

# Growth and field emission of carbon nanotubes on electroplated Ni catalyst coated on glass substrates

Jaemyung Kim<sup>a)</sup> and Kwangsoo No

*Department of Materials Science and Engineering, KAIST, Taejeon 305-701, South Korea*

Cheol Jin Lee

*School of Electrical Engineering, Kunsan National University, Kunsan 573-701, South Korea*

(Received 19 March 2001; accepted for publication 7 June 2001)

Carbon nanotubes are grown on Ni catalyst coated on soda-lime glass substrates using chemical vapor deposition of  $C_2H_2$  gas at  $550^\circ C$ . Ni film is coated on the surface of Ag film using the electroplating method. Ni was etched by ammonia ( $NH_3$ ) gas in order to form nanometer sized catalytic particles before carbon nanotube growth. Pd film is applied as a gas activator to decrease the growth temperature of carbon nanotubes. The carbon nanotubes grown on Ni catalyst particles showed a multiwalled structure with defective graphite sheets at the wall. The turn-on voltage was about  $2.8 V/\mu m$  with an emission current density of  $10 \mu A/cm^2$ , and the threshold voltage was about  $4.0 V/\mu m$  with an emission current density of  $10 mA/cm^2$ . The Fowler-Nordheim plot showed a good linear fit, indicating that the emission current of carbon nanotubes follows Fowler-Nordheim behavior. The calculated field enhancement factor was 2850. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389761]

## I. INTRODUCTION

Since the first observation of carbon nanotubes (CNTs),<sup>1</sup> extensive research has been done on the synthesizing methods: arc discharge,<sup>2,3</sup> laser vaporization,<sup>4</sup> pyrolysis,<sup>5</sup> and plasma-enhanced or thermal chemical vapor deposition (CVD).<sup>6–12</sup> Among these synthesis methods, CVD has many advantages such as high purity, high yield, simple process, selective growth, vertical alignment, and large area uniformity. The reaction temperature of thermal CVD is generally as high as  $700$ – $1000^\circ C$ . Recently, the growth of CNTs using the plasma-enhanced CVD method was reported at  $660^\circ C$ .<sup>6</sup>

One of the most attractive applications of CNTs is an electron emitter for flat panel displays such as field emission display (FED) and vacuum fluorescent display (VFD).<sup>13–16</sup> Kim *et al.*<sup>14</sup> reported FED having CNT emitters which mixed with organic binder. Wang *et al.*<sup>16</sup> used a carbon nanotube-epoxy mixture as an electron emitter for FED. Kim and Wang used the screen printing method to coat Ag thick film as a cathode on the glass substrate. They mixed CNTs, which were synthesized by the arc discharge method, with an organic binder (or epoxy binder) and then printed the CNT organic mixture paste on the Ag thick film. Soda-lime glass, which has softening at  $550^\circ C$ , is commonly used as the substrate of flat panel displays because of its low price and good vacuum sealing. In order to apply the direct grown CNTs to an electron emitter sealed by a soda-lime glass substrate, the growth temperature must be lower than  $550^\circ C$ . Because of this temperature limitation, most of the researchers used pre-made CNT as an electron emitter. In this work we introduced a fabrication method of a CNT emitter making for a field emission display that will be suitable for mass production.

Lee *et al.*<sup>17</sup> reported low temperature CNT growth by thermal CVD below  $550^\circ C$  using a gas activator, such as Pd, Pt, etc. In this work, Ag thick film was coated using the screen printing method on the glass substrate and then Ni thin film was also coated on the Ag film using the electroplating method. CNTs were grown on the Ni coated Ag/soda-lime glass using thermal CVD at  $550^\circ C$ . This method is suitable for mass production of a large area electron emitter for FED.

## II. EXPERIMENTAL PROCEDURES

A  $25 \times 25$  mm sized soda-lime glass was used as a substrate. Ag film, which is used as a cathode electrode, was printed by the screen-printing method of Ag paste (DS-7068, Daejoo Korea) on the glass substrate. The printed pattern was a stripe type,  $500 \mu m$  wide with  $500 \mu m$  pitch. After printing the Ag film it was dried at  $150^\circ C$  for 10 min and heated at  $550^\circ C$  for 10 min. The final thickness of the Ag film was about  $5 \mu m$  on the glass substrate.

