Electronic, chemical and structural characterization of CNTs grown by SiC surface decomposition.

A. Policicchio, T. Caruso, R.G. Agostino, E. Maccallini, G. Chiarello, E. Colavita, V. Formoso, M. Castriota, E. Cazzanelli.

CNISM-Dipartimento di Fisica, Università della Calabria, Ponte Bucci, Cubo 33c, I-87036 Arcavacata di Rende (CS), Italy

Abstract. The electronic, chemical and structural properties of Carbon Nano Tubes (CNTs) synthesized by Silicon Carbide surface decomposition were analyzed by Scanning Electron Microscopy (SEM), Scanning Tunneling Microscopy/Spectroscopy (STM/STS), Electron Energy Loss (EEL) and Raman spectroscopy. A clear relationship between the bonding features and the growth condition (temperature and growth time) is obtained. The morphology of the sample investigated by SEM reveals a well-packed and aligned structure of the CNTs. Different lengths of the CNTs are observed depending on the local temperature of the sample surface. The longest observed CNTs were 500/600 nm. The STS measurements show I-V diode-like characteristic curve which can be used, for instance, as an electron collector in solar cells applications. As a perspective metallic electrode, gold, will be deposited on top of the CNTs in the future, to collect the electron current and investigated by the same techniques.

1. Introduction
The growth of Carbon Nanotubes (CNTs) by Silicon Carbide (SiC) surface decomposition appears to be a promising method to scale up CNT production with accurate control [1]. In order to efficiently utilize the great properties of CNTs in applications such as photovoltaics, the problem of physical support of the CNTs must be overcome. The new frontier in photovoltaic devices is the development of molecular, polymeric and inorganic-organic hybrid thin film systems, because of their potential low-cost and easy processability [2] also, furthermore, dye-sensitized-heterojunctions is one of the hotter subjects in the photovoltaic field. Thinking beyond simple heterojunctions, the collection of the photo-separated charges can be improved by using nanostructured materials, as their high structural organisation can increase charge separation and mobility by orders of magnitude. Specifically, by growing carbon nanotubes (CNTs) directly on substrates it is possible to avoid problems due to interfacial states while at the same time induce high charge mobility through a highly delocalized electronic structure. In this experimental work, the electronic, chemical and structural properties of synthesized carbon products are investigated by several experimental techniques (Electron Energy Loss (EEL), Raman Spectroscopy, Scanning Tunneling Microscopy/Spectroscopy (STM/STS) and Scanning Electron Microscopy (SEM)) and compared with experimental results recently obtained on single/multi –walled carbon nanotubes (SWCNT/MWCNT) [3, 4] as a function of the heating temperature and growth time.

2. Experimental
The investigated samples were grown by heating the SiC sample through current passage. Related to the resistance of the sample (a few KOhm) we used ~1 Ampere (~ 45 Volt) current. SiC substrate of
1 cm squared was utilized and heated in UHV at temperatures ranging between (1150-1550) °C. The final temperature was reached with steps of 100 °C. During this heating procedure it is recommended to avoid the heating of the sample at ~1000 °C for long time, because graphitic layers can be formed, inhibiting CNT growth. Prior to the above mentioned heating procedure, the sample was annealed at ~ 400/500 °C for few hours to remove the contamination due to the air exposure of the sample surface.

EEL and Auger spectra were acquired using an electron gun and hemispherical analyzer mounted in our UHV chamber. The SEM/EDX measurements were collected by FEI QUANTA FEG 400 F7. The STM/STS and Raman measurements were obtained by using a Schafer microscope equipped in air and Raman microprobe Jobin-Yvon Labram (He-Ne laser - 632.8 nm emission).

3. Results and discussion

The EEL measurements were obtained by using an electron beam energy of 1000 eV. In this way, the signal coming out is from the topmost surface layers (~ 10-20 Å). In figure 1 the evolution of the EEL spectra as a function of temperature, during the heating of the SiC substrate to 1550 °C, are shown. All the spectra show two main peaks at ~6 eV and ~23 eV due to \(\pi\) plasmon excitation which are typical of graphitic-like structures [3].

