

Screen printed carbon nanotube field emitter array for lighting source application

Jae-Hong Park, Gil-Hwan Son, Jin-San Moon, Jae-Hee Han, Alexander S. Berdinsky, D. G. Kuvshinov, Ji-Beom Yoo,^{a)} and Chong-Yun Park
Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, 300 Chunchun-Dong, Jangan-Gu, Suwon 440-746, Korea

Joong-Woo Nam, Jonghwan Park, Chun Gyoo Lee, and Deok Hyeon Choe
Technology Development 3, Corporate R&D Center, Samsung SDI 428-5, Gongse-Ri, Kiheung-Eup, Yongin 449-902, Korea

(Received 1 October 2004; accepted 30 November 2004; published 7 April 2005)

We have investigated carbon nanotube (CNT)-field emitter array (FEA) for the application of lighting system like back light unit (BLU) in liquid crystal display (LCD). The photosensitive CNT paste was synthesized by mixing of multiwalled carbon nanotubes (MWNTs), spin on glass (SOG), organic vehicle, photosensitive monomers, photosensitive oligomers and photo initiators. Uniform CNT paste films were obtained by using backside exposure technique and emission properties of CNT paste were evaluated depending on variation in SOG content and firing conditions. Then we prepared line patterned CNT-FEAs using photolithography and measured their $I-V$ characteristics and brightness. © 2005 American Vacuum Society. [DOI: 10.1116/1.1851535]

I. INTRODUCTION

Liquid crystal display (LCD) requires a light source from its backside because LCD is not an emissive display. The back light unit (BLU) for LCD has been remarkably investigated for a recent few years because of development of large area LCD TV. The light sources for BLU such as cold cathode fluorescent lamp (CCFL), external electrode fluorescent lamp (EEFL) and flat lamp have been widely used. A suitable BLU must have low power consumption, light-weight and uniform brightness. Recently, principal constructions of BLU using light emitting device based on carbon nanotube (CNT), gallium nitride (GaN) light emitting diode (LED) and modified CCFL were reported. Bonard and co-workers demonstrated a fully sealed luminescent tube based on CNT field emitter.¹ Wei's group also reported the household light bulb with CNT filaments.² The flat lamp using CNT-field emitter array (FEA) can be used for large area LCD BLU because of its superior performances such as ultra slim features, simple structure, low power consumption and etc.³ CNT-FEA was fabricated by two typical methods such as a chemical vapor deposition (CVD) using catalytic metals and a screen-printing technique using CNT paste. The screen-printing method has many advantages for fabrication of emitters in terms of easy manufacturing process, mass production, low cost and uniformity in large area.⁴

In this study, we prepared photosensitive CNT paste with spin on glass (SOG) and investigated their emission properties depending on SOG content and firing conditions. Moreover, we have investigated the potential of diode type FEA using CNT paste for the application in lighting system like BLU in LCD.

II. EXPERIMENT

We prepared the photosensitive CNT paste by mixing of MWNTs, SOG, organic vehicle, photosensitive monomers, photosensitive oligomers, and photo initiators. MWNTs powders grown by CVD and SOG were used as an electron emission source and inorganic binder, respectively. In the case of CNT paste, glass frit was typically used as an inorganic binder to enhance the adhesion between CNT and the substrate after firing. However, CNT paste with a glass frit has shown a poor uniformity in cathode film formation and the emission characteristics after firing in air. Therefore, photosensitive CNT paste was prepared by using SOG as an advanced inorganic binder instead of a glass frit. The mixture of CNT powders, organic vehicles and inorganic binder were premixed through solder paste softener for 15 min. Then the three-roll mill process was carried out for mixing and dispersion of CNT powders in organic vehicle as polymer matrix. Detailed process for the preparation of CNT paste were described in our previous report.⁵ Mechanically well-dispersed CNT paste was printed onto an indium thin oxide (ITO) coated soda lime glass. To obtain the uniform thickness of CNT paste film, backside exposure and development process were carried out after printing and drying of CNT paste in forced convection oven for 15 min at 90 °C. The residue of organic vehicle leads to problems such as outgassing and arcing during a field emission measurement. Organic materials in paste have to be removed in order to obtain the stable emission characteristics. Therefore, the CNT paste film was fired at 400–450 °C in air or nitrogen (N₂) ambient.

