (Φ), and the voltage drop (ΔV). When a high voltage is applied to the CNTs, the potential barrier of the hafnium oxide protective layer is bent by the Schottky effect. Electrons at the Fermi level position of the CNTs, which are closer to the conduction band minimum (CBM) of wide band gap coating materials, are injected from the interface between the coating and CNTs into the conduction band of the hafnium oxide protective layer by the tunneling effect. Thus, electrons are transported by the applied
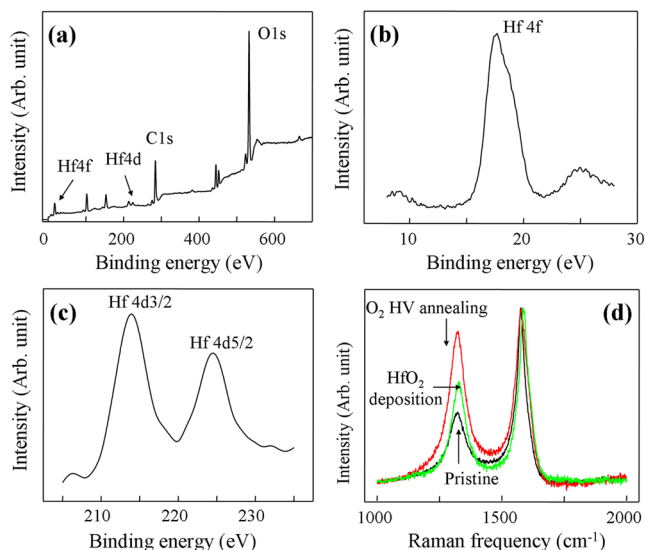

FIG. 2. (Color online) (a) The wide-scan and (b), (c) magnified XPS spectra of the hafnium oxide coated carbon nanotubes. (d) Raman spectra of the pristine, oxygen high vacuum annealed and hafnium oxide coated nanotubes using a 532 nm laser line.
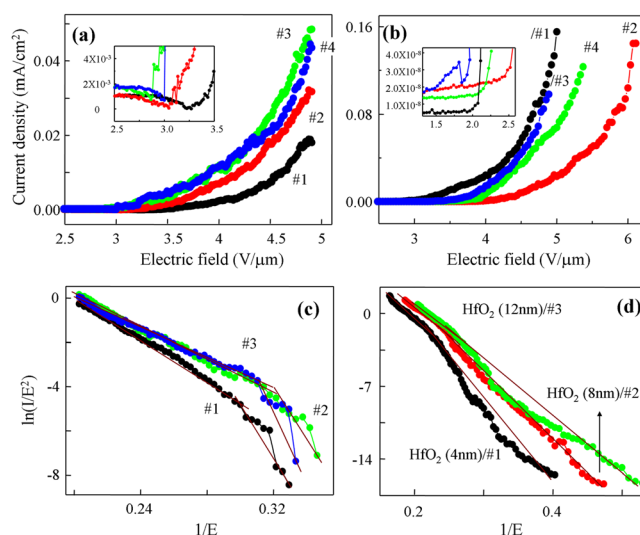

FIG. 3. (Color online) The current-voltage field emission curves of the CNT emitters (a) before and (b) after hafnium oxide coating and (c), (d) their corresponding Fowler-Nordheim (F-N) plots. Insets in (a) and (b) show the magnified current-voltage field emission curves.

electric field from the CBM to the vacuum level in wide band gap materials. Electron field emission then occurs from the CBM of the hafnium oxide layer at the interface between the hafnium oxide and the vacuum. Because of a voltage drop (ΔV) across the hafnium oxide dielectric layer, the energy of the emitted electrons is linearly proportional to the applied voltage.[18,19] Therefore CNTs coated with wide band gap materials could improve the electron field emission and current stability in high performance flat-panel devices.

In conclusion, we have demonstrated that CNT emitters coated with a layer of hafnium oxide showed significantly enhanced field emission properties. Electron field emission occurs from the CBM of the hafnium oxide layer at the interface between the hafnium oxide and the vacuum, because of a voltage drop across the dielectric hafnium oxide layer. The CNT emitter with a 12 nm thick coating exhibited the highest field enhancement factor and lowest turn-on field. We therefore expect that the low turn-on voltage, high current density, and long-term current stability of hafnium oxide coated CNT emitters will make them an excellent cathode material for commercially available flat-panel display devices in the near future.

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[20]See supplementary material at http://dx.doi.org/10.1063/1.3650471 for the experimental details, the elemental distribution profile, the field enhancement factors and turn-on field and illustration of the field emission, and simple band diagram for the field emission mechanism.