

Field emission effects of nitrogenated carbon nanotubes on chlorination and oxidation

S. C. Ray,^{1,a)} U. Palnitkar,¹ C. W. Pao,¹ H. M. Tsai,¹ W. F. Pong,^{1,b)} I-Nan Lin,¹ P. Papakonstantinou,² Abhijit Ganguly,³ L. C. Chen,³ and K. H. Chen⁴

¹Department of Physics, Tamkang University, Tamsui 251, Taiwan

²NRI, School of Electrical and Mechanical Engineering, University of Ulster at Jordanstown, Newtownabbey, County Antrim BT370QB, Northern Ireland, United Kingdom

³Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan

⁴Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan

(Received 17 April 2008; accepted 23 July 2008; published online 24 September 2008)

With reference to our recent reports [Appl. Phys. Lett. **90**, 192107 (2007); Appl. Phys. Lett. **91**, 202102 (2007)] about the electronic structure of chlorine treated and oxygen-plasma treated nitrogenated carbon nanotubes (N-CNTs), here we studied the electron field emission effects on chlorination (N-CNT:Cl) and oxidation (N-CNT:O) of N-CNT. A high current density (J) of 15.0 mA/cm² has been achieved on chlorination, whereas low J of 0.0052 mA/cm² is observed on oxidation compared to $J=1.3$ mA/cm² for untreated N-CNT at an applied electric field E_A of ~ 1.9 V/ μ m. The turn-on electric field (E_{TO}) was ~ 0.875 . The 1.25 V/ μ m was achieved for N-CNT:Cl and N-CNT:O, respectively, with respect to $E_{TO}=1.0$ V/ μ m for untreated one. These findings are due to the formation of different bonds with carbon and nitrogen in the N-CNT during the process of chlorine (oxygen)-plasma treatment by the charge transfer, or else that changes the density of free charge carriers and hence enhances (reduces) the field emission properties of N-CNTs:Cl (N-CNTs:O). © 2008 American Institute of Physics. [DOI: 10.1063/1.2981090]

I. INTRODUCTION

Conventional cathode ray tubes are gradually being replaced by flat panel displays,¹ where a continuous or patterned film of nanotubes provides a large number of independent electron beams. For this type of instruments, the field emission is one of the most promising applications for nanostructured carbon-based thin films. This can be attributed to the recent development of cheap and robust field emitting materials. Carbon nanotubes (CNTs) in particular have received much attention. In this process, when a high electric field in the order of 10⁷ V/cm is applied on a solid surface with a negative electrical potential, electrons inside the solid are emitted into vacuum by the quantum mechanical tunneling effect. The CNTs are capable of emitting such high (electrons) currents (up to 1 A/cm²) at low fields (~ 5 V/ μ m) that are favorable for field emitters because of their high aspect ratio, sharp tip, high chemical stability, and high mechanical strength. In particular CNT emitters² are reported to be ideal candidates for the next generation of field emission flat panel displays.³ Many experimental studies have reported field emission from multiwall (MW) and single-wall CNTs (SWCNTs),⁴⁻⁷ but the breakthrough for this technology came in 1998 when a crude display using nanotubes as emitters was first announced by Bonard *et al.*² For good emitter displays it is very essential to have the materials that behave with high emission current density. At the same time the emission should be at very low threshold applied electric

field. One process of field emission enhancement is the functionalization of CNT using different precursors. Gohel *et al.*⁸ observed that the N₂ treated MWCNT shows significant improvement in field emission properties, while the Ar⁺ treated MWCNT displays poorer field emission characteristics compared to untreated MWCNT. Kurt *et al.*⁹ showed that the film of nitrogenated CNTs (N-CNTs) behaves with better field emission characteristics compared to CNT. Several field emission studies have been reported to demonstrate the capability of CNTs to emit electrons with a high current density and threshold electric fields in the range of 1–10 V/ μ m.²⁻⁹ In the present work, we have studied the field emission effects on chlorine and oxygen-plasma treatment of MW N-CNT, where we have found that the turn-on applied electric field is less than 1.0 V/ μ m.

