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Enhanced field emission from carbon nanotubes by electroplating of silver nanoparticles

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The authors report that the field emission of carbon nanotubes (CNTs) is significantly improved by electroplating. The electroplating leads to a decrease of the turn-on electric field from 2.95 to 1.0 $V/\mu m$ and an increase of the emission-current density from 0.224 to 0.8112 mA/cm^2 at an applied electric field of 8 $V/\mu m$. It is found that after 23 days the current density of the CNT emitters prepared with electroplating only decreases by 10%, whereas that of the CNT emitters prepared without electroplating decreases by more than 80%. The improvement of the field emission of CNTs is due to the electroplating-enabled strong adhesion between the CNTs and the substrate. This has been verified by the measurement of the contact resistance. © *2011 American Vacuum Society.* [DOI: 10.1116/1.3610841]

I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991, there have been extensive studies on their fundamental properties and applications.[1–5] Owing to their unique electrical, mechanical, thermal, and chemical properties, CNTs are good candidates for many device applications, including flat-panel display devices,[6,7] X-ray tubes,[8,9] and microwave amplifiers. Field emission is one of the promising applications of CNTs, but for practical CNT-based field-emission devices it is necessary to improve the emission-current density, uniformity, and stability over long periods. According to the Fowler–Nordheim (FN) theory,[10] field-emission-current density depends on both the field-enhancement factor and the work function of the CNT emitters. The fine contact resistance between CNTs and the substrate may be another key problem in the cold cathode emitters based on CNTs. Low electrical-contact resistance between CNTs and the substrate can also enhance field-emission density and stability and, therefore, electrical contact between CNTs and the substrate has become one of the most important issues in nanoelectronics and has been studied theoretically[11,12] and experimentally.[13–15] In general, the reported electrical-contact resistances between the CNTs and the substrates are very large,[16–19] and such high resistance greatly prevents CNT-based devices from reaching the intrinsic electronic properties of CNTs. The field-emission current of CNTs deposited on substrates will be greatly tailored by this contact effect.[20] For these reasons, this article presents a simple and effective method based on complementary electroplating to enhance the adhesion between CNT emitters and the substrate. The field-emission properties of the CNT field emitters made using a combination of electrophoresis and electroplating was significantly improved compared to that of electrophoresis only. This efficient method is very simple, low cost, and suitable for the production of a large-scale CNT-based field-emission cold cathode.

II. EXPERIMENTAL PROCESSES

The commercial CNTs synthesized by the chemical vapor deposition (CVD) method were used as the electron-emission source and were typically 20–80 nm in diameter and 10–30 μm in length. First, the raw CNTs were purified by ultrasonic agitation in solution with 1:3 volume ratio of concentrated nitric and sulfuric acid. Second, the CNTs were washed with de-ionized water and dried in air at 120 °C for 12 h and the treated CNTs were dispersed in a solution of isopropyl alcohol that contained dissolved $Mg(NO_3)_2 \cdot 6H_2O$ at a concentration of $1 \times 10^{-4} M$. Last, a small amount of dissolved ethyl cellulose was added to the suspension to disperse the CNTs and the suspension was ultrasonically dispersed for about 1 day and then centrifuged for 20 min at

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3000 rpm in order to remove the large-sized CNT conglomerations. The top fraction of the suspension was used in the electrophoresis procedures.

The first step in the sample preparation was the electrophoretic deposition (EDP) of CNTs on an indium-tin oxide-coated (ITO) glass substrate. An ITO-coated glass substrate (cathode) and a stainless-steel plate (an anode) were immersed into the CNT electrophoresis suspension at room temperature. The two electrodes were kept in parallel with a gap of 1 cm held constant by two glass spacers. The deposition was carried out by applying a constant dc voltage of 60 V and the deposition time was kept at 3 min. In the second step, the electroplating process was carried out at room temperature to enhance the adhesion between CNTs and the substrate. The electrolyte used was a 0.5 wt % $AgNO_3$ aqueous solution and an electrodeposition current density of 2 mA/cm^2 was supplied by a dc power source for 45 s, while the complementary Ag nanoparticles were deposited selectively on the surfaces of CNTs and also on the ITO-coated glass substrate. In comparison, Ag nanoparticles were deposited on a bare ITO substrate by electroplating. All samples were annealed in ambient N_2 at 200–400 °C for 1 h to induce strong adhesion with the substrate.