![Figure 1: EEL spectra of SiC and CNTs growth by SiC substrate. The image show the spectra changes step by step with the temperature (see text).](image)

The \(\pi\) plasmon starts to appear in the figure 1 (spectrum b), increases in intensity and moves at higher energy loss with increasing temperature. Recently it was shown that in graphitic structures (graphite and CNTs) this excitation is at higher energy loss values than nanostructured amorphous carbon [4]. The upshift of the \(\pi\) plasmon in figure 1 at higher temperature is associated with good graphitization of the CNTs. In addition, the increase of the intensity is compatible with an increase of CNTs amount and ordering. The increase of \(\pi + \pi\) plasmon intensity is in agreement with the previous changes on \(\pi\) plasmon excitation. The energy loss position of the \(\pi\) plasmon starts to move at 1150 °C (figure 1(spectrum b)) and it fixes its position at annealing temperature between 1400-1500°C (figure 1(spectrum c)). Afterwards only changes in the peak intensity are observed (figure 1 spectrum d-e).

From the EEL spectra inspection, we have an indirect evidence of the ordering effect [4] and on the CNT lengthening above 1400°C. SEM analysis on inhomogenously heated SiC surfaces (not shown) give evidence of CNT with different length, short CNT on areas heated below 1400°C and regular growth in the areas with higher temperatures.

All the following experimental results obtained with the remaining techniques have been carried out on sample of the spectrum f in figure 1.

The good quality of CNTs is connected to the absence of the oxygen atoms which binds to the defect present in the CNTs structures and Auger (not shown here) and EDX measurements (C 88.67 % and Si 11.33% in thicker region and C 82.60 % and Si 17.40% in thinner region of the sample) exclude its presence. SEM and EDX analysis results connect the morphological and chemical properties of the samples.
The SEM images were acquired with 20 kV acceleration voltage and X-ray fluorescence spectra were acquired over 0-10 keV, in order to obtain the bulk elemental composition of the samples.

At lower magnification (figure 2a) a very packed and rough surface is observed. The inset of figure 2b shows the profile of the growth CNTs which have micrometric length (~ 400 nm). The CNTs seem to have different characteristics throughout the sample: in some areas the CNTs are long (~ 400-500 nm whereas in other areas they are shorter (~ 200-300 nm). The difference in length can depend in the temperature gradient along the sample. In both case the film is uniform and well packaged.

Mechanical defects were induced to the sample to have CNTs images along its axis (see figure 2b and c). In figure 2b some isolated CNTs can be distinguished with an approximate diameter size of few nanometers and a length of few microns.

STM/STS measurements were carried on the same sample. The STM images were acquired in different regions where the CNTs laid on the substrate (see figure 3a) or are perpendicular to the substrate (see figure 3b and inset). The figure 3a shows CNTs with diameter of ~2-3 nm which is in agreement with the cap size of the CNTs shown figures 3b. At higher areas, the morphology of CNT is flat and the roughness of the sample is ~4nm.

The STS is, somehow, connected to the STM and I-V characteristic curve can be related to each structure obtained in the STM image. By using simple models characteristic electronic properties of the sample like the band gap value and the density of the states (DOS) shape, can be extracted from the I-V curve utilizing peculiar models [5]. In general the top view of the sample shows everywhere I-V diode-like characteristic curve (see figure 3c). In figure 3d the normalized conductance of this curve is plotted. The dashed line represents the normalized conductance of metals (=1). In this way, in analogy with metals, the band gap value of semiconductor is measured. In the present case, the cap of the tube presents a gap value of 1.4 eV. The DOS in the occupied states is narrower since it can explain the high tunnelling current at negative voltage. An additional explanation of this high tunnelling current is the higher mobility of the electron carriers along the tube axis.