The  $200$  nm thick Ni film was only coated on the patterned Ag film as a stripe line using the electroplating method. It makes self-aligned CNTs grow on the line patterned Ni/Ag film. The electroplating bath consists of nickel sulfate ( $NiSO_4 \cdot 6H_2O$ )  $150 g/l$ , ammonium chloride ( $NH_4Cl$ )  $15 g/l$ , and boric acid ( $H_3BO_3$ )  $15 g/l$ .<sup>18</sup> The temperature and pH of the electroplating bath were  $40^\circ C$  and 4.5, respectively. In the electroplating bath, an anode (+) of dc power source (HC-1330A, Heungchang Korea) was connected to a Ni metal plate and a cathode (–) was connected to the Ag coated glass substrate. The dc current  $\sim 20$  mA at 2 V was applied for 20 s.

Palladium (Pd),  $100$  nm thick, was deposited on the alumina substrate using the thermal evaporation under a

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: ducking@kaist.ac.kr

vacuum of  $1 \times 10^{-6}$  Torr. The Pd film lowered the deposition temperature of CNTs due to contributing  $C_2H_2$  gas activation and benzene coupling reaction.<sup>17,19</sup>

The Ni/Ag/glass substrate and the Pd deposited alumina substrate were loaded in a face-to-face direction on an alumina setter and inserted into a quartz tube reactor. The surface of the Ni/Ag/glass substrate was directed facedown, while Pd coated alumina substrate was directed faceup. The distance between the two substrates was 5 mm.

Argon(Ar) gas was passed through the quartz reactor in order to prevent the oxidation of the Ni catalyst and Pd gas activator while the temperature increased. To make Ni catalytic particles,  $NH_3$  gas was supplied to the quartz reactor at 550 °C with a flow rate of 100 sccm for 5–20 min. And then the CNTs were grown using  $C_2H_2$  gas with a flow rate of 20 sccm, for 10 min at 550 °C. Then the reactor was cooled down slowly to room temperature under Ar gas ambient.

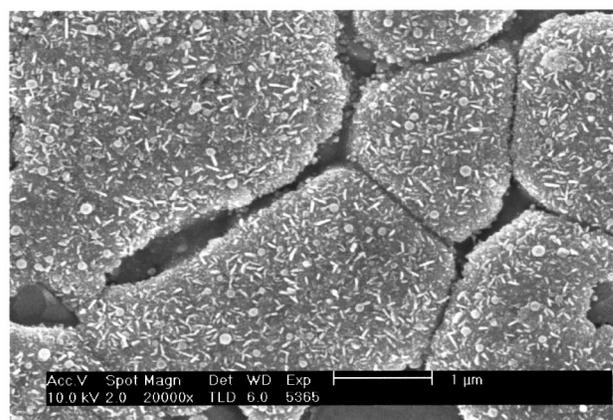
CNTs were examined by a scanning electron microscope (SEM) (Philips XL30SFEG) to measure the tube length and the diameter. A Raman spectrometer was also used to evaluate the structure and crystallinity. Field emission measurement was performed by taking voltage–current ( $V$ – $I$ ) curves with a Keithley 237 (maximum 1100 V) source-measure unit at a vacuum chamber.

### III. RESULTS AND DISCUSSION

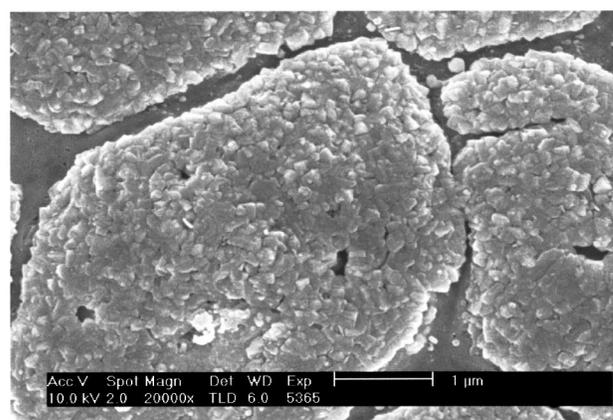
Figure 1 shows SEM micrographs of the surface morphology of Ni catalyst particles on the Ag/glass substrates after  $NH_3$  pretreatment. We etched Ni film with a  $NH_3$  gas at a flow rate of 100 sccm for 10 and 20 min at 550 °C. In Fig. 1(a), Ag grains of several micrometer size and Ni catalyst particles of several nanometer size are formed on the Ag grains. If etching time was over 20 min, Ni catalyst on the Ag grain was removed as seen in Fig. 1(b).