Field emission scanning electron microscopy (FESEM) was employed for the characterization of CNT paste. Figure 1 shows SEM images of screen-printed CNT paste films that were obtained from different firing conditions. The CNT paste film was fired at temperature of 400–450 °C under air

^{a)}Author to whom correspondence should be addressed; electronic mail: jbyoo@skku.ac.kr

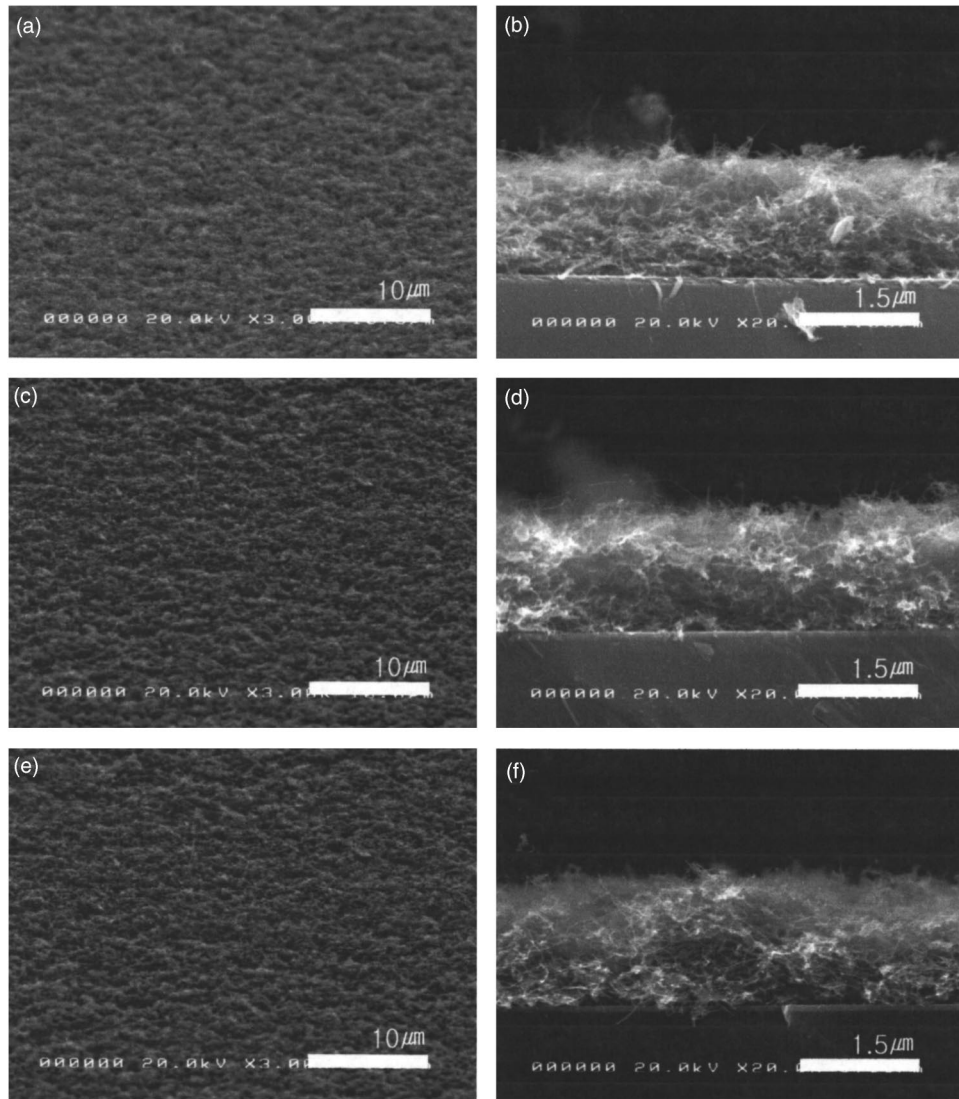


FIG. 1. SEM images of screen-printed CNT paste films with different firing conditions; (a), (b) 400 °C in air, (c), (d) 450 °C in air, and (e), (f) 450 °C in N₂.

