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ScienceDirect
Surface & Coatings Technology 201 (2007) 5378–5382
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Growth of carbon nanotubes by atmospheric pressure plasma enhanced chemical vapor deposition using NiCr catalyst

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Available online 1 September 2006

Abstract

Carbon nanotubes (CNTs) were grown as a function of NiCr thickness using a modified atmospheric pressure plasma containing NH_3 (210 sccm)/N_2(100 sccm)/C_2H_2(150 sccm)/He(8 slm) at low substrate temperatures (≤500 °C), and their physical and electrical characteristics were investigated for possible applications to field emission devices. The number of defects in the grown CNTs was decreased with increasing substrate temperature and the highest CNT growth rate of 1.0 μm/min was obtained at 500 °C with 10 nm thick NiCr. The turn-on electric fields of the CNTs grown at 450 and 500 °C with 10 nm thick NiCr were 2.6 V/μm and 3.7 V/μm, respectively.

PACS: 52 The physics of plasmas and electric discharges
Keywords: Carbon nanotubes(CNTs); Field emission; PECVD

1. Introduction

One of the important applications among the many potential applications of carbon nanotubes (CNTs) being developed by industry is field emission displays (FED). Generally, two methods are being developed for applying CNTs as field emitters in FED. One is to screen-print the CNTs mixed with organic vehicles [1] and the other is to directly grow the CNTs onto the patterned catalyst layer by chemical vapor deposition (CVD) [2]. The former is more widely investigated as it is simpler, less expensive, and lower temperature process compared to the CNTs growth by the CVD. However, the former is also encountering problems in the application to FED such as non-uniform dispersion of CNTs, poor adhesion, etc.

In this study, to improve the abovementioned problems of CVD, an atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) method utilizing a modified dielectric barrier discharge (DBD) configuration was used as a direct CNT growth method [3]. The physical and electrical characteristics of the grown CNTs were investigated for the possible application to the FED emitter.

2. Experiment

The modified DBD system used in this study to grow CNTs at atmospheric pressure is similar to a typical planar dielectric barrier discharge (DBD) system except for using a capillary-type dielectric plate as the dielectric plate covering the power electrode as shown in Fig. 1 [4–6]. The powered electrode and the ground electrode were made of stainless steel. The top electrode (cathode) was connected to an alternating current (AC) (20–100 kHz, 3 kW) power supply while the bottom electrode was grounded. The power electrode was covered with a capillary-type dielectric plate containing a number of parallel small holes (the aspect ratio of the holes was 10:1), which were used to form ion beam-like high-density plasma in the hole and to distribute the reactive gases. The temperature of substrate was heated from 350 to 500 °C using a heating block located under the ground electrode and the substrate temperature was detected by an optical pyrometer (Luxtron, Model 100C-non-contact type).

0.5 to 40 nm thick NiCr (Ni:Cr=8:2) thin films were used as the catalyst for the growth of CNTs. The NiCr thin films were

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doi:10.1016/j.surfcoat.2006.07.191

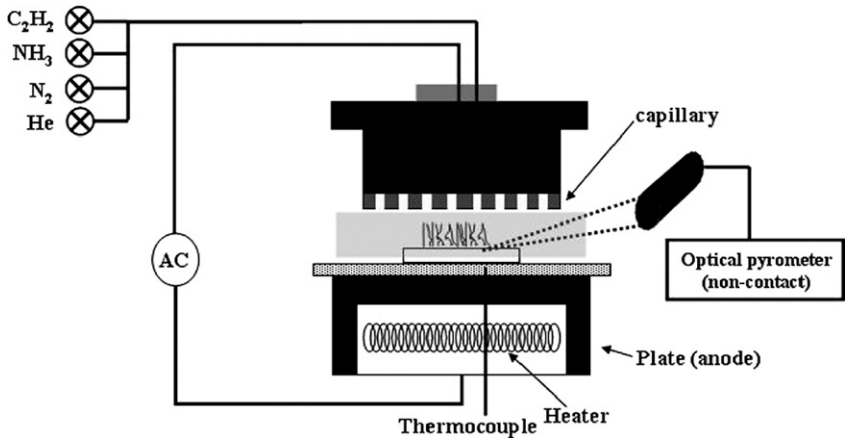

Fig. 1. Schematic diagram of the capillary dielectric discharge-type AP-PECVD system used in this study.