II. EXPERIMENTAL DETAILS

Electron field emission characteristics were performed using a Keithley power supply (Keithley: model 237). The cathode voltage was applied by an analog programmable 1.0 kV power supply under computer control, and the measured emission current was logged at each voltage. The measurements were carried out under a low 10⁻⁶ torr ambient pressure. The movement of the anode tip (1 mm diameter) was measured digitally, and the gap between emitter and collector was confirmed by optical microscope. During the measurements the anode and cathode distance in the field emission system was fixed at 200 μ m, which is the thickness of the microglass spacer used to isolate the cathode from the anode. Raman spectra were obtained using the visible laser light with wavelength 633 nm. For the sample preparation, ini-

^{a)}Author to whom correspondence should be addressed. Electronic mail: raysekhar@rediffmail.com.

^{b)}On leave at Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA.

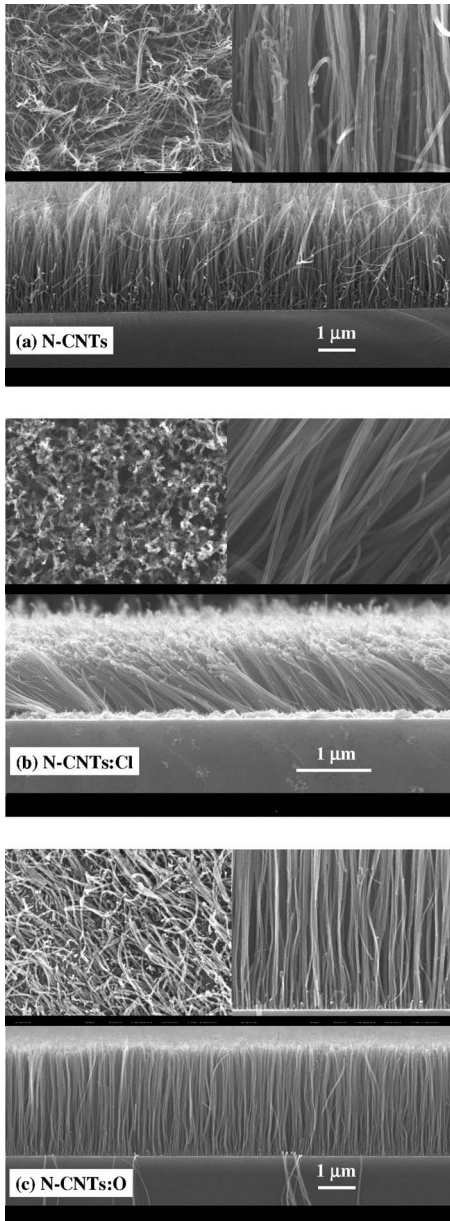


FIG. 1. Typical SEM images of (a) N-CNT, (b) N-CNT:Cl, and (c) N-CNT:O.

tially the vertically oriented N-CNT was synthesized by microwave-plasma enhanced chemical-vapor deposition on a silicon substrate using Fe catalyst.¹⁰ Afterward, the obtained N-CNTs were chlorinated in an inductively plasma coupled reactor at a 5 SCCM (SCCM denotes cubic centimeter per minute at STP) flow rate of chlorine gas for periods of 5 min. During chlorination the total pressure was 40 mTorr, and the applied input power was 150 W. Oxygen treatment was performed under the air-atmospheric plasma conditions for 5 s at a discharge power of ~ 0.5 kW using a dielectric barrier discharge system.^{11,12}

III. RESULTS AND DISCUSSION

Figures 1(a)–1(c) show the typical scanning electron microscopy (SEM) images of N-CNT, N-CNT:Cl, and N-CNT:O, respectively. It is clearly observed from the cross-