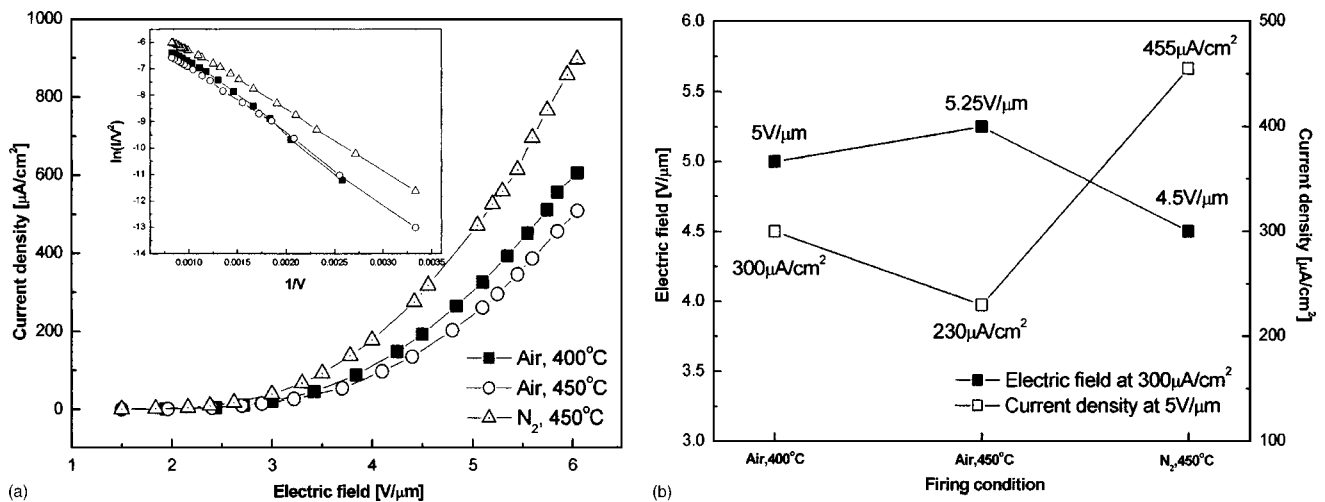


FIG. 2. (a) *I*–*V* characteristics and (b) variation of emission properties of CNT paste under different firing conditions. Inset (a) is of the Fowler–Nordheim plot of the emission current.