deposited using RF-magnetron sputtering on the sodalime glass substrates after the deposition of Cr (100 nm) films to the glass substrate to enhance the adhesion of NiCr films. The growth conditions of CNTs are listed in Table 1. The growth of CNTs was consisted of two steps: (1) NH_3 plasma pretreatment step: the formation of catalyst metal nanoparticles using a NH_3 (150 sccm)/He(8 slm) plasma for 15 min in the AP-PECVD chamber and (2) CNT growth step : the growth of CNTs using a NH_3(210 sccm)/N_2(100 sccm)/C_2H_2(150 sccm)/He(8 slm) plasma for 2–8 min. When the substrate temperature was varied, the treatment temperature was maintained the same as the CNT growth temperature.

Field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700) was used to analyze the growth characteristics of CNTs and FT-Raman spectroscopy (Renishaw RM1000-InVia) was used to analyze the structure of the grown CNTs. The field emission characteristics of CNTs were measured using direct current in a vacuum chamber with a parallel diode-type configuration at 2×10^{-6} Torr. The CNT emitter area was 1×1 cm^2 and the distance between the CNT emitter and the ITO coated glass electrode was 200 μm.

3. Results and discussion

CNTs were grown using the AP-PECVD with NH_3 (210 sccm)/N_2(100 sccm)/C_2H_2(150 sccm)/He(8 slm) for 8 min as functions of substrate temperature, thickness of NiCr, and growth time. Fig. 2(a)–(d) shows the effect of substrate temperature of (a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 500 °C on the growth of CNTs investigated in a previous study [7]. The pretreatment conditions and other growth conditions are summarized in Table 1. He was used for sustaining glow discharge at low voltages, C_2H_2 as carbon source for CNT growth, NH_3 and N_2 for the formation of NiCr nanoparticles during the

Table1
CNT growth conditions for the capillary-type AP-PECVD system

		Pretreatment	CNT growth
Temperature (°C)		350–500	350–500
Gas (sccm)	NH_3	150	210
	C_2H_2	0	150
	He	8000	8000
	N_2	0	100
Time (min)		15	2–8
AC power (kV)		5.0	6.0

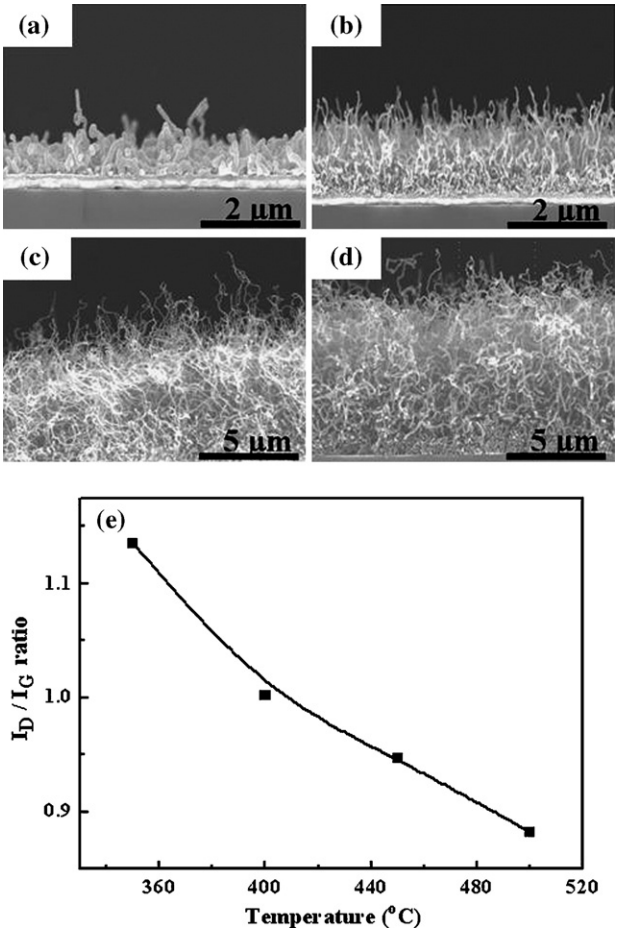

Fig. 2. SEM images of the CNTs grown as a function of substrate temperature by a modified AP-PECVD. (a) 350 °C, (b) 400 °C, (c) 450 °C, (d) 500 °C and (e) I_D/I_G ratio of FT-Raman spectra for the CNTs in (a)–(d).