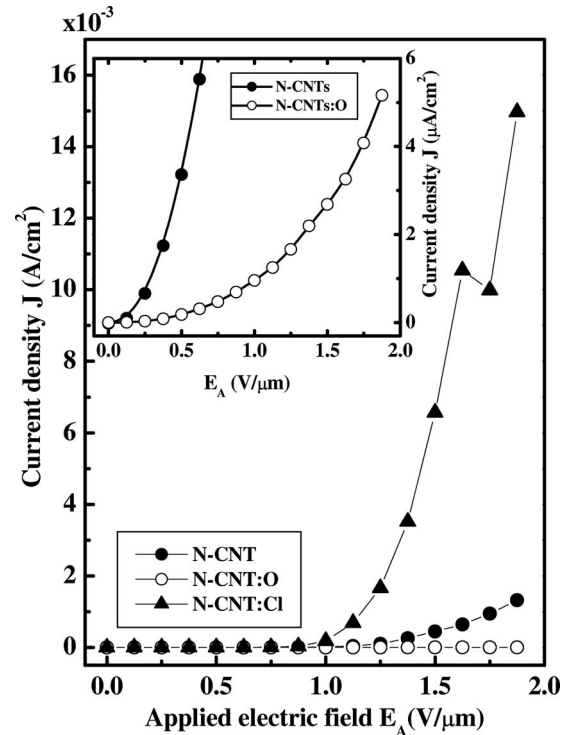


FIG. 2. The emission current density (J) with applied electrical field (E_A) of N-CNT, N-CNT:Cl, and N-CNT:O. Inset shows the magnified lower part of J vs E_A of N-CNT and N-CNT:O.

sectional SEM images that the vertical alignment of N-CNT is changed on chlorine-plasma treatment, but strong vertical alignment is formed when the treatment was performed with oxygen-plasma. In general, the mechanism of the highly vertically aligned growth is mainly attributed to the high density of CNT being grown from the densely packed catalytic nanoparticles. As the nanotubes lengthen, they interact with nearby nanotubes, presumably by van der Waals forces, to form a large bundle with some rigidity, which enables them to keep growing along the same direction.¹⁰ On the basis of this growth mechanism, the alignment is changed on chlorine/oxygen-plasma treatments. Simultaneously, the density as well as the lengths of the tubes is decreased on chlorination, but on oxidation it increased; those can be observed from the overview and cross-section SEM images shown in Fig. 1. The increase (decrease) in length and density of the nanotubes can be explained with respect to their growth mechanism. The diffusion and precipitation of the reactive carbon species are faster (slower) in oxidation (chlorination), resulting in faster (slower) growth rate and increase (decrease) in nanotube length as well as nanotube density. During the process of oxidation (chlorination), probably larger (smaller) numbers of active carbon species are in nucleation site that enhance (reduce) the nanotube density. However, it seems that the diameters of the tubes are slightly increased (~ 29 nm) and decreased (~ 21 nm) on chlorine and oxygen treatments, respectively, with respect to nontreated N-CNT (~ 26 nm) due to a change in CNT density.

Figure 2 shows the results of the field emission measurements, the current density (J) versus applied electric field (E_A). Figure 3 shows the Fowler-Nordheim (F-N) plot for the

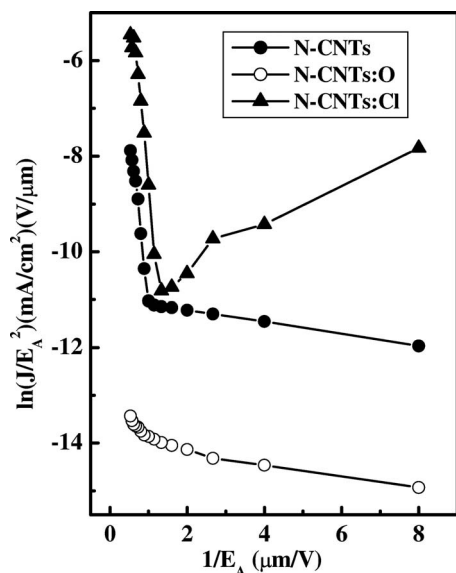


FIG. 3. Field emission F-N plots, i.e., $(1/E_A)$ vs (J/E_A^2) of N-CNT, N-CNT:Cl, and N-CNT:O.

