Enhanced Carbon Nanotube Field Emitter With Adsorbed Au Nanoparticles

Sheng-Joue Young, *Member, IEEE*, Zheng-Dong Lin, Chih-Hung Hsiao, and Chien-Sheng Huang

***Abstract*— Field emission was achieved utilizing vertically aligned carbon nanotubes (CNTs), whose external surface was decorated with Au nanoparticles (NPs). It was found that the average length and diameter of the CNTs were ∼4.52 μm and 45 nm, respectively. Au NPs (around 5 nm) were coated onto CNT surfaces for field emission. The turn-ON field and current density of the Au-coated CNTs clearly indicate that the Au NPs considerably enhanced field emission. Au NP decoration effectively decreased the work function and turn-ON field.**

***Index Terms*— Au nanoparticles (NPs), carbon nanotubes (CNTs), field emission, work function.**

I. Introduction

FIELD electron emission from carbon nanotubes (CNTs) has received interest, because CNTs are an ideal emitter material [1]. Since their discovery in 1991 by Iijima [2], CNTs have many potential applications due to their excellent physical and chemical characteristics [3], [4]. CNTs as field emitters have a very low turn-ON field due to their high melting point, high field enhancement factor (which originates from their high geometric aspect ratio and small radii of curvature at the tips), and high thermal conductivity. CNTs thus have a high emission current without melting. In cold cathodes, electrons are liberated by tunneling from the cathode material at room temperature under an intense electric field, which is termed electron field emission. The advantages of cold cathode field emitters over the conventional thermionic emitters are reduced electrical field and energy consumption [5].

According to the Fowler–Nordheim (F–N) theory [6], the emission capability of an emitter strongly depends on the field enhancement factor β and the work function ϕ. It can be predicted that if they are combined with their high field enhancement factor, work function of CNTs reduces and field emission would be greatly enhanced. Decorating the external surface of CNTs with metal nanoparticles (NPs) has attracted considerable attention, because CNTs have a high work function of about 5 eV. The CNT surface can be modified by depositing a thin coating of metal NPs that have a low work function [7].

In this paper, we report the vapor–liquid–solid growth of CNTs on an SiO_2/Si substrate. The surfaces of these CNTs are decorated with Au NPs for field emission. Detailed growth procedures and the emission properties of the fabricated devices are discussed.

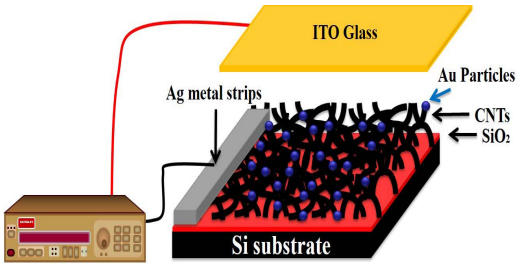

Fig. 1. Schematic of configuration for field-emission measurements.

II. Experiment

Before CNTs were grown, an Si (100) substrate was cleaned by immersion in boiled acetone for 10 min, and then in boiled isopropyl alcohol for 10 min. The chemically cleaned substrate was then rinsed in deionized water and dried in a flow of nitrogen. The substrate was then thermally oxidized to form approximately a 20-nm-thick SiO_2 layer to act as a catalyst diffusion barrier, before a 10-nm-thick Fe layer was deposited by sputtering [8], [9]. This pretreatment process was conducted at 600 °C. When a growth temperature of 700 °C was reached, the flow of N_2 was switched OFF, and the flow of C_2H_2 reactant was switched ON at a rate of 30 sccm at 3.5 torr for 10 min [10]. An electron beam was utilized to evaporate a controlled load of Au NPs all over the CNTs to an equivalent nominal thickness of ∼5 nm. The field-emission properties of these CNTs were then measured in a vacuum chamber with a pressure of $<5 \times 10^{-6}$ torr at room temperature. Fig. 1 schematically shows the experimental configuration for field-emission measurements. During these measurements, indium–tin oxide glass was used as the anode, while a Keithley 237 high-voltage source was used to provide the sweeping electric field and to monitor the emission current. The distance between the anode and the sample was kept at 130 μm.

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S.-J. Young and Z.-D. Lin are with the Department of Electronic Engineering, National Formosa University, Yunlin 632, Taiwan (e-mail: shengjoueyoung@gmail.com).

C.-H. Hsiao is with the Center for Micro/Nano Science and Technology, Advanced Optoelectronic Technology Center, Department of Electrical Engineering, Institute of Microelectronics, National Cheng Kung University, Tainan 701, Taiwan.