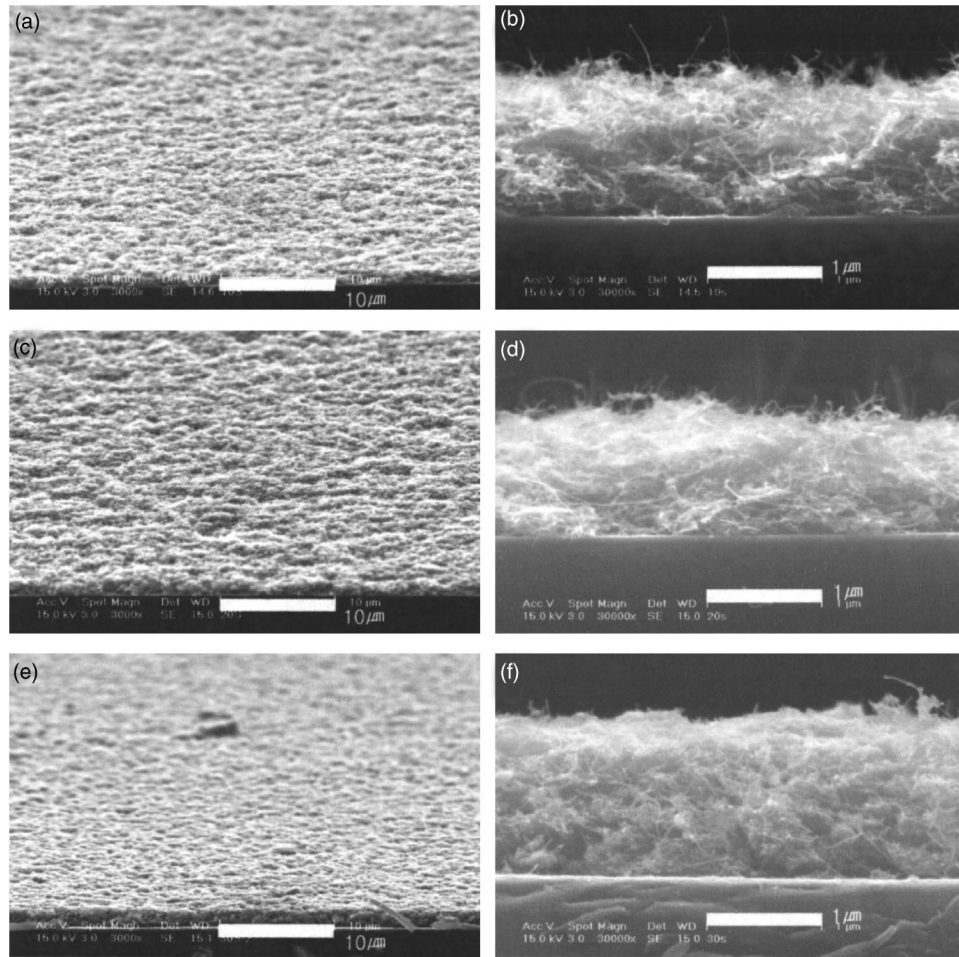


FIG. 3. SEM images of CNT paste films with different SOG content; (a),(b) 10 wt. % SOG, (c), (d) 20 wt. % SOG, and (e), (f) 30 wt. % SOG.

or N_2 ambient. CNT paste with SOG easily formed a uniform thick film and firing was carried out at relatively high firing temperature of $450^\circ C$ in air, as shown in Figs. 1(c) and 1(d).

The emission characteristics and brightness of screen-printed CNT FEA were measured in a vacuum chamber with a parallel diode-type configuration at a pressure of 5×10^{-6} Torr after surface activation treatment using adhesive tape.^{6,7}

III. RESULTS AND DISCUSSION

It is well known that screen printed CNT-FEA generally needs a special surface treatment such as laser irradiation,⁸ ion irradiation,⁹ and surface rubbing with adhesive tape^{6,7} for high emission current density and uniform emission site through protrusion of CNT. We carried out activation treatment using adhesive tape. The emission characteristics of CNT paste films were measured after surface activation treatment. We have adopted pulsed voltage with a duty cycle of 1/500. The distance between anode and cathode was $200 \mu m$. Emission characteristics of CNT paste were changed depending on firing temperature and ambient as shown in Fig. 2. Figure 2(a) shows current voltage (I - V) characteristics of CNT paste depending on the firing condi-