field emission on chlorine/oxygen treated and nontreated N-CNT. Chlorine treated N-CNT shows that field emission is enhanced, whereas on oxygen treatment this field emission is reduced compared to the nontreated N-CNT. The inset of Fig. 2 is the magnified lower part of J versus E_A of N-CNT and N-CNT:O to see the difference of J among them. The turn-on electric field (E_{TO}) of nontreated N-CNT is $1.0 \text{ V}/\mu\text{m}$ that we obtain from the F-N plot, as plotted in Fig. 3. Interestingly, this E_{TO} is significantly reduced to $0.875 \text{ V}/\mu\text{m}$ on chlorine treatment and increased slightly to $1.25 \text{ V}/\mu\text{m}$ on oxygen treatment of N-CNT. Further, we have also obtained the field emission current density in the mA/cm^2 range for chlorine treated and nontreated N-CNT, but this current density is reduced to $\mu\text{A}/\text{cm}^2$ on oxygen treatment. In terms of magnitude concern, the emission current density is enhanced for chlorine treated N-CNT ($\approx 15 \text{ mA}/\text{cm}^2$) in comparison to nontreated N-CNT ($\approx 1.3 \text{ mA}/\text{cm}^2$) at $E_A = 1.9 \text{ V}/\mu\text{m}$. However, in contrast, for our oxygen treated N-CNT the electric current density is reduced drastically ($\sim 0.0052 \text{ mA}/\text{cm}^2$) at same $E_A = 1.9 \text{ V}/\mu\text{m}$ obtained from Fig. 2. It is noted that all these measurements were confirmed by repeating them at several points through the samples' surfaces. This enhancement and reduction in field emission on chlorine/oxygen treatment not only is attributed to the change in physical properties but also depends on the change in chemical properties that occur during the process of treatment. In terms of physical changes, it is observed from the SEM images as discussed above that the density is decreased, the nanotube length is shortened, and the orientation is changed on chlorine treated N-CNT, whereas opposite trends are observed for oxygen treated N-CNT, as shown in Figs. 1(b) and 1(c), respectively. The N-CNT:Cl may be considered as the medium density based nanotubes, as explained by Bonard *et al.*¹³ There have been several reports that show that the density and the orientation of the CNTs affect the emission characteristics.^{13–15} The CNT thin films with high density show poorer quality of

emission compared to one that has medium density due to screening effects.^{1,2} On the basis of density concern, it was observed by Bonard *et al.*² that the field amplification factor optimizes when the intertube distance is twice the height of the CNTs and drops rapidly as the distances among the nanotubes decrease. Moreover, the nanotubes cannot be too far apart as well since the number density of emitters decreases with increasing intertube distance. Again, if the numbers of emitters are very few, then nanotube films become an ineffective cathode. Based on this argument, the field emission can be enhanced by properly reducing the surface density of the nanotubes, which partially can explain why the chlorine treated N-CNT has higher field emission and lower turn-on field compared to nontreated N-CNT. In the case of oxygen treated N-CNT, the density and length of tubes become higher than those of nontreated and chlorine treated N-CNT as we observed in the SEM images shown in Fig. 1. As a result, the field emission is reduced compared to pure N-CNTs and N-CNT:Cl. Chen and Zhou¹⁶ discussed that aligned/randomly oriented CNT with less densities have higher emission due to two sources: (i) the small fraction of the CNT that points to the current collector due to simple statistical distribution and (ii) due to the field induced alignment. Several experiments have shown that the CNTs can be easily bent and aligned to the electric field direction under a moderate electric field. Another advantage of this type of cathode is the large number of CNT available for emission, which can lead to a longer lifetime.