C.-S. Huang is with the Graduate School of Electronic and Optoelectronic Engineering, National Yunlin University of Science and Technology, Douliu 64002, Taiwan.

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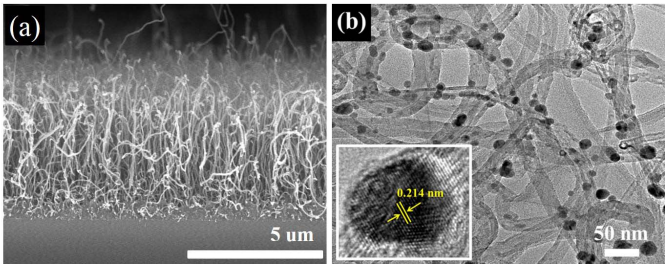

Fig. 2. (a) Cross-sectional FESEM. (b) TEM images of Au-CNTs. Inset: highly part of high-resolution TEM image of Au NP on the CNT surface.

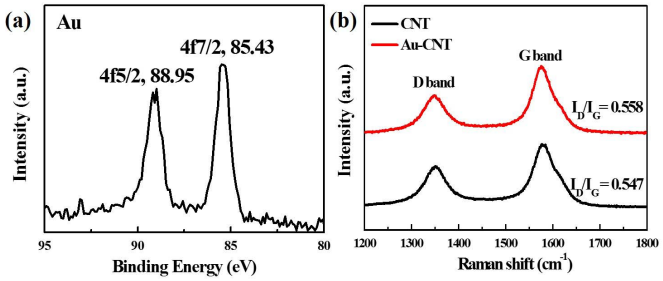

Fig. 3. (a) XPS Au4f spectra of Au-coated CNTs. (b) Raman spectra of pure and Au-coated CNTs at room temperature.

III. Results and Discussion

Fig. 2(a) and (b) shows a cross-sectional field-emission scanning electron microscopy (FESEM) image and a transmission electron microscopy (TEM) image of CNTs coated with Au NPs, respectively. The average length and diameter of the CNTs were approximately 4.5 μm and 45 nm, respectively. Fig. 2 clearly indicates that some of the Au NPs on the CNT surfaces were isolated, while some were connected with each other, increasing their size to close to 5 nm. Fig. 2(b) (inset) shows a high-resolution TEM image with an enlarged Au NP on the sidewall. The lattice spacing was found to be 0.214 nm, corresponding to a face-centered cubic lattice structure [11].

The Au-NP-coated CNTs were further characterized using X-ray photoelectron spectroscopy (XPS). In Fig. 3(a), the XPS spectrum of the Au-coated CNTs includes the Au 4f 7/2 and 4f 5/2 doublet, with binding energies of 85.43 and 88.95 eV, respectively. This doublet is typical of all Au peaks [11], [12].

Fig. 3(b) shows the Raman spectra of pure CNTs and Au-coated CNTs. Both the typical disorder-induced D-band ($\sim$1350 cm^{-1}) and the E_{2g} G-band ($\sim$1580 cm^{-1}) for multiwalled CNTs appear [13], [14]. The fitting of Gaussian components yielded the peak values and I_D/I_G ratio, which is an index of the graphitization of CNTs. A smaller I_D/I_G ratio indicates greater graphitic crystallinity of CNTs. Without Au, the I_D/I_G ratio was 0.547. The Au NPs increase this ratio to 0.558 without significantly damaging the CNT structure. The slight increase of the D-band intensity is likely caused by the Au NPs. However, the Raman spectra indicate good crystallinity with a subtle change of peak intensities with Au NP decoration.

Fig. 4 shows the current–voltage (I–V) characteristics of CNTs before and after Au deposition. The resistance of

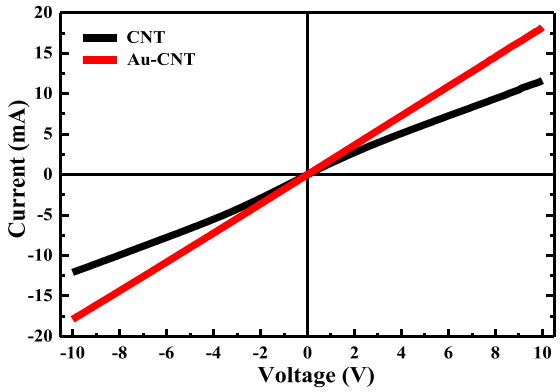

Fig. 4. I–V characteristics of CNT field-emission device before and after Au NP deposition.