The CNTs were grown using  $C_2H_2$  gas with a flow rate of 20 sccm for 10 min at 550 °C. Figure 2 shows SEM micrographs of the CNTs grown on a Ni/Ag/glass substrate at 550 °C in the presence of a Pd gas activation layer. Figure 2(a) is a low magnification SEM micrograph. CNTs were not grown on the bare glass surface but grown only on the Ni/Ag surface. Figure 2(b) is the magnified view of Fig. 2(a). Figure 2(b) shows two types of CNTs: a straight shape with a large diameter in the range 100–200 nm and a noodle shape with a small diameter in the range 30–40 nm. The carbon nanotubes are not vertically oriented to the substrate, but a few CNTs are randomly directed perpendicular to the substrate.

Figure 3 shows Raman spectrum of the CNTs grown on the Ni/Ag/glass substrate. The wavelength of the excitation laser was 488 nm. The peak of tangential C–C stretching (G) modes appears at  $1580\text{ cm}^{-1}$ . There is no evidence for a radial breathing mode at  $\sim 190\text{ cm}^{-1}$ , suggesting that the carbon nanostructures are multiwalled tubes or fibers. It is known that the D mode corresponding to  $1335\text{ cm}^{-1}$  is related to the defects or carbonaceous particles on the surface of tubes. A Raman spectrum reveals that CNTs have a multiwalled structure with some defective graphite sheets at the wall.



(a)

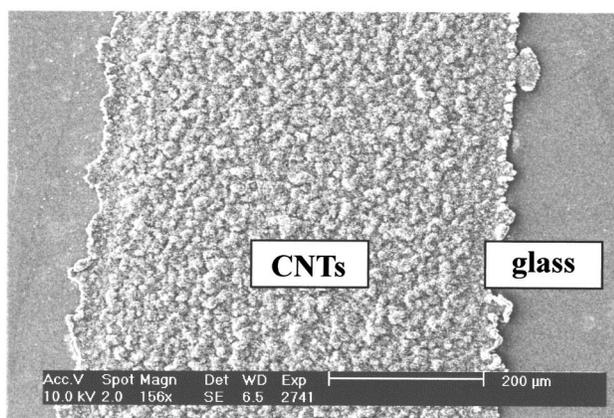


(b)

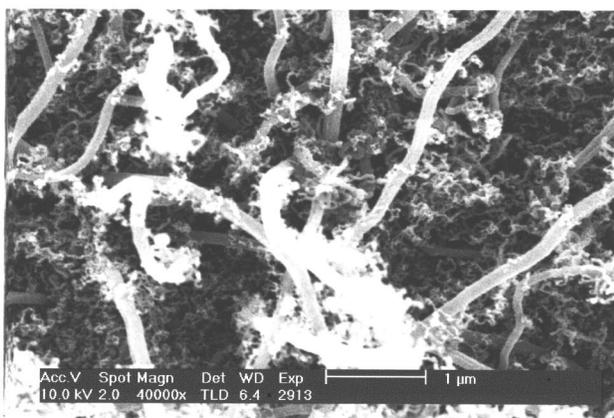
FIG. 1. SEM micrographs of the Ni catalyst particles on the Ag film after  $NH_3$  treatment. (a) Surface morphology of Ni/Ag/glass etched for 10 min using  $NH_3$  gas. Ni catalyst particles are identified on the surface. (b) Surface morphology of Ni/Ag/glass etched for 20 min using  $NH_3$  gas. No Ni particles remain on the surface due to the over etch.