However, the optimal surface morphology is not the only reason for the enhancement/reduction in field emission characteristics, but the chemical functionalizations or chemical doping sites also have to be taken into account for the enhanced field emission. We measured the Raman spectra using the laser excitation energy with wavelength of 633 nm , as shown in Fig. 4, and found that all N-CNTs have D -peak ($\sim 1330 \text{ cm}^{-1}$) and G -peak ($\sim 1583 \text{ cm}^{-1}$) along with a very weak T -peak (1156 cm^{-1}). We observed that the I_D/I_G ratio changes from 1.34 (N-CNT) to 1.44 (N-CNT:Cl) and 1.40 (N-CNT:O) on chlorination and oxidation, respectively. Probably, this higher I_D/I_G ratio in the case of N-CNT:Cl increased the number of defects that enhance the field emission properties of N-CNT:Cl.¹⁷ In our earlier reports we discussed the electronic structure of N-CNT, N-CNT:Cl, and N-CNT:O with the help of experimental results of x-ray absorption near edge structure (XANES) spectroscopy, scanning photoelectron microscopy (SPEM), and also theoretical calculation of density of states of N-CNT/ N-CNT:Cl/ N-CNT:O.^{11,12} The overall field emission improvement of N-CNT:Cl is due to an etching effect on Cl-plasma treatment with the formation of C–Cl bonding after reducing the α -C content and overall increase in density of states.^{11,12} We had seen an extra peak in between π^* and σ^* peak of C K -edge XANES spectra, and the peak was attributed to the C–Cl rather than to other bonding, which was formed by the substitution of C–C bonds. In the case of N-CNT:O, the π^* feature was quite close to that of highly oriented pyrolytic graphite and lay below the π^* feature of nontreated N-CNT by $\sim 1.1 \text{ eV}$, which was caused by the charge transfer process and the formation of C–N/N–O and/or C–O bonds. We

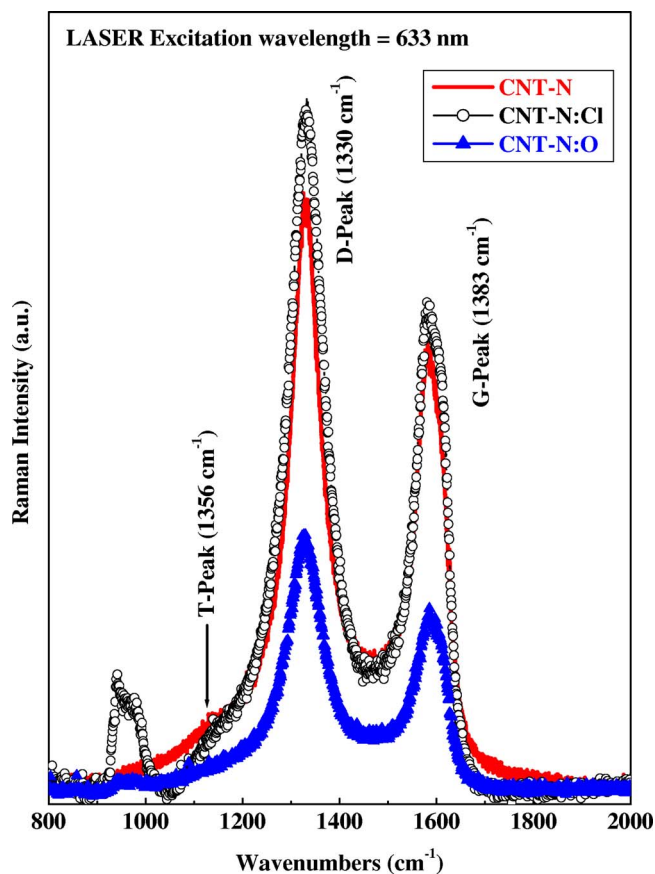


FIG. 4. (Color online) Room temperature Raman spectra of N-CNT, N-CNT:Cl, and N-CNT:O at a laser excitation energy of 1.96 eV ($\lambda=633$ nm from He-Ne laser).