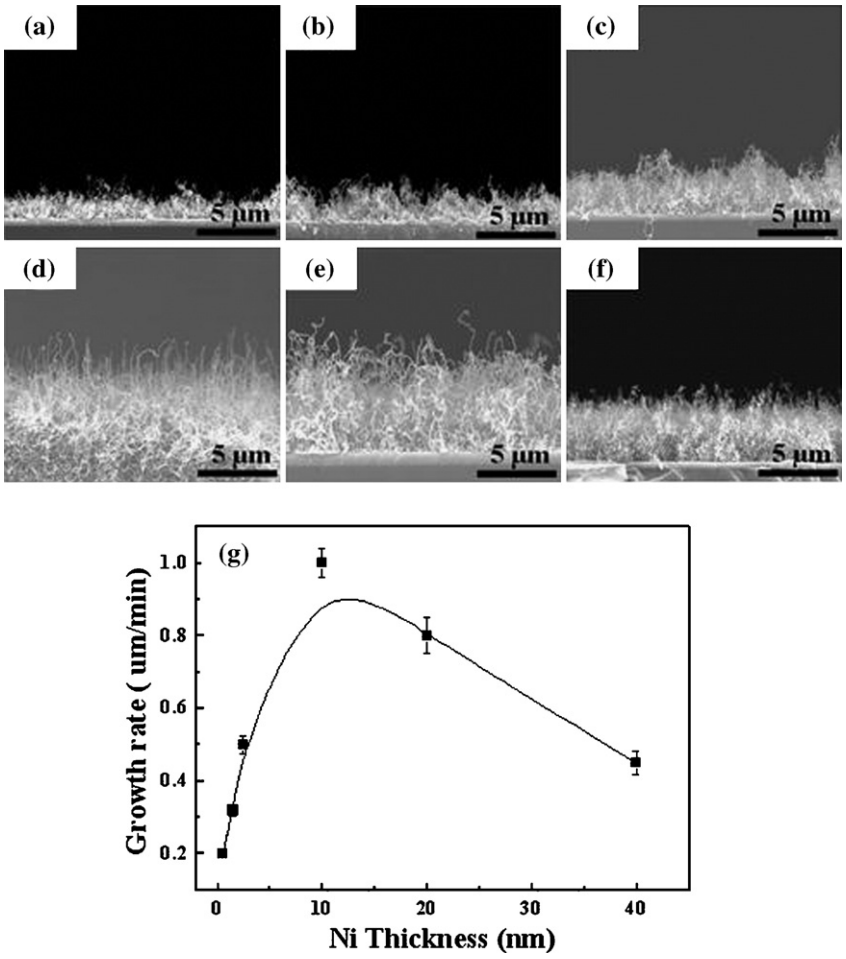

Fig. 3. SEM images of the CNTs grown at different NiCr thicknesses: (a) 0.5 nm, (b) 2.5 nm, (c) 5 nm, (d) 10 nm, (e) 20 nm, and (f) 40 nm. All samples were grown at 500 °C for 8 min and the growth rates as a function of the NiCr thickness are shown in (g).

pretreatment and for the activation of CNT growth. As shown in Fig. 2(a)–(d), with the increase of the substrate temperature from 350 to 500 °C, the CNT length was increased from 1± 0.5 μm to 8±1 μm while the diameter of the CNTs was decreased from 100±10 nm to 40±5 nm. The increase of CNT growth length is believed to be related to the increase of carbon reaction rate and the diffusion to the catalyst metal [8] while the decrease of the CNT diameter is related to the decrease of catalyst nanoparticle size during the pretreatment [9]. In general, the increase of substrate temperature increases the size of the catalyst nanoparticle by the increased agglomeration of NiCr nanoparticles. However, in our experiment, the catalyst nanoparticle size was decreased with increasing substrate temperature by the reaction of the catalyst with NH_3 during the NH_3 plasma pretreatment [10].

