PINE-LIKE MORPHOLOGIES BASED ON NITROGEN-DOPED CARBON NANOTUBES: ELECTRON-FIELD EMISSION ENHANCEMENT

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Introduction

Aligned carbon nanotubes (ACNTs) carpets represent a new and interesting materials with a great potential of applications in electronic devices. The production of this material is carried out by means of chemical deposition (CVD) method. The control of the synthesis parameters combined with new ideas on the experimental setups have allowed the production of carpets of ACNTs with fascinate morphologies.[1] Another route to produce carpets of ACNTs is the realization of CVD experiment on a pre-fabricated substrates with micro pattern array or on already synthesized vertically aligned nanotubes.[2-5] These microarrays with CNTs grown in specific sites have been considered as good candidates for device fabrication, such as field electron emission, due to high emission currents, low turn on voltages and better emission stability.[4,6-7] There exist different reports on the fabrication of micro patterns based on CNTs: 1) CNTs grown on supports that wet in water, creating tipped array morphologies by capillarity;[8-10] 2) CNTs grown on deposited diamond or graphite as seeds for produce sp^2 and sp^3 carbon generating hybrid structures by hot filament CVD[11], and 3) CNTs grown on deposited nanoparticles .[12-13] In general, they showed that small changes can modify substantially the morphology of carbon nanotube structures.

In this work, a single step modified CVD method is proposed to synthesize carpets containing micro-mountains formed by vertical stacked nitrogen-doped carbon nanotubes with varied lengths, adopting pine-like morphologies. Electron field emission properties of pine-like morphologies will be discussed.

Experimental

Figure 1 displays a schematic representation of the chemical vapor deposition (CVD) method used for the synthesis of multiwalled carbon nanotubes (CNx) carpets with pine morphology arrays. In this set up, the atomized solution (97.5% of benzylamine and 2.5% of ferrocene) is transported by an Ar flow of 2.5 l/min inside of quartz tube and pyrolized during 20 min. using a tubular Thermoline Minimite furnace at 850 °C. The CNx were grown on Si/SiO_2 substrates previously distributed along the quartz tube axis (labeled by 1, 2 and 3 regions),. These substrates were placed in the second zone of the furnace (right side, 2 cm from the middle), separated 1 cm between them. The main modification in our CVD experiment is performed on the exit or trap zone (enclosed by the red square). In the conventional CVD method, the exit zone contains a half-filled bubbler with acetone (only one container), in our modified CVD method, the first container was emptied and a second container was added and filled with ethanol; in addition, the exhaust gas was forced to pass through a small diameter glass nozzle (i. d. ~ 0.6 mm).