also measured the relative sp^2 -content from the earlier reported XANES spectroscopy^{11,12} and found that sp^2 -content decreases from 7.23 (N-CNT) to 7.09 (N-CNT:O) and 6.63 (N-CNT:Cl) on oxidation and chlorination, respectively. In principle, the FE is enhanced with an increase in sp^2 -content due to an increase in graphitization in CNTs. However, in our present case, this hypothesis does not support for N-CNT:Cl. So, the mechanism is different and due to a formation of C–Cl bonding on chlorination that enhances FE properties. These findings are further confirmed by the theoretical calculation of PDOS of both N-CNT:Cl and N-CNT:O.^{11,12} This evidence clearly indicated that the chlorine treated N-CNT is chemically functionalized and has formed a C–Cl bond that increases the density of free charge carriers and is responsible for the enhancement in field emission characteristics. In oxygen treated N-CNT, the field emission is reduced due to a decrease in the density of free charge carriers by the formation of more and comparatively dense nanotubes, as observed in SEM micrograph in Fig. 1(c), along with different bonds after chemical oxidation on the surface of nanotubes wall. During the Cl-plasma process, Cl ions with energy corresponding to the applied plasma power bombarded the tube wall, took carbon atoms away, and changed into forms of C–Cl bonds. Due to a lack in carbon in the ambience, a large fraction of C–Cl was taken out of the chamber with the Cl, which resulted in some nanotubes, and thus the CNT films became thin and dilute. Meanwhile,

a small fraction of C–Cl was redeposited on the survived tube surface, which consequently caused many nanoscale particles along the remained tubes. These nanoscale particles also may be due to an enhancement in field emission characteristics. We also observed in SPEM results that the spectra of N-CNT:Cl (N-CNT:O) broaden (shrink) and shift at higher (lower) energy of the σ bond feature and also increase (decrease) its intensity. The change in the σ -bond feature is associated with chlorine-derived (oxygen-derived) σ states and can be caused by the formation of C–Cl (N–O) bonds by the substitution of C–C bonds. It was explained that the broadening of σ bond in N-CNT:Cl may be brought about by the formation of sp^3 -like bond instead of sp^2 -like configuration, typical for graphitelike, as proposed by Obraztsov and co-workers.^{18,19} This change in coordination would decrease the height of the potential barrier and hence increase the field emission properties. The opposite features were observed for the N-CNT:O as it results in the reduction of field emission properties. The formation of N–O (C–Cl) on oxidation (chlorination) could also explain the Pauline electronegativity process. The formation of N–O and probably sp^3 C–N bonds is caused by the transfer of electrons from the tube walls due to higher electronegativity of oxygen/nitrogen than carbon [$O(3.44) > N(3.04) > C(2.55)$], whereas the C–Cl and sp^2 C–N bonds are due to higher electronegativity of chlorine/nitrogen than carbon [$Cl(3.16) > N(3.04) > C(2.55)$]. The increase (decrease) in length and density of CNT-N may also be due to a chemical interaction with Cl and O with N-CNT that forms C–Cl/N–Cl and N–O/C–O, respectively. The N–O and sp^3 C–N may cause the reduction in field emission properties of N-CNT:O by the decrease in density of free charge carriers, and the C–Cl with sp^2 C–N bonds causes the increase in electron affinity by the increase in density of free charge carriers and hence enhances the field emission properties of N-CNT:Cl.

IV. CONCLUSION

We have studied the electron field emission effects on chlorination (N-CNT:Cl) and oxidation (N-CNT:O) of N-CNT. On chlorination high current density (J) of 15.0 mA/cm² has been achieved, but on oxidation the current density (J) is reduced to 0.0052 mA/cm² compared to $J=1.3$ mA/cm² for N-CNT at an applied electric field E_A of ~ 1.9 V/ μ m. The turn-on electric fields are changed from $E_{TO}=1.0$ V/ μ m for untreated N-CNT to ~ 0.875 and 1.25 V/ μ m on chlorination and oxidation, respectively. These findings are due not only to the change in optimal surface morphology but also to the formation of different bonds with carbon and nitrogen in the N-CNT during the process of chlorine (oxygen)-plasma treatment that changes the density of free charge carriers and hence enhances (reduces) the field emission properties of N-CNTs:Cl (N-CNTs:O).

ACKNOWLEDGMENTS

The author (W.F.P.) would like to thank the National Science Council of Taiwan for financially supporting this research under Contract No. NSC96-2112-M032-012-MY3.