Fig. 2(e) shows the I_D/I_G ratio of FT-Raman spectra for the CNTs shown in Fig. 2(a)–(d). The CNTs grown by the AP-PECVD showed two peaks near 1582 cm^{-1} related to the graphite peak (G-band) originated from sp^2 bonding and near 1350 cm^{-1} related to the defect peak (D-band) originated from a-C. As shown in the figure, with increasing substrate temperature from 350 to 500 °C, the relative intensity of the two bands (I_D/I_G) was decreased from 1.135 at 350 °C to 0.882 at 500 °C, therefore, the quality of the grown CNTs was improved with increasing substrate temperature.

Fig. 3(a)–(f) shows the SEM images of the CNTs grown at 500 °C as a function of the catalyst layer thickness of (a) 0.5 nm, (b) 2.5 nm, (c) 5 nm, (d) 10 nm, (e) 20 nm, and (f) 40 nm and Fig. 3(g) shows the CNT growth rate as a function of the thickness of the catalyst layer measured from Fig. 3(a)–(f). As shown in the figure, the increase of the catalyst layer thickness up to 10 nm increased the CNT growth rate up to 1 μm/min while the further increase of the catalyst layer thickness decreased the growth rate. The lower growth rate of CNTs obtained with the catalyst layer thickness lower than 10 nm is believed to be related to the catalyst surface oxidation due to the air exposure of the catalyst layer before the NH_3 pretreatment and the growth of CNTs. However, the higher CNT growth rate obtained with the thinner catalyst layer for the catalyst layer thicker than 10 nm is believed to be related to the smaller catalyst nanoparticles formed for the thinner catalyst layer. It is due to the fact that smaller number of carbon atoms is required for the growth of smaller diameter CNTs associated with the thinner catalyst layer [11,12]. Therefore, in our experiment, highest CNT growth rate was obtained with 10 nm thick NiCr catalyst layer.

The effect of growth time on the CNT growth length was investigated for the substrate temperature of 500 °C and with 10 nm thick NiCr catalyst layer and the results are shown in Fig. 4(a)–(d) for the SEM images and in Fig. 4(e) for the growth length as a function of growth time. The growth time was varied from 2 to 8 min. As shown in the figure, the growth length was increased almost linearly with the increase of growth time. Therefore, the length of the CNTs could be controlled by adjusting CNT growth time for the application to field emission emitter.

Using the CNTs grown at 450 °C and 500 °C by the AP-PECVD for 8 min with 10 nm thick NiCr layer, the field emission properties were investigated and the results are shown in Fig. 5. Fig. 5(a) shows the results on electric field (E) vs. current density (J) for the CNTs grown at 450 °C and 500 °C, Fig. 5(b) shows the current density of the CNTs grown at 450 °C as a function of time at 700 V of anode voltage, and Fig. 5 (c) shows the its field emission images measured at the applied voltage of 600, 650, 700, and 750 V for the CNTs grown at 450 °C. As shown in the inset of Fig. 5(a), the Flower–Nordheim plot of the CNT emission showed a linear relationship signifying the electron is field emitted by tunneling