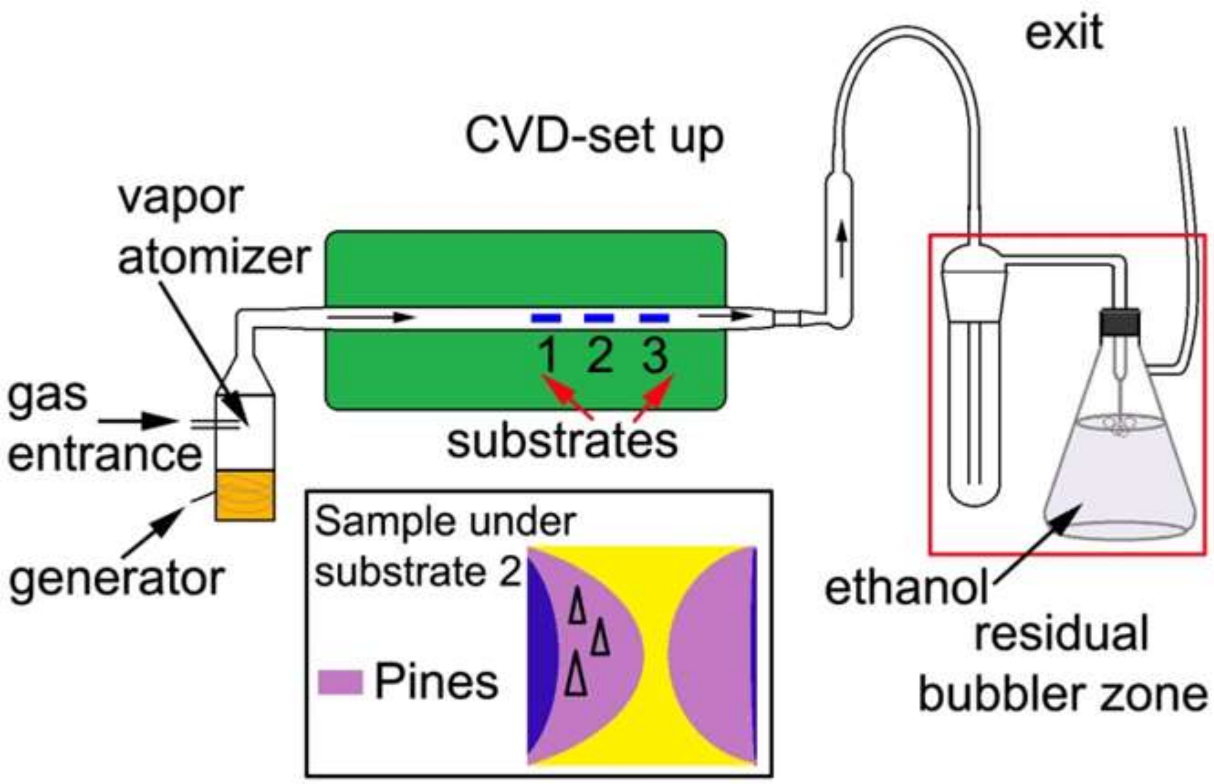

Figure 1. Schematic representation of the modified chemical vapor deposition (CVD) method setup for the synthesis of pine-like CNx structures. These structures grow under the substrates with better defined pines in substrate labeled by 2. The CVD modification consists in addition of a double trap (see exit zone).

The CNx were grown on both sides, superior and inferior parts of the substrates. On the superior part, a typical aligned CNx were found. On the inferior part, different structures were observed. Inset in figure. 1 displays a schematic representation of the sample under substrate wafer in zone 2, showing the region where the pine-like morphologies were obtained (purple zone). The other substrates (1 and 3) presented similar distribution structure although at microscopic level the morphologies are different.

Results

Figure 2 shows SEM images of the morphology observed under substrate 2, focusing in the pines zone (see inset in figure 1, purple color). Notice that the SEM images show pine-like structure distributed randomly. These pine structures are mainly composed by CNx with different lengths and diameters, which possibly were growing at different rates or at different stages in the synthesis process. The pine base and length averages are 29.42 ± 5.86 μm, with 39.47 ± 5.73 μm, respectively, and composed by CNx which diameter average is 33.95 ± 5.43 nm. Figure 2b depicts a SEM image magnification taken from the rectangular enclosed area in figure 1.

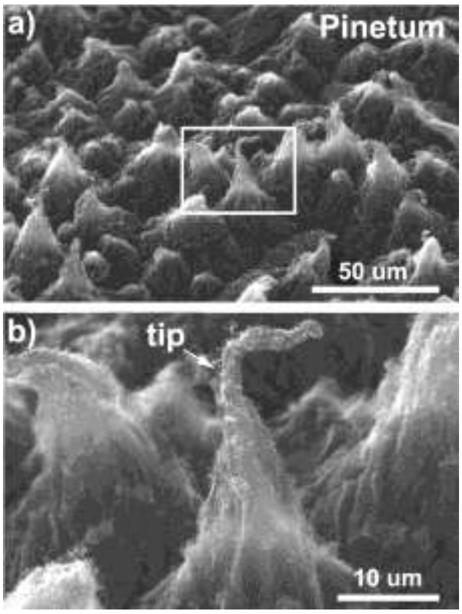

Figure 2. SEM images of pine-like structure morphologies. **(a)** Pine structures array and **(b)** close up image taken from the marked rectangle in **(a).** The pine structures are made of several CNx with different heights.

It is worth to mention that the morphology in the inferior part of substrate 1 (not showed) presented also conic structure with an amorphous carbon thin layer covered its surface, while in the case of substrate 3 (inferior part too) forest of CNx is formed with not clear defined pine structures (not showed). In general, different morphologies were obtained depending on the position of each substrate. We believe that depending of the substrate position, it experiments different flux gas turbulence and atomized mixture (benzylamine and ferrocene) composition variation which could influence in the pine structure formation. Apparently, in substrate 1, the atomized mixture is passing under it and forming CNx with some pine structure possibly due to the reduced small space,[13] but also producing amorphous carbon after some time. In substrate 2, the CNx formation is possibly due to the type-cloud mixture that it was not altered and it is passing by the superior part of substrate 1 and the mixture that is emerging from the inferior part of substrate 1. Other structures have been produced taking advantage of type-space confinement or peculiar surface tratments.[12-13] In the case of the substrate 3 should be similar than substrate 2, but in this case the cloud mixture passing below the substrate 2 is participating with less intensity and the CN_X are fabricated below the substrate 3 by the mixture that comes from above. However, more investigations on the formation mechanism of pine structures are now needed.