The samples were characterized and analyzed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The field-emission characteristics were measured with the diode structure in a vacuum chamber maintained at a pressure of 1×10^{-5} Pa at room temperature. The CNT emitters and ITO glass were used as the cathode and anode, respectively, with a distance between the cathode and the anode of 100 μm. The emission current was measured by a Keithley 237 source measure unit and contact resistances were measured using the four-wire method.

III. RESULT AND DISCUSSION

Figure 1(a) shows the SEM images of the CNT emitters prepared by the EDP on the substrate with an enlarged image of CNT emitters fabricated by EDP and EDS shown in the right inset. It can be seen that the CNTs loosely lay on the surface of the ITO-covered glass substrate. The CNTs attached by EDP alone have weak adhesion, mainly due to the van der Waals force[21] at the interface between the CNTs and the substrate. Figure 1(b) shows the SEM image of the CNT emitters fabricated by EDP and subsequent electroplating. In the right inset of Fig. 1(b), it can be seen that Ag nanoparticles with a size of 10–20 nm cover both the substrate of ITO and the surface of the CNTs. Composition of the Ag nanoparticles is confirmed by EDS where it is seen that other elements (Na, O, and Mg) were mixed with Ag during the process of electrophoresis and electroplating. In order to further confirm the presence of Ag nanoparticles on the CNT surfaces, Ag nanoparticles were deposited on a bare ITO substrate through electroplating. Figure 1(c) shows a SEM image of the Ag nanoparticles covering a bare ITO substrate. It can be seen that the morphology of Ag nanoparticles deposited on a bare ITO substrate is similar to that of Ag nanoparticles on the surface of CNTs. Composition of the Ag nanoparticle is also confirmed by an EDS in the right inset. Based on comparison of the EDS of a CNT sample prepared by the combination method and a bare ITO substrate after the electroplating, it can be confirmed that Ag nanoparticles on the CNT surface come from the electroplating process. In the image in the right inset of Fig. 1(b) it can be seen that the CNT roots were embedded into Ag nanoparticles and fully encased by Ag nanoparticles after electroplating deposition. CNTs were fixed on the substrate by Ag nanoparticles and the sticking tips could act to stabilize the field-electron-

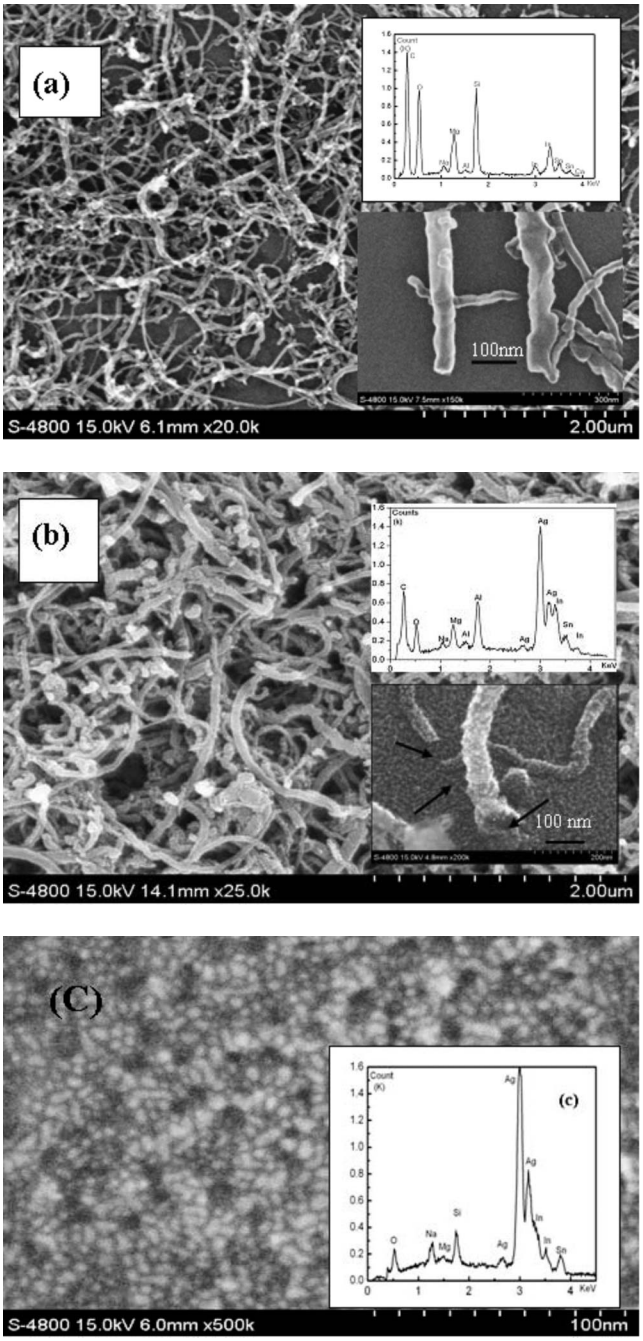

FIG. 1. SEM images of CNT emitters fabricated by (a) EDP-only, (b) the combination method (c), and Ag nanoparticles on the bare ITO substrate. An enlarged image of CNT emitters before and after electroplating [(a) and (b)], as well as the EDS [(a)–(c)] are shown in the right inset.