tions. Firing at $450^\circ C$ in N_2 ambient shows better emission characteristics than firing at other conditions. Organic vehicle can be more easily removed at the higher firing temperature and N_2 ambient protected the CNT emitter while CNT emitter was burned out in O_2 presented ambient. Variation of emission property with different firing conditions was evaluated as the electric field where emission current density was $300 \mu A/cm^2$ and as the current density at the electric field of $5 V/\mu m$. The maximum emission current density of $895 \mu A/cm^2$ at $6.05 V/\mu m$ was obtained from CNT paste fired at $450^\circ C$ in N_2 ambient. When the firing temperature was decreased from 450 to $400^\circ C$ in an ambient of air, emission property of CNT paste was enhanced due to decrease in thermal damage and oxidation of CNT. When firing ambient was changed from air to N_2 , an electric field at the emission current of $300 \mu A/cm^2$ was decreased from 5.25 to $4.5 V/\mu m$. Current density at the electric field of $5 V/\mu m$ was increased from 203 to $455 \mu A/cm^2$ in N_2 ambient in contrast to air. The reason for these phenomena is that we have more emission site in N_2 ambient. Through Fowler-Nordheim (F-N) plots [inset of Fig. 2(a)], we confirmed that field emission was done by quantum tunneling mechanism. We optimized the firing condition for CNT pastes with various conditions such as ambient and tempera-

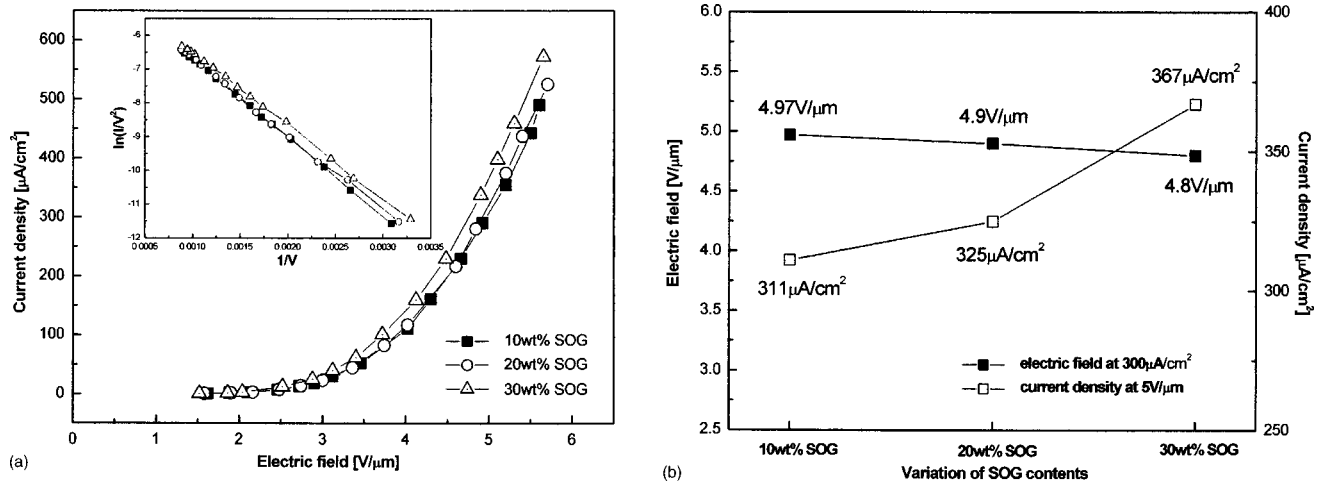


Fig. 4. (a) I - V characteristics and (b) variation of emission property of CNT paste with different SOG content. Inset (a) is of the Fowler-Nordheim plot of the emission current.

ture. According to our results, a firing at 450°C under N_2 is the most suitable condition for photosensitive paste with CVD-MWNTs.

We prepared CNT pastes with different SOG content, and investigated their microstructure and emission properties. Figure 3 shows SEM images of CNT paste films with different SOG content. The thickness of CNT paste films was slightly increased as of SOG content increases. Morphology of CNT paste with different SOG content seems to be quite similar.

Figure 4 shows I - V characteristics (a) and variation of emission property of CNT paste films with different SOG content. The increase in SOG content leads to enhancement of field emission properties of CNT paste. As SOG content increases from 10 to 30 wt. %, the applied electric field that produces the emission current of $300\mu\text{A}/\text{cm}^2$ decreased from 4.97 to $4.8\text{V}/\mu\text{m}$ and the current density at $5\text{V}/\mu\text{m}$

increased from 311 to $367\mu\text{A}/\text{cm}^2$. An inset of Fig. 4(a) shows an electron emission from CNT paste was done by the tunneling mechanism.