Figure 4 illustrates the electron emission current density versus electric field curve from the CNTs grown on Ni/Ag/glass substrate. Field emission measurement was conducted in a vacuum chamber at  $2 \times 10^{-5}$  Torr.  $25 \times 25$  mm sized indium-tin oxide (ITO) coated glass was placed above the CNTs. An Ag electrode was connected to a cathode(–) and an ITO electrode was connected to an anode(+). The distance between the ITO film and the CNT tips was about 100  $\mu\text{m}$ . In this case, a 100 nm thick ITO film which is a transparent electrode has a resistivity of  $3 \times 10^{-4}\ \Omega\text{ cm}$ .

The turn-on voltage was about 2.8 V/ $\mu\text{m}$  with an emission current density of 10  $\mu\text{A}/\text{cm}^2$ . The electron emission current increased dramatically above 3 V/ $\mu\text{m}$  and arrived at 1 mA/ $\text{cm}^2$  at an applied electric field 3.3 V/ $\mu\text{m}$ . Maximum emission current density was 10 mA/ $\text{cm}^2$  at 4.0 V/ $\mu\text{m}$  before electrical breakdown, which is sufficient for the electron emitter of the FED. The inset of Fig. 4 shows a good linear fit, indicating that the emission current of CNTs follows the Fowler–Nordheim behavior. The field enhancement factor ( $\beta$ ) can be calculated from the slope of the FN plot.<sup>20</sup> The



(a)



(b)

FIG. 2. SEM micrographs of the CNTs grown on the Ni/Ag/glass substrate at 550 °C using C<sub>2</sub>H<sub>2</sub> gas with a flow rate of 20 sccm for 10 min, in the presence of a Pd gas activator. (a) SEM image of CNTs on the substrate. CNTs are selectively grown on the Ni catalytic metals. (b) A magnified SEM image ( $\times 40\,000$ ) of CNTs.

total current  $I$  as a function of the local field at the emitter surface  $F$  is approximately given by  $I \propto (F^2/\Phi) \exp(B\Phi^{3/2}/F)$  with  $B = 6.83 \times 10^9 [\text{V eV}^{-3/2} \text{m}^{-1}]$ , where  $\Phi$  is the work function.  $F$  is usually taken as  $F = \beta E$

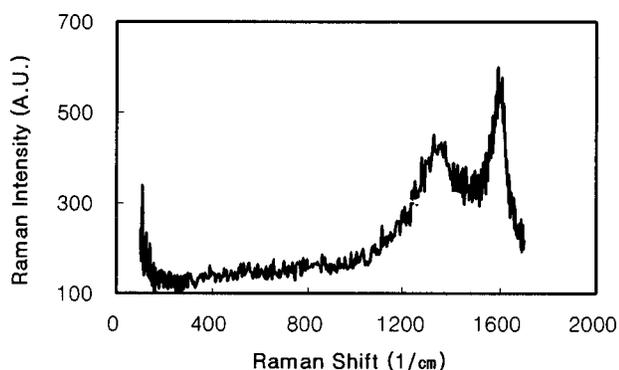


FIG. 3. Raman spectrum of the CNTs grown on the Ni/Ag/glass substrate. Raman spectrum reveals that CNTs have a defective graphite structure at the wall.

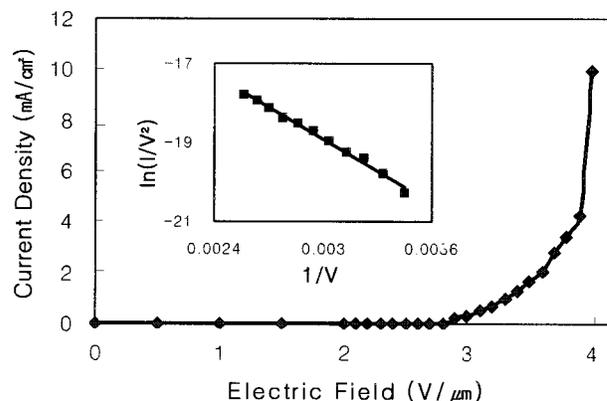


FIG. 4. Electron emission current density versus applied electric field curve from the CNTs grown on Ni/Ag/glass substrate. Turn-on voltage is about 2.8 V/ $\mu\text{m}$  and maximum current density is 10 mA/cm<sup>2</sup> at an applied electric field 4.0 V/ $\mu\text{m}$  before electric breakdown.