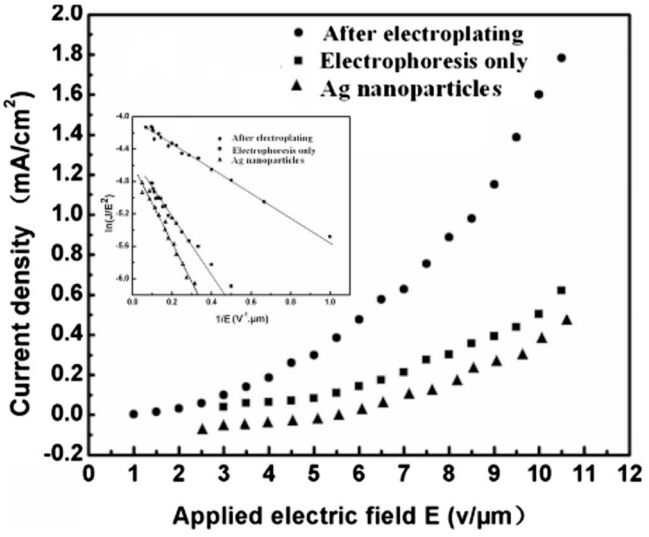

FIG. 2. Emission–current density versus applied electric field curves for the CNTs prepared by EDP-only, combination of the electrophoresis and subsequent electroplating, and Ag nanoparticles a bare ITO substrate. The corresponding FN plots are shown in the inset.

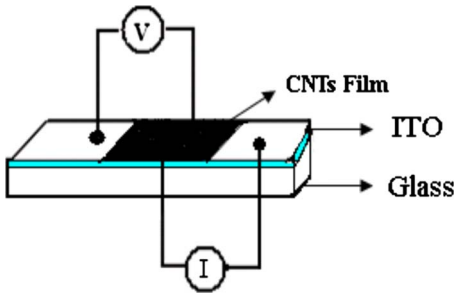

FIG. 3. (Color online) Schematic of the four-wire measurement structure used to measure contact resistance between CNT emitters and the substrate.

emission sources. Clearly, this method has the potential to improve the adhesion of CNTs to the substrate while decreasing the contact resistance between CNTs and the substrate.

The field-emission-current density versus applied-electric field curves for the CNTs prepared by EDP-only and with subsequent electroplating are shown in Fig. 2. It is found that the turn-on electric field, at which the emission-current density reaches 10 $\mu A/cm^2$, is decreased from 2.95 to 1.0 $V/\mu m$ and the emission-current density with an applied electric field 8 $V/\mu m$ increased from 0.224 to 0.812 mA/cm^2 for the EDP-only and with subsequent electroplating, respectively. The corresponding FN plots are shown in the inset of Fig. 2. Each plot can be well fitted by using a straight line with different slopes. These straight lines indicate that the emitted electrons mainly result from field emission. The field-emission-current density of the CNT emitters prepared by electrophoresis and with subsequent electroplating was more than three times higher than that of CNT emitters prepared by EDP-only with an applied electric field of 8 $V/\mu m$ because of the good electrical contact between CNTs and the substrate. These results suggest that CNT field-emission properties can be dramatically improved by electroplating.