The minimum size of the pattern by conventional screen-printing method using normal paste is below $100\mu\text{m}$.¹⁰ When we used a photosensitive paste and photolithography techniques such as backside exposure and development, a much smaller patterning was possible. Figure 5(a) shows an optical microscopic image of line patterned CNT FEA after back side exposure and development process. The width and pitch of CNT paste stripes were 50 and $50\mu\text{m}$, respectively. The thermal evaporated chromium (Cr) layer [the bright region in Fig. 5(a)] with thickness of 200nm was used for a self-aligned photo mask and supplementary electrode to the ITO electrode. The thickness of line patterned CNT paste stripes [the dark region in Fig. 5(a)] was approximately $1.6\mu\text{m}$.

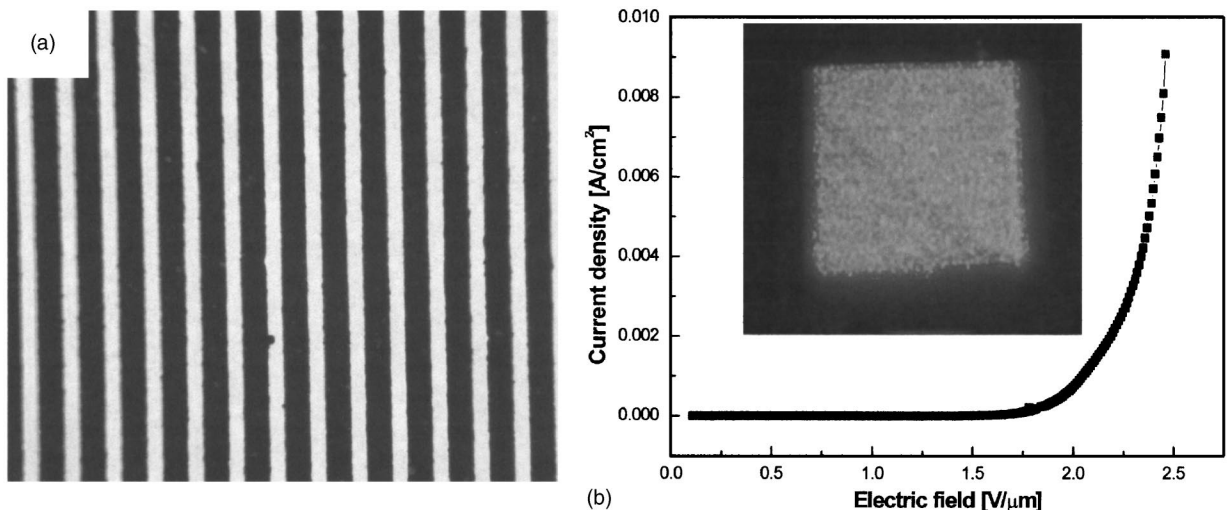


Fig. 5. (a) The optical microscopic image of CNT-FEA and (b) I - V characteristic of the fabricated CNT-FEA. Inset (b) is of the emission image from CNT-FEA at the anode voltage of 1200V .

The I - V characteristics and brightness of the CNT-FEA were measured by the parallel diode-type configuration in a high vacuum chamber after surface treatment using adhesive tape. We have adopted dc voltage in this case. The area of CNT paste films was $2 \times 2 \text{ cm}^2$ and the space between anode and cathode was $500 \text{ }\mu\text{m}$. The conventional green phosphors for cathode ray tube (CRT) were deposited on the ITO electrodes of front glass to form an anode faceplate. The I - V characteristics of this sample were represented in Fig. 5(b). The turn-on electric field, E_{to} , is defined as the electric field at $10 \text{ }\mu\text{A}/\text{cm}^2$ of current density. As shown in Fig. 5(b), the E_{to} of CNT-FEA corresponds to approximately $1.56 \text{ V}/\mu\text{m}$ and maximum current density was approximately $9.08 \text{ mA}/\text{cm}^2$ at $2.46 \text{ V}/\mu\text{m}$. The inset of Fig. 5(b) indicates the emission image from CNT-FEA with an anode voltage of 1200 V . The uniform emission pattern was observed from the whole cathode area and the measured brightness was $18\,000 \text{ cd}/\text{m}^2$. The fabricated CNT-FEA showed relatively high brightness at low operating voltage.