$=\beta V/d$ , where  $V$  is the applied potential,  $d$  is the distance between cathode and anode,  $\beta$  the field enhancement factor, and  $E = V/d$  the macroscopic field. The calculated field enhancement factor was 2850, for the work function of CNT to be 5 eV, the same as that of graphite or C<sub>60</sub>.<sup>21</sup> This value is similar to the reported value.<sup>20</sup>

In summary we have grown carbon nanotubes on Ni coated Ag/glass substrates at 550 °C using thermal chemical vapor deposition. Ag film was screen-printed on the glass substrate and Ni catalyst was electroplated on the Ag film. We could realize carbon nanotubes growth below the softening temperature of soda-lime glass using a Pd gas activator. We suggest that this method is good for mass production of a CNT emitter.

The CNT had good emission characteristics even though it reveals not so good crystalline structure. The threshold voltage was about 4.0 V/ $\mu\text{m}$  with an emission current density of 10 mA/cm<sup>2</sup>. The Fowler–Nordheim plot shows a good linear fit, indicating that the emission current of CNTs follows the Fowler–Nordheim behavior, the calculated field enhancement factor was 2850.

<sup>1</sup>S. Iijima, *Nature (London)* **354**, 56 (1991).

<sup>2</sup>S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993).

<sup>3</sup>D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature (London)* **363**, 605 (1993).

<sup>4</sup>A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, D. T. Colbert, G. Scuseria, D. Tomanek, J. E. Fisher, and R. E. Smalley, *Science* **273**, 483 (1996).

<sup>5</sup>M. Terrones, N. Grobert, J. Olivares, J. P. Zhang, H. Terrones, K. Kordatos, W. K. Hsu, J. P. Hare, P. D. Townsend, K. Prassides, A. K. Cheetham, H. W. Kroto, and D. R. M. Walton, *Nature (London)* **388**, 52 (1997).

<sup>6</sup>Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, *Science* **282**, 1105 (1998).

<sup>7</sup>S. L. Sung, S. H. Tsai, C. H. Tseng, F. K. Chiang, X. W. Liu, and H. C. Shih, *Appl. Phys. Lett.* **74**, 197 (1999).

<sup>8</sup>C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, *Nature (London)* **388**, 756 (1997).

<sup>9</sup>W. Z. Li, S. S. Xie, L. X. Qain, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996).

<sup>10</sup>S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tomblor, A. M. Casell, and H. Dai, *Science* **283**, 512 (1999).

<sup>11</sup>C. J. Lee, D. W. Kim, T. J. Lee, Y. C. Choi, Y. S. Park, W. S. Kim, W. B.

- Choi, N. S. Lee, J. M. Kim, Y. G. Choi, S. C. Yu, and Y. H. Lee, *Appl. Phys. Lett.* **75**, 1721 (1999).
- <sup>12</sup>W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996).
- <sup>13</sup>Y. Saito and S. Uemura, *Carbon* **38**, 169 (2000).
- <sup>14</sup>J. M. Kim, W. B. Choi, N. S. Lee, and J. E. Jung, *Diamond Relat. Mater.* **9**, 1184 (2000).
- <sup>15</sup>J. L. Kwo, M. Yokoyama, W. C. Wang, F. Y. Chuang, and I. N. Lin, *Diamond Relat. Mater.* **9**, 1270 (2000).
- <sup>16</sup>Q. H. Wang, A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, E. W. Seelig, and R. P. H. Chang, *Appl. Phys. Lett.* **72**, 2912 (1998).
- <sup>17</sup>C. J. Lee, J. H. Park, J. M. Kim, Y. Huh, J. Y. Lee, and K. S. No, *Chem. Phys. Lett.* **327**, 277 (2000).
- <sup>18</sup>*Plating Handbook* (Kijeonsa, Korea, 1989), p. 242.
- <sup>19</sup>C. J. Baddeley *et al.*, *Surf. Sci.* **400**, 166 (1998).
- <sup>20</sup>J. M. Bonard *et al.*, *Appl. Phys. Lett.* **73**, 918 (1998).
- <sup>21</sup>B. W. Gadzuk, E. W. Plummer, C. R. Seances Acad. Sci., Ser. B **278**, 659 (1974).