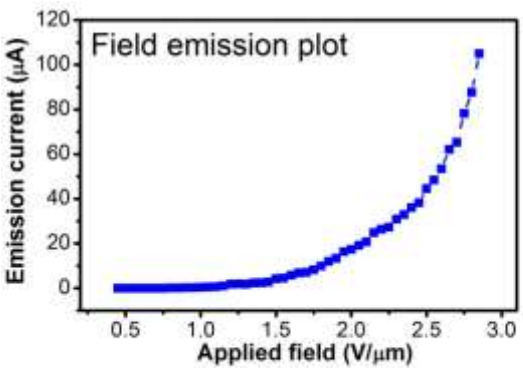

Figure 3. The field emission current as a function of the applied field for pine structures containing CNx.

Due to their conic geometry, the pine-like structures are expected to have good field emission (FE) properties.[14-15] Their FE characteristics were evaluated by measuring the I-V plot in an area of 2×2 mm^2 of substrate labeled as 2 containing the pine structure. A homemade field emission chamber with a high vacuum system (around 5×10^{-8} Torr), a distance of 200 µm between the anode and the sample, and an area of 1 cm^2 were fixed.

Figure 3 shows the FE curve of pine structures . The curve shows exponential behavior of current for increasing voltage, achieving a turn-on voltage of 0.7 V/µm. This value is lower than other materials, such Ga doped ZnO nanopins (1.92 V/µm).[16] It is also lower than a CNx forest (1.80 V/µm),[17] but is in the range of pure non-aligned MWCNT (0.75 V/µm).[18] However, it is lower than the turn-on voltage of long individual bundles of CNT (0.18V/µm).[19]

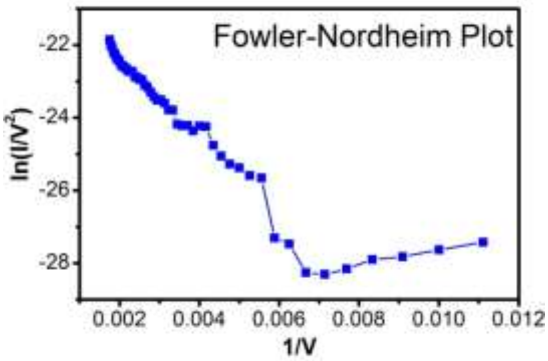

Figure 4. Fowler-Nordheim plot calculated from the FE plot of pine structures.

The FE properties of the samples were analyzed using the model of Fowler-Nordheim (FN) by plotting 1/V versus $\ln(I/V^2)$ (see figure 4). From this plot, the field enhancement factor β was calculated from $B = -\beta\varphi^{3/2}d/s$, where s is the slope of the linear region; B is a constant (6.83×10^9 V $eV^{3/2}$ m^{-1}), φ is the work function (5 eV, taken from graphite),[19] and d is the distance between electrodes (200 µm). The field enhancement factor of our pines based on CNx was near to 7000, which is superior to that reported for forest of CNx (2000).[17]

Figure 5 exhibits the current stability versus time for pines measured approximately by four days. This plot suggests that our pines have good stability for a range current of 4-10 µA. Raman was also measured along the pines (not shown). I_D/I_G was approximately of 0.83 along the shape.

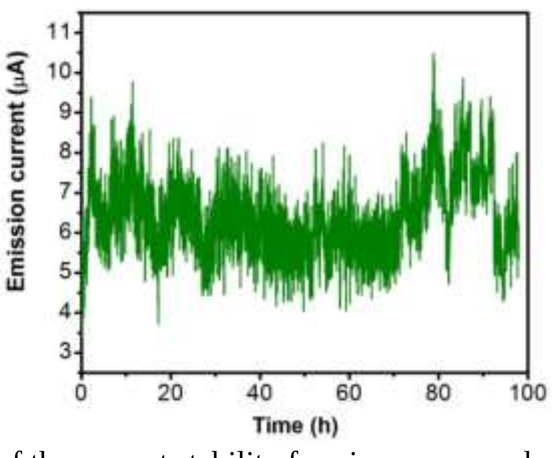

Figure 5. Time dependence of the current stability for pines measured approximately for four days.

Conclusions

A modified chemical vapor deposition method was employed in order to synthesize pine-like morphologies formed by nitrogen-doped carbon nanotubes. These pines like structures were grown in the inferior side of a Si/SiO_2 substrate. The inferior side of substrate and the quartz tube form a confined space which was not directly exposed to the flow gas feedstock. SEM characterization showed that the pine morphology is formed by vertical well stacked CNx following a length conical distribution. The field emission measurements revealed that pine-morphologies are better emitters than CNTs previously reported[16-18], showing low turn-on voltage (0.7 V/µm) and large field enhancement factor (~7000). A more detailed account on experimental setup and growth mechanism of these fascinate structures will be published elsewhere.[20]

References

[1] Zhang L, Resasco DE. Single-Walled Carbon Nanotube Pillars: A Superhydrophobic Surface. *Langmuir* 2009; 25(8):4792–8.