IV. CONCLUSION

We prepared the photosensitive CNT paste by mixing MWNTs, SOG, organic vehicle, photosensitive monomers, photosensitive oligomers, and photo initiators. Uniform CNT paste films were obtained by using screen-printing method and backside exposure technique. We also investigated their emission property depending on variation of SOG content and firing conditions. Firing at $450 \text{ }^\circ\text{C}$ in N_2 was the most suitable condition for case of paste with CVD-MWNTs. Thickness and emission current density of CNT paste films were slightly increased with an increase in SOG content. The

fabricated CNT-FEA showed relatively good emission properties and high brightness at low operating voltage. These reliable results will be used for the fabrication of CNT-FEA based flat lamp for the BLU of LCD in the near future.

ACKNOWLEDGMENTS

This research was supported by a grant (M1-02-KR-01-0001-02-K18-01-016-1-2) from Information display R&D Center, one of the 21st Century Frontier R&D program funded by the Ministry of Science and Technology of Korea government and KOSEF through CNNC (Center for Nanotubes and Nano structured Composite) at Sungkyunkwan University.

- ¹M. Croci, I. Arfaoui, T. Stöckli, A. Châtelain, and J.-M. Bonard, *Microelectron. J.* **35**, 329 (2004).
- ²J. Wei, H. Zhu, D. Wu, and B. Wei, *Appl. Phys. Lett.* **84**, 4869 (2004).
- ³N. S. Lee, D. S. Chung, I. T. Han, J. H. Kang, Y. S. Choi, H. Y. Kim, S. H. Park, Y. W. Jin, W. K. Yi, M. J. Yun, J. E. Jung, C. J. Lee, J. H. You, S. H. Jo, C. G. Lee, and J. M. Kim, *Diamond Relat. Mater.* **10**, 265 (2001).
- ⁴W. B. Choi, D. S. Chung, J. H. Kang, H. Y. Kim, Y. W. Jin, I. T. Han, Y. H. Lee, J. E. Jung, N. S. Lee, G. S. Park, and J. M. Kim, *Appl. Phys. Lett.* **76**, 3129 (1999).
- ⁵S. K. Kang, J. H. Choi, J. H. Park, J. H. Han, J. B. Yoo, J. W. Nam, C. K. Lee, and J. M. Kim, *J. Vac. Sci. Technol. B* **22**, 1345 (2004).
- ⁶T. J. Vink, M. Cillies, J. C. Krieger, and H. W. J. J. van de Laar, *Appl. Phys. Lett.* **83**, 3552 (2003).
- ⁷K. B. Kim, Y. H. Song, C. S. Hwang, C. H. Chung, J. H. Lee, I. S. Choi, and J. H. Park, *J. Vac. Sci. Technol. B* **22**, 1331 (2004).
- ⁸W. J. Zhao, N. Kawakami, A. Sawada, and M. Takai, *J. Vac. Sci. Technol. B* **21**, 1734 (2003).
- ⁹D. H. Kim, C. D. Kim, and H. R. Lee, *Carbon* **42**, 1807 (2004).
- ¹⁰Y. R. Cho, J. H. Lee, C. S. Hwang, Y. H. Song, H. S. Uhm, D. H. Kim, S. D. Ahn, C. H. Chung, B. C. Kim, and K. I. Cho, *Jpn. J. Appl. Phys., Part 1* **41**, 1532 (2002).