Figure 2 also shows that the field-emission properties of the CNT emitters prepared by EDP-only are better than that of Ag nanoparticles on the bare ITO substrate because some protruding CNTs can greatly contribute to the field-emission-current density. It is also confirmed that CNT field-emission enhancement for the sample using the combination method mainly comes from the improvement of contact resistance, although Ag nanoparticles on both the surfaces of the CNTs and the ITO substrate can contribute to field-emission-current density. The electron transport and emission process occurs, first, when electrons are injected from the ITO substrate into a single CNT and transported in the CNT under the electric field. It is assumed that the properties of the CNT/Ag heterojunction are similar to a Schottky barrier with a height of about 1 eV.[22] Second, the conduction electrons in CNTs tunnel into the Ag nanoparticles through the Schottky barrier and are emitted into the vacuum from the Ag nanoparticles. The electron tunneling probability will become small due to the Schottky barrier, so the field-emission electrons into the vacuum will be limited by the CNT/Ag heterojunction. The low work function of Ag (4.7 eV) (Ref. 23) nanoparticles is beneficial to the field emission, but the work function of Ag is nearly equal to that of CNTs (4.9 eV);[24] therefore, we conclude that the Ag nanoparticle covering on the surface of the CNTs can contribute little to enhancing the electron field emission. After Ag nanoparticle coating, some protruding CNT roots are embedded into the Ag nanoparticles which means that a robust contact was constructed between the tubes and the substrate. CNTs covered with Au nanoparticles contribute to an impressive field-emission property,[25] although the work function of Au (5.1 eV) (Ref. 26) is higher than that of the CNTs (4.9 eV). It is believed that the CNT field-emission enhancement is mainly attributed to the fine electrical-contact resistance.

In order to verify contact resistance improvement by electroplating, we measured contact resistance using the four-wire measurement method as shown in Fig. 3.[27,28] Copper wires were connected to the ITO surface and the CNT emitters film using silver paint. The Keithley 237 source measure unit was chosen as dc source and the voltage drop across the contact area between the ITO and the CNT film is measured using digital voltmeters. The measurement was repeated many times and an average value for contact resistance of the EDP-only sample was found to be about 3.46 Ω/mm^2. However, the contact resistance for the combination method was only about 0.352 Ω/mm^2, showing that contact resistance was reduced to about 10% of the value after electroplating. Based on the results of our experiments, we can confirm that the contact resistance can be dramatically improved after electroplating.

Figure 4 shows the emission-current degradation of the CNT emitters measured at a current density of 1 mA/cm^2 and at a pressure of 1×10^{-5} Pa. The current densities decrease for the two cases of EDP-only and after electroplating in the lifetime measurement over a period of 23 days. The

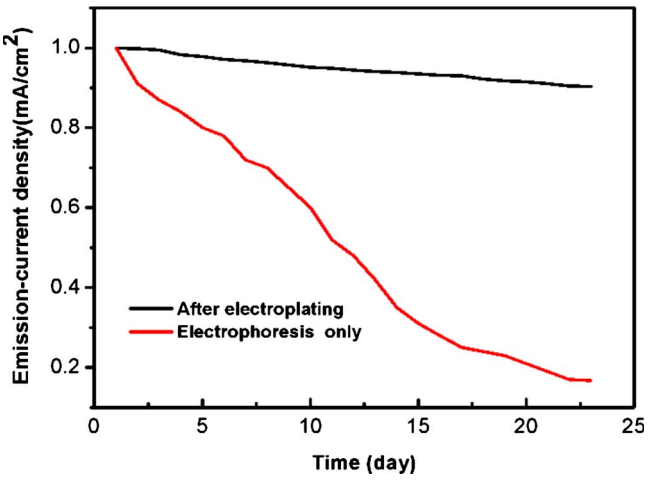

FIG. 4. (Color online) Emission-current density degradation for the two cases of the CNTs emitters prepared by EDP-only and the combination method.

emitting current density of CNT emitters fabricated by EDP-only decreased to 16.8% of the initial current during the measurement period; however, after electroplating, the current fluctuation is lower and the average current shows only a 10% degradation during this period. This better stability and long lifetime can be explained by the strong adhesion between CNTs and the substrate. After electroplating, the CNT roots are embedded into the Ag-nanoparticle-covered substrate, which means that a robust contact was constructed between the tubes and the substrate. The CNTs attached by EDP-only have weak adhesion, mainly due to the van der Waals force at the interface between the CNTs and the substrate. The CNT emitters are easily detached from the electrode during the device operation, so this method can offer a new possibility for the simple and reliable fabrication of high-quality cold cathodes by using EDP and electroplating.

IV. CONCLUSION

In summary, a novel technique was successfully developed to assemble CNT coated with Ag nanoparticles on glass substrates by a combination of electrophoresis and subsequent electroplating. The field-emission properties of the CNT field emitters made using the combination method is significantly improved compared to that with EDP-only, including a decreased turn-on electric field from 2.95 to 1.0 $V/\mu m$ and an increased emission-current density from 0.224 to 0.812 mA/cm^2 with an applied electric field of 8 $V/\mu m$. It is considered that the greatly enhanced field-emission properties of this combination method were mainly caused by reducing contact resistance, and the experimental results further verified this conclusion. This efficient process is a promising candidate for production of large-area CNT-based electron sources, due to the ease of the process, the low cost, and the ease of scaling up.

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