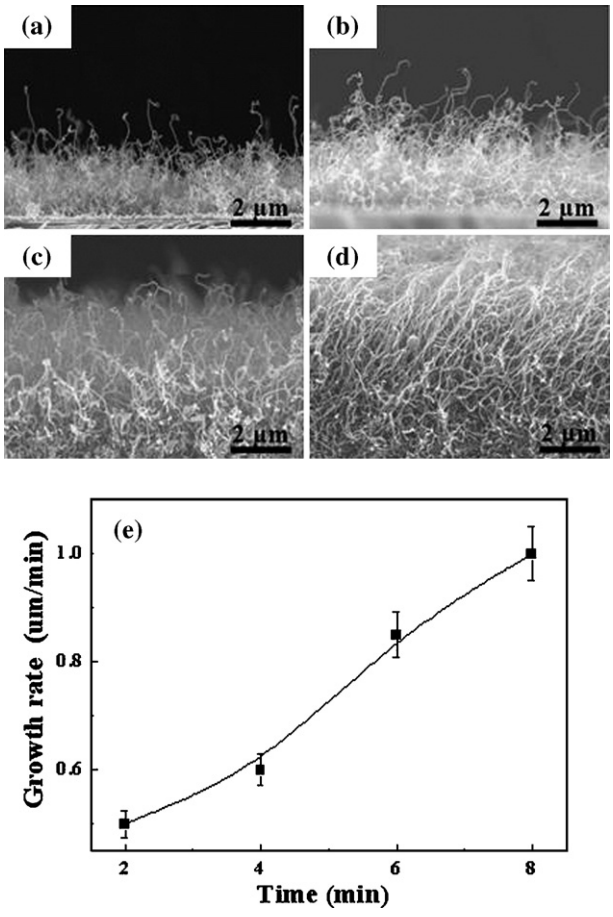

Fig. 4. SEM images of the CNTs grown as a function of growth time by the modified AP-PECVD. (a) 2 min, (b) 4 min, (c) 6 min and (d) 8 min. All samples were grown at 500 °C with 10 nm thick NiCr. The growth length measured as a function of growth time is shown in (e).

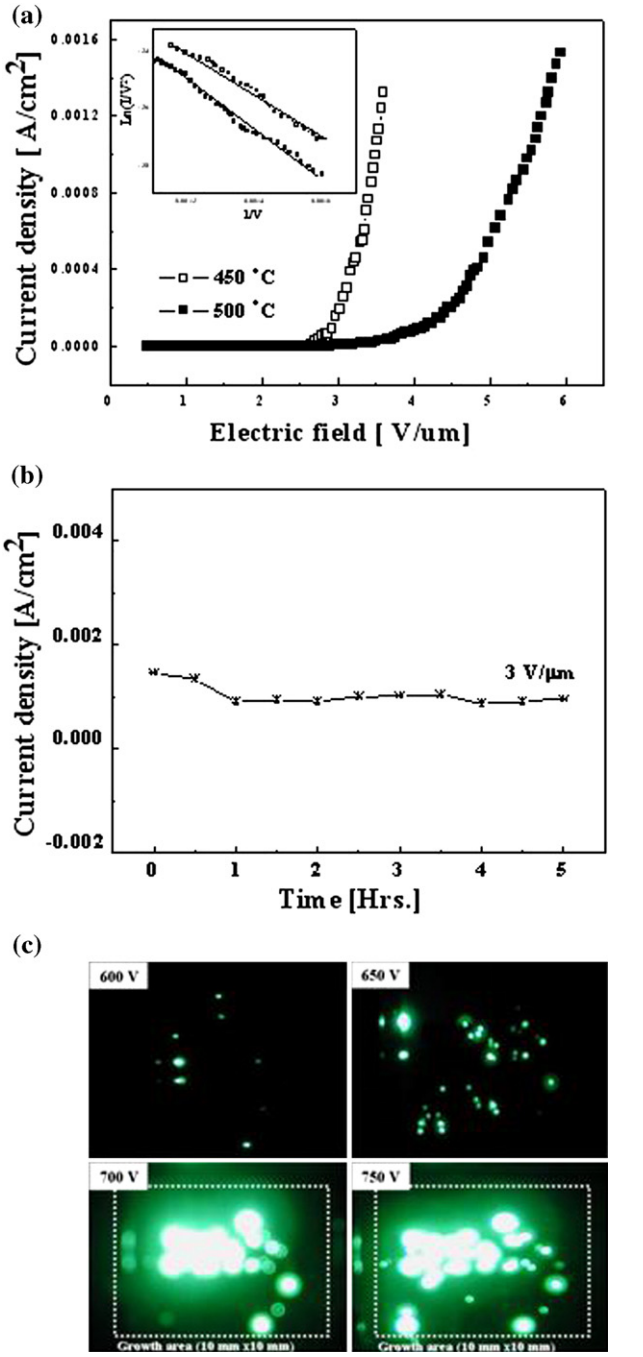

Fig. 5. (a) Field emission characteristics of the CNTs grown by the AP-PECVD at 450 °C and 500 °C with 10 nm thick NiCr. (b) Electron emission as a function of time for the CNT grown at 450 °C with 10 nm thick NiCr at the anode voltage of 700 V and (c) its field emission images measured at the applied voltage of 600, 650, 700, and 750 V.

