Field emission energy distributions from nanodiamond-covered single wall carbon nanotubes

A. Fiori[1], , M. L. Terranova[1], S. T. Purcell[2], P. Vincent[2], A. Ayari[2]

[1]Dept. of Chemical Science and Technologies, University of Rome Tor Vergata, 1 via della Ricerca Scientifica 00133 Rome, Italy and Micro and NAano System laboratory (MINASlab)
[2]Laboratoire de Physique de la Matière Condensée et Nanostructures, Université Lyon 1; CNRS, UMR 5586, Domaine Scientifique de la Doua, F-69622 Villeurbanne cedex; France

angelamaria.fiori@uniroma2.it

Carbon materials have recently gained a leading position among the ever increasing family of novel cold cathode materials [1]. After the first experimental works of the early 90s [2-4] demonstrating low threshold field emission, different forms of diamond have been shown to have excellent qualities as field emission sources. As a consequence, much effort has been focussed on both the synthesis of diamond nanostructures to increase the field enhancement factor [5-7] and on understanding the emission mechanism in these nominally insulating materials. Different hypotheses have been proposed to explain the controversial experimental data, which varies widely between different sample types [8-14], but so far very few reports of field emission energy distribution supporting or discarding them have appeared [4, 12-14].
Carbon nanotubes, on the other side, exhibit an unrivalled advantage in field enhancing due to their high aspect ratio and have shown very high field emission metallic performances [1]. Covering nanotubes with nanodiamond would represent a way of getting nanometer-sized diamond grains on nanoscale protrusions in order to benefit from the field enhancement in a reproducible way.
By means of a modified Hot Filament Chemical Vapor Deposition apparatus, we recently set-up a method for growing, in one synthesis step, nanodiamond-covered Single Wall Carbon Nanotube (SWNT) bundles [15]. Careful morphological and structural characterization of both phases has been carried out by means of Scanning Electron Microscopy (SEM), Raman spectroscopy and Reflection High Energy Electron Diffraction (RHEED) [15]. In short these studies showed that the nanograins are high quality crystalline diamond.
The field emission investigation involved the recording of the emission patterns, current stability and the total energy distributions (TED) at different applied voltages.
Due to the field enhancing effect of the SWNT bundles, the emission came from numerous localised sites spread over the 2 mm^2 emission zone. The emission was very stable over the meaurement cycles of several of hours.
The Fowler-Nordheim plot of the total current was shown to be rather straight leading one to assume semimetallic behaviour. However, an extremely original and remarkable feature of the emission was the displacement of the energy spectra of emitted electrons from the Fermi level which measures the voltage drops created by the passing emission currents. The spectra consisted of many separate peaks from the different emitters spread over 20 to 500 Volts below the Fermi level. The higher value is more than two orders of magnitude larger than previously reported for other diamond emitters. This remarkably large shifting is a clear sign of the highly insulating nature of our nanodiamond.
Successive spectra taken as a function of applied voltages shift from the Fermi level with a nonlinear behaviour. We propose that this is due to both a resistive drop and field penetration. Moreover, an x-y map of the TEDs of the sample demonstrated that the peaks are related to precise zones of the sample and so to different emitters or groups of emitters.
Further work including a measure of the current coming from an individual emitter, temperature dependent measurements, laser illumination and simulations are needed to clarify the details of the electronic transport leading to such spectacular TEDs.

References:
[1] N. S. Xu, S. Ejaz Huq, Materials Science and Engineering R, **48** (2005) 47
[2] C. Wang, A. Garcia, D. C. Ingram, M. Lake, M. E. Korfesch, Electron. Lett. **27** (1991) 1459
[3] Ken Okano, Kimihiko Hoshina, Masamori Iida, Satoshi Koizumi, and Tadao Inuzuka, Appl. Phys. Lett. **64** (1994) 2742
[4] N. S. Xu, Y. Tzeng, R. V. Lantham J. Phys. D: Appl. Phys. **27** (1994) 1988
[5] Y. Ando, Y. Nishibayashi, A. Sawabe, Diamond Relat. Mater. **13** (2004) 633
[6] H. Masuda, T. Yanagishita, K. Yasui, K. Nishio, I. Yagi, Y. N. Rao, A. Fujishima, Adv. Mater. **13** (2001) 247
[7] Y. K. Chih, C. H. Chen, J. Hwang, A. P. Lee, C. S. Kou, C. S. Diamond Relat. Mater. **13** (2004) 1614
[8] M. W. Geis, N. N. Efremow, K. E. Krohn, J. C. Twichell, T. M. Lyszczarz, R. Kalish, J. A. Green, M. D. Tabat, Nature **393** (1998) 431
[9] A. V. Karabutov, V. D. Frolov, V. I. Konov, Diamond Rel. Mat. **10** (2001) 840
[10] J. B. Cui, , J. Ristein, L. Ley, J. Phys. Rev. B **60** (1999) 16135
[11] J. Y. Shim, H. K. Baik, K. M. Song J. Appl. Phys. **87** (2000) 7508
[12] R. Schlesser, M. T. McClure, B. L. McCarson, Z. Sitar J. Appl. Phys. **82** (1997) 5763
[13] C. Bandis, B. B. Pate Appl. Phys. Lett. **69** (1996) 366
[14] O. Gröning, L.-O. Nilsson, O. Grönong, L. Schlapbach, Solid-State Electronics **45** (2001) 929
[15] M. L. Terranova, S. Orlanducci, A. Fiori, E. Tamburri, V. Sessa, M. Rossi, A. S. Barnard, Chem. Mater. **17** (2005) 3214-3220

Figures:

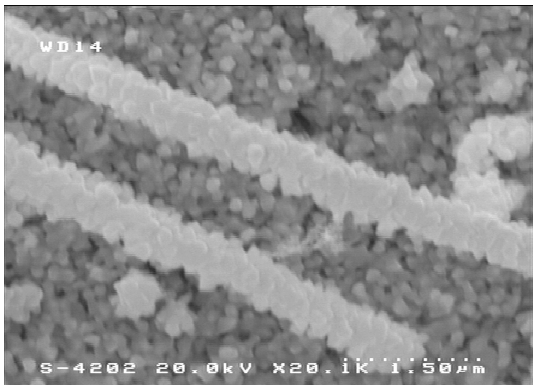

Fig. 1 A SEM image of two SWNT bundles covered by nanocrystalline diamonds

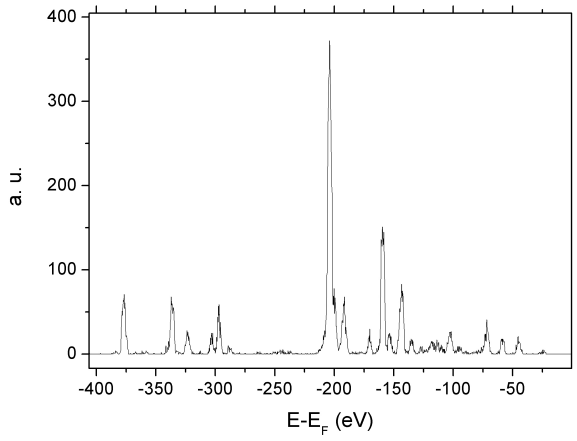

Fig. 2 A typical TED obtained by the investigated sample