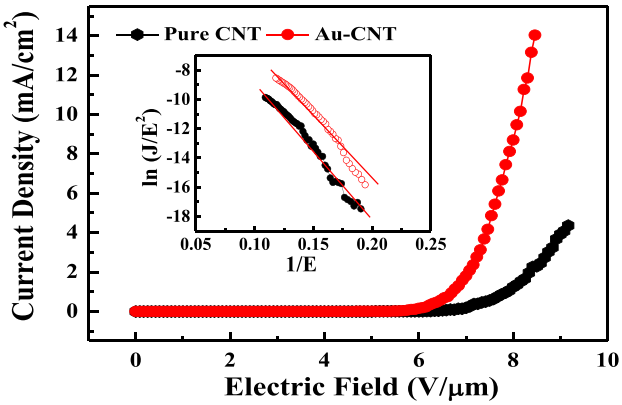

Fig. 5. Current density versus electric field curve of bare and Au-coated CNTs. Inset: corresponding F–N plots.

pure CNTs is roughly 809 Ω, indicating typically good CNT conductivity. The resistance of the Au-coated CNTs is only 549 Ω. The microscopy images show that the Au nanoclusters did not form interconnected conducting pathways between the Au-coated CNTs, so the decrease in resistance must result from a net charge transfer between the Au nanoclusters and the Au-CNTs.

Fig. 5 shows the dramatically improved field emission from the Au-coated CNTs. The turn-ON electric field (E_{to}), at which the emission current density reaches 10 μA/cm^2, decreased from 5.33 to 4.84 V/μm, and the threshold electric field (E_{th}) corresponding to 1 mA/cm^2 decreased from 7.91 to 6.76 V/μm, for the pure CNTs and Au-coated CNTs, respectively. The field-emission current density of the Au-coated CNT emitters was more than eight times higher than that of pure CNT emitters with an applied electric field of 8 V/μm because of the good electrical contact between the CNTs and the substrate [15]. Both the turn-ON field and the current density of the Au-coated CNTs clearly indicate that Au NPs considerably enhanced field emission. The current density versus applied field characteristics of both samples were analyzed using the F–N theory [6]

$$J = AE^2\varphi^{-1}\exp\left(\frac{-B\varphi^{\frac{3}{2}}}{\beta E}\right) \tag{1}$$

where J represents the emission current density, ϕ refers to the work function, A and B are constants, E is the applied

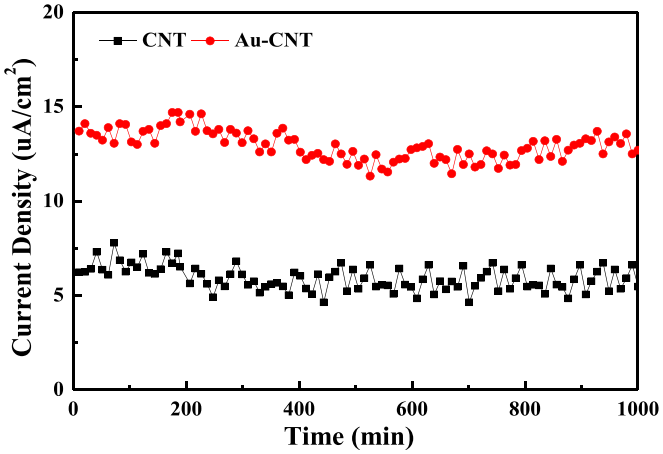

Fig. 6. Stable field-emission current.

field between the cathode and the anode, and β denotes the effective field enhancement factor, which reflects the ability of the emitters to enhance the local electric field, and can be calculated from the F–N plot as

$$\ln\frac{J}{E^2} = -\frac{B\varphi^{3/2}}{\beta}\frac{1}{E} + \ln\frac{A\beta^2}{\varphi}. \tag{2}$$

According to this equation, a plot of $\ln(J/E^2)$ versus $1/E$ is linear. Fig. 5 (inset) shows the corresponding F–N plots. The slope of the F–N plot shows that the field enhancement factor β of pure CNTs is ~767.57. To further investigate the field-emission behavior, based on the measured slopes for the CNTs, we obtained a $\phi^{3/2}/\beta$ value of 0.0147 in the applied electric field [16]. The work function of the CNTs is estimated to be ~5 eV [17]. The $\phi^{3/2}/\beta$ value of CNTs in the applied electric field is 0.0134. Since the surface morphologies of the two types of CNT are similar, it is assumed that the β value of Au-coated CNTs is also 767.57. With this assumption, it is found that the work function ϕ of the Au-coated CNTs is 4.74 eV. Decoration with Au NPs decreased the work function from 5 to 4.74 eV. The improved emission current density and relatively low turn-ON voltage are attributed to the lower work function [18].