[2] im X, Gary-Foo HW, Chia GH, Sow CH. Capillarity-Assisted Assembly of Carbon Nanotube Microstructures with Organized Initiations. *ACS Nano* 2010; 4(2):1067–75.

[3] E. Muñoz-Sandoval, V. Agarwal, J. Escorcia-García, D. Ramírez-González, M. M. Martínez-Mondragón, et al. Architectures from Aligned Nanotubes Using Controlled Micropatterning of Silicon Substrates and Electrochemical Methods. *Small* 2007; 37(7):1157–63.

[4] Fan S, Chapline MG, Franklin NR, Tombler TW, Cassell AM, Dai H. Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties. *Science* 1999; 283(5401):512-4.

[5] We i BQ, Vajtai R, Jung Y, Ward J, Zhang R, Ramanath G, Ajayan PM. Microfabrication technology: Organized assembly of carbon nanotubes. *Nature* 2002; 416:495-6.

[6] Jeong HJ, Lim SC, Kim KS, Lee YH. Edge effect on the field emission properties from vertically aligned carbon nanotube arrays. *Carbon* 2004; 42:3003–42.

[7] Pandey A, Prasad A, Moscatello J, Ulmen B, Yap YK. Enhanced field emission stability and density produced by conical bundles of catalyst-free carbon nanotubes. *Carbon* 2010; 48(1):287-92.

[8] Nguyen-Vu TDB, Chen H, Cassell AM, Andrews R, Meyyappan M, Li J. Vertically aligned carbon nanofiber arrays: an advance toward electrical–neural interfaces. *Small* 2006; 2(1):89–94.

[9] De Volder M, Tawfick SH, Park SJ, Copic D, Zhao Z, Lu W, et al. Diverse 3D microarchitectures made by capillary forming of carbon nanotubes. *Adv. Mater.* 2010; 22(39):4384–9.

[10] Lim X, Foo HWG, Chia GH, Sow CH. Assisted assembly of carbon nanotube microstructures with organized initiations. *ACS Nano* 2010; 4(2):1067-75.

[11] Hiraki H, Jiang N, Wang HX, Hiraki A. Electron emission from nano-structured carbon composite materials an important role of the interface for enhancing the emission. *J. Phys. IV France* 2006; 132:111–5.

[12] Cervantes-Sodi F, Vilatela JJ, Jiménez-Rodríguez JA, Reyes-Gutiérrez LG, Rosas-Meléndez S, Íñiguez-Rábago, et al. Carbon nanotube bundles self-assembled in double helix microstructures. *Carbon* 2012; 50(10):3688-93.

[13] Zhao MQ, Zhang Q, Tian GL, Huang JQ, Wei F. Space Confinement and Rotation Stress Induced Self-Organization of Double-Helix Nanostructure: A Nanotube Twist with a Moving Catalyst Head. *ACS Nano* 2012, 6(5); 4520–9.

[14] Carbon nanotube electron sources and applications. Jonge N, Bonard JM. *Phil. Trans. R. Soc. Lond. A* 2004; 362:2239–66.

[15] Eletskii AV, Bocharov GS. Emission properties of carbon nanotubes and cathodes on their basis. *Plasma Sources Sci. Technol.* 2009; 18(3):034013-20.

[16] Sun X. Designing efficient field emission into ZnO. SPIE Newsroom, *The International Society for Optical Engineering* 2006:1-4.

[17] Ghosh P, Tanemura M, Soga T, Zamri M, Jimbo T. Field emission property of N-doped aligned carbon nanotubes grown by pyrolysis of monoethanolamine. *Sol. Sta. Comm.* 2008; 147(1–2):15-9.

[18] Lahiri I, Seelaboyina R, Hwang JY, Banerjee R, Choi W. Enhanced field emission from multi-walled carbon nanotubes grown on pure copper substrate. *Carbon* 2010; 48(5):1531-8.

[19] Perea-López N, Rebollo-Plata B, Briones-León JA, Morelos-Gómez A, Hernández-Cruz D, Hirata GA, et al. Millimeter-long carbon nanotubes: outstanding electron-emitting sources. *ACS Nano* 2011; 5(6):5072–7.

[20] García-Betancourt M. L., et al. 2013.