- ¹A. A. Talin, K. A. Dean, and J. E. Jaskie, *Solid-State Electron.* **45**, 963 (2001).
- ²J.-M. Bonard, H. Kind, T. Stöckli, and L.-O. Nilsson, *Solid-State Electron.* **45**, 893 (2001).
- ³W. 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.* **75**, 3129 (1999).
- ⁴P. G. Collins and A. Zettl, *Appl. Phys. Lett.* **69**, 1969 (1996).
- ⁵Y. Saito, K. Hamaguchi, K. Hata, K. Uchida, Y. Tasaka, F. Ikazaki, M. Yumura, A. Kasuya, and Y. Nishina, *Nature (London)* **389**, 554 (1997).
- ⁶Y. Saito, K. Hamaguchi, T. Nishino, K. Hata, K. Tohji, A. Kasuya, and Y. Nishina, *Jpn. J. Appl. Phys., Part 2* **36**, L1340 (1997).
- ⁷J. M. Bonard, J. P. Salvetat, T. Stoeckli, W. A. De Heer, L. Forro, and A. Chatelain, *Appl. Phys. Lett.* **73**, 918 (1998).
- ⁸A. Gohel, K. C. Chin, Y. W. Zhu, C. H. Sow, and A. T. S. Wee, *Carbon* **43**, 2530 (2005).
- ⁹R. Kurt, J. M. Bonard and A. Karimi, *Thin Solid Films* **398–399**, 193 (2001).
- ¹⁰L. C. Chen, C. Y. Wen, C. H. Liang, W. K. Hong, K. J. Chen, H. C. Cheng, C. S. Shen, C. T. Wu, and K. H. Chen, *Adv. Funct. Mater.* **12**, 687 (2002).
- ¹¹S. C. Ray, C. W. Pao, H. M. Tsai, J. W. Chiou, W. F. Pong, C. W. Chen, M.-H. Tsai, P. Papakonstantinou, L. C. Chen and K. H. Chen, *Appl. Phys. Lett.* **91**, 202102 (2007); "A comparative study of the electronic structures of oxygen- and chlorine-treated nitrogenated carbon nanotubes by x-ray absorption and scanning photoelectron microscopy," *Virtual J. Nanoscale Sci. Technol.* **16**(22), (2007).
- ¹²S. C. Ray, C. W. Pao, H. M. Tsai, J. W. Chiou, W. F. Pong, C. W. Chen, M.-H. Tsai, P. Papakonstantinou, L.C. Chen, K. H. Chen and W. G. Graham, *Appl. Phys. Lett.* **90**, 192107 (2007); "Electronic structures and bonding properties of chlorine-treated nitrogenated carbon nanotubes: X-ray absorption and scanning photoelectron microscopy study," *Virtual J. Nanoscale Sci. Technol.* **15**(20), (2007).
- ¹³J.-M. Bonard, N. Weiss, H. Kind, T. Stöckli, L. Forró, K. Kern, and A. Châtelain, *Adv. Mater. (Weinheim, Ger.)* **13**, 184 (2001).
- ¹⁴P. J. de Pablo, S. Howell, S. Crittenden, B. Walsh, E. Graugnard and R. Reifenberger, *Appl. Phys. Lett.* **75**, 3941 (1999).
- ¹⁵D. N. Davydov, P. A. Sattari, D. AlMawlaw, A. Osika, L. Haslett, and M. Moskovits, *J. Appl. Phys.* **86**, 3983 (1999).
- ¹⁶Y. Cheng and O. Zhou, *C. R. Phys.* **4**, 1021 (2003).
- ¹⁷C. P. Juan, C. C. Tsai, K. H. Chen, L. C. Chen, and H. C. Cheng, *Jpn. J. Appl. Phys., Part 1* **44**, 8231 (2005).
- ¹⁸E. D. Obraztsova, J.-M. Bonard, V. L. Kuznetsov, V. I. Zaikovskii, S. M. Pimenov, A. S. Pozarov, S. V. Terekhov, V. I. Konov, A. N. Obraztsova, and A. S. Volkov, *Nanostruct. Mater.* **12**, 567 (1999).
- ¹⁹A. N. Obraztsov, A. P. Volkov, I. Y. Pavlovskii, A. L. Chuvilin, N. A. Rudina, and V. L. Kuznetsov, *JETP Lett.* **69**, 411 (1999).