The enhanced field-emission properties of Au-coated CNTs were mainly caused by the lower effective work function. The effective work function ($\Phi_{\text{eff}} = \Phi/\beta$) of the films was calculated from the slope of the F–N plot, where Φ is the true work function and β is the field enhancement factor of the material [19]. The Φ_{eff} values of the bare and Au-coated CNTs obtained from the F–N plot are 0.00651 and 0.00584 eV, respectively. It is believed that the CNT field-emission enhancement is mainly attributed.

Fig. 6 shows the stable field-emission current of pure and Au-coated CNTs obtained at current densities of 5 and 15 μA/cm^2 after 1000 min. The current fluctuation is lower, and the average current shows only a 5% degradation during this period. This better stability and long lifetime can be explained by the strong adhesion between the CNTs and the substrate.

Fig. 7 shows the schematic band diagram of Au-decorated CNTs. When a high external electric field is applied, the band

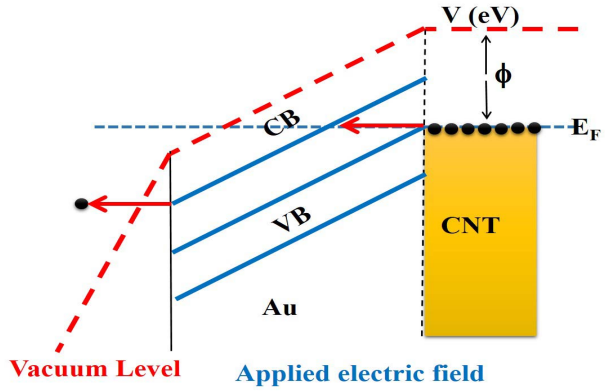

Fig. 7. Schematic band diagram of Au-decorated CNTs.

bending effect lowers the vacuum level. Electrons are injected from the Fermi level of the CNTs to the conduction band of Au. The injected electrons thermalize to the conduction band minimum of Au. Finally, the electrons are emitted by field emission at the Au and vacuum interface. Therefore, electrons more easily tunnel at lower electric fields, enhancing field emission [20], [21].

IV. Conclusion

This paper reported the growth of high-density CNTs on an oxidized Si substrate, which were coated with Au NPs. With Au adsorption, the turn-ON electric field, at which the emission current density reaches 10 μA/cm^2, decreased from 5.33 to 4.84 V/μm. Decoration with Au NPs decreased the work function from 5 to 4.74 eV. The enhanced field-emission properties of Au-coated CNTs are mainly caused by a lower effective work function.

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Sheng-Joue Young (M'10) received the B.S. degree from the Department of Physics, National Changhua University of Education, Changhua, Taiwan, in 2003, and the M.S. and Ph.D. degrees from the Institute of Electro-Optical Science and Engineering and the Institute of Microelectronics, National Cheng Kung University, Tainan, in 2005 and 2008, respectively.

He is currently an Associate Professor with the Department of Electronic Engineering, National Formosa University, Yunlin, Taiwan, in 2010.

Zheng-Dong Lin was born in Taipei, Taiwan, in 1988. He received the M.S. degree from the Institute of Electronic Engineering, National Formosa University, Yunlin, Taiwan, in 2012.

His current research interests include semiconductor physics, carbon-based material, sensor devices, optoelectronic devices, and nanotechnology.

Chih-Hung Hsiao was born in Taipei, Taiwan, in 1982. He received the M.S. degree from the Institute of Electronic Engineering, National Yunlin University of Science and Technology, Yunlin, Taiwan, in 2007, and the Ph.D. degree from the Institute of Microelectronics, National Cheng Kung University (NCKU), Tainan, Taiwan, in 2010.

He currently serves as a Post-Doctoral Researcher with the Institute of Microelectronics, NCKU.

Chien-Sheng Huang received the B.S., M.S., and Ph.D. degrees from the Department of Electrophysics, Institute of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, in 1989, 1991, and 1998, respectively.

He is currently an Assistant Professor with the Department of Electronic Engineering, National Yunlin University of Science and Technology, Yunlin, Taiwan. His current research interests include optoelectronic devices and nanotechnology.