![Figure 2. SEM images of CNTs grown by SiC surface decomposition. In (b) and (c) mechanical cut of the sample was carried out.](image)

![Figure 3. STM and STS images of CNTs grown by SiC substrate decomposition. The topographies were acquired with set point 0.1 nA and 3.5 V. (a) Topography 65x65 nm of laid CNTs on SiC substrate. (b) topography 56x56 nm (top view of the sample); inset: topography 26x26 nm. (c) I-V curve and (d) normalized conductance obtained in the inset of figure 3b.](image)
In figure 4 representative Raman spectra corresponding to different sample zones are reported. In the optical microscope, the (a)-(e) zone showed darker color than (f) zone because the sample is thicker and thinner respectively. In figure 4(1) the range (200-1000) cm$^{-1}$ is reported while in figure 4(2) the range (1000-1900) cm$^{-1}$ is plotted. Only the spectrum collected on the (f) zones shows Raman features at ~768, 789 and 967 cm$^{-1}$ and a shoulder at 798 cm$^{-1}$. Such bands have been assigned to the silicon carbide substrates [6, 7]. This means that the layer of the grown CNTs film on the (f) zone is thinner. The absence of the radial breathing mode at lower wave number excludes the growth of SWCNTs, in agreement with STM images. The spectra obtained at higher frequency region (see figure 4(2)) confirm the differences between the (f) and the others zones. All the spectra show features at about 1328 (strong), 1580 (strong) and 1615 (shoulder) cm$^{-1}$ attributed to the presence of MWCNTs and multiwalled nanofibers [8]. Those bands present remarkable difference in the (f) zone showing additional features which could be attributed to the SiC substrate and different carbon species like CNTs with less wall (for instance Double Walled CNTs) and condensed aromatic ring [9, 10].

![Raman spectra](image)

Figure 4. Representative Raman spectra collected on the different spots in the ranges (a) (200-1000) cm$^{-1}$, (b) (1000-1900) cm$^{-1}$.

4. Conclusion

CNTs grown by SiC surface decomposition are very packed on the surface, as it is shown in SEM and STM images. In addition the EEL spectra show the good quality of the sample, confirmed from Auger and EDX spectra. The investigated CNTs show diode-like I-V characteristics and show electron collector behavior. In the future we plan to deposit a gold electrode to use this system as an electron electrode collector in solar cells devices.

Acknowledgements

The authors are grateful to Abate Salvatore and Desiderio Giovanni (LICRYL – Liquid Crystal Laboratory INFM-CNR) for precious help during SEM measurements, to Barone Tiziana for Raman measurements and to Faisal Alamgir (Brookhaven National Laboratory) for the useful discussions.

References

[1] M. Kusunoki, T. Suzuki, T. Hirayama, N. Shibata – Phys. B 323 (2002) 296–298.
[2] Nelson, J. The Physics of Solar Cells; Imperial College Press: London, 2003.
[3] G. Chiarello, E. Maccallini, R.G. Agostino, V. Formoso, A. Cupolillo, D. Pacile, E. Colavita, L. Papagno, L. Petaccia, R. Larciprete, S. Lizzit, A. Goldoni - Carbon 41 (2003) 985–992.
[4] R.G. Agostino et al. - Phys. Rev. B 68, 035413 (2003).
[5] Stroscio, A. J.; Kaiser, W. J. – Scanning Tunneling Microscopy; Academic Press:San Diego, 1993.
[6] M. Dudley, W. Huang, S. Wang, J. A. Powell, P. Neudeck and C. Fazi; J. Phys.D., 28, A56 (1995).
[7] M. W. Russel, J. A. Freitas Jr., W. J. Moore and J. E. Butler; Adv. Mat. Opt. Elec., 7, 195 (1997).
[8] L. Delzeit, I. McAninch, B. A. Cruden, D. Hash, B. Chen, J. Han and M. Meyyappan; Journal of Appl. Phys., 91, 6027 (2002).
[9] L. Song, L. Ci, C. Jin, P. Tan, L. Sun, W. Ma, L. Liu, D. Liu, Z. Zhang, Y. Xiang, S. Luo, X. Zhao, J. Shen, J. Zhou, W. Zhou and S. Xie; Nanotechnology, 17, 2355 (2006).
[10] C. Mapelli, C. Castiglioni, E. Meroni and G. Zerbi; J. Mol. Struct., 80-481, 615 (1999).