of electrons from CNTs. The turn-on fields (defined as the electric field at 1 μA/cm^2 of the emission current density) were 2.6 V/μm for 450 °C and 3.7 V/μm for 500 °C. The higher turn-on field at the higher substrate temperature appears to be related to the lower defects on the CNTs grown at the higher substrate temperature. The current density of CNTs required for the field emission device is known to be 1 mA/cm^2 [13]. The current densities of CNTs grown at 450 °C and 500 °C at 1 mA/cm^2

were 3.5 V/μm and 5.54 V/μm, respectively. When the current density was measured as a function of time while keeping the 700 V of the anode voltage for the CNTs grown at 450 °C, as shown in Fig. 5(b), the current density remained similar at 0.90 mA/cm^2 for 5 h even though there was an initial slight decrease of current density possibly due to the field stress effect [14]. However, as shown in Fig. 5(c), even though the increase of anode voltage from 600 to 750 V increased the emission area, the emission area less than 30% was emitting due to the differences in the height of grown CNTs. Therefore, to apply for the FED emitters, the grown CNTs need to be conditioned to have similar height using the method such as oxygen plasma treatment.

4. Conclusions

In this study, CNTs were fabricated using an capillary-type AP-PECVD at a low temperature (≤500 °C) in He(8 slm)/C_2H_2 (150 sccm)/NH_3(210 sccm)/N_2(100 sccm) as a function of NiCr layer thickness. The CNTs grown on the 10 nm thick NiCr catalyst layer showed the highest growth rate. Also, the higher substrate temperature showed the higher growth rate with smaller diameter and with smaller defect density. The CNT grown at 500 °C showed the growth rate of 1.0 μm/min and the I_D/I_G of 0.82 measured by FT-Raman. The turn on field of CNTs grown were 2.6 V/um for 450 °C and 3.7 V/um for 500 °C, and 1 mA/cm^2 required for FED application could be obtained at 3.5 V/μm for 450 °C and 5.54 V/μm for 500 °C.

Acknowledgements

This work was supported by the National Research Laboratory (NRL) Program of the Korea Ministry of Science and Technology.

References

[1] T.J. Vink, M. Gillies, J.C. Kriege, H.W.J.J. Van de laar, Appl. Phys. Lett. 83 (17) (2003) 3553.
[2] M.P. Siegal, D.L. Overmyer, P.P. Provencio, Appl. Phys. Lett. 80 (12) (2002) 2171.
[3] H. Hesamzadeh, B. Ganjipour, S. Mohajerzadeh, A. Khodadadi, Y. Mortazavi, S. Kiani, Carbon 42 (2004) 1043.
[4] C.H. Yi, Y.H. Lee, G.Y. Yeom, Surf. Coat. Technol. 163 (2003) 723.
[5] Y.H. Lee, G.Y. Yeom, J. Korean Phy. Soc. 47 (2005) 74.
[6] Y.H. Lee, C.H. Yi, M.J. Chung, G.Y. Yeom, Surf. Coat. Technol. 474 (2001) 146.
[7] S.J. Kyung, Y.H. Lee, C.W. Kim, J.H. Lee, G.Y. Yeom, Carbon 44 (8) (2006) 1530.
[8] C.J. Lee, J.H. Park, Y. Huh, J.Y. Lee, Chem. Phys. Lett. 343 (2001) 33.
[9] Y.C. Choi, Y.M. Shin, Y.H. Lee, B.S. Lee, G.S. Park, W.B. Choi, et al., Appl. Phys. Lett. 76 (2000) 2367.
[10] Z.Y. Juang, I.P. Chien, J.F. Lai, T.S. Lai, C.H. Tsai, Diamond Relat. Mater. 13 (2004) 1203.
[11] M. Chhowalla, K.B.K. Teo, C. Ducati, N.L. Rupesinghe, G.A.J. Amarutunga, A.C. Feffari, et al., J. Appl. Phys. 90 (10) (2001) 5309.
[12] V.K. Kayastha, Y.K. Yap, Z. Pan, L.N. Lvanov, A.A. Puretzky, D.B. Geohegan, Appl. Phys. Lett. 86 (2005) 253105.
[13] C.J. Lee, J. Park, Appl. Phys. Lett. 77 (2000) 3397.
[14] J.M. Kim, W.B. Choi, N.S. Lee, J.E. Jung, Diamond Relat. Mater. 9 (2000) 1184.