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Application of sprayed carbon nanotubes to light detector

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Summary. — Nanomaterials, likes carbon nanotubes (CNTs), are interesting for the development of new generation photodetectors. A study of CNT films deposited at low temperature by spray technique, starting from a nanodispersion of nanotube powder in a non-polar 1,2-dichloro-ethane solvent, is presented. Transmission and Scanning Electron Microscopy images are reported to show the morphological properties of the deposited CNTs. Light detectors have been prepared on silicon substrates. The nanotubes layer has been covered with an indium tin oxide layer to obtain ohmic contact. Electrical device characteristics, both in dark and on light irradiation, are reported.

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1. – Introduction

High aspect ratio, extremely small radius of curvature, chemical inertness, high mechanical strength and high electrical conductivity make carbon nanotubes (CNT) suited to many applications. They possess the great advantage to support high values of current densities (up to $1\,\mathrm{GA/cm^2}$) without overheating and a higher emission stability [1-4] making them very interesting for photodetector development. Another peculiar characteristic of the Multi Wall Carbon Nanotubes (MWCNTs) is their sensitivity to the electromagnetic radiation from UV to IR, depending on their diameter (D) and chirality (χ) [5]. As a consequence, properly tuning the D and χ values, it could be possible to fabricate a wide range of radiation detectors for space, high energies physics, medical instrumentation and more general technological applications.

The spray deposition technique used in the present work allows to easily deposit CNTs on large areas, with a very good adhesion and without emission tips degradation and intermediate layer [6].

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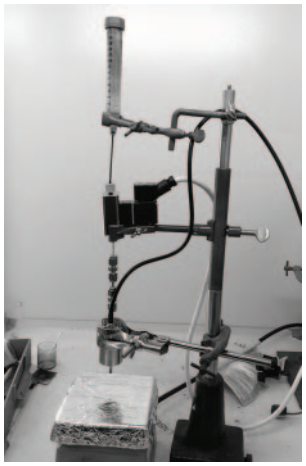

Fig. 1. – Spray system for the deposition of CNTs.

In order to exploit the properties due to monodimensional CNTs [7-9], the non-polar solvent 1,2-dichloroethane (DCE) has been chosen because the interactions between the solvent molecules and CNTs proved to be stronger than interactions between nanotubes themselves [10]. DCE has been also chosen because it is easily vapourized in ambient conditions and it has low surface tension that gives rice to good wettability of CNTs. In order to perform the chemical and morphological characterizations of the resulting films, X-Ray Photoelectron Spectroscopy (XPS), Electron Microscopy in Scanning (SEM) and Transmission (TEM) modes were used, respectively.

A description of detectors obtained by depositing MWCNTs with the spray technique is presented,together with the results of their Current-Voltage (I-V) characterizations.

2. – Experimental details

The dispersion to be sprayed was prepared starting from a commercial powder MWCNT (COMETOX) with a purity degree greater than 95%. The nanotubes were 5–15 μm long with a diameter between 10 and 30 nm.

To remove the water inside the powder, that push the non-polar CNTs up to form bundles, preliminarily standard drying process was followed [6]. The dispersion was prepared following the procedure reported with more details in [11].

A Sonaer ultrasonic device, with a nozzle working frequency of 60 kHz, was used to spray the dispersed nanotubes on the substrates (fig. 1). In order to reach better film uniformity and a fast drying of the solution, the substrates were heated at about 120 °C during the deposition. Homemade aluminum masks were used to select the CNT deposition area. Because of the presence of dangerous substances such as DCE and CNTs, the whole deposition system was placed inside a fume hood.

TEM (FEI Tecnai G^2 Spirit, 120 kV energy) has been used to evaluate the CNTs dispersion degree in the film. Optical Microscopy and SEM (Zeiss-Σigma microscope with inlens detector, 20 μm aperture, 10 kV energy) and XPS (Thermo VG Theta Probe spectrometer equipped with a microspot monochromatized Al $K\alpha$ source, spot size 300 μm) were used to obtain the surface morphology and its chemical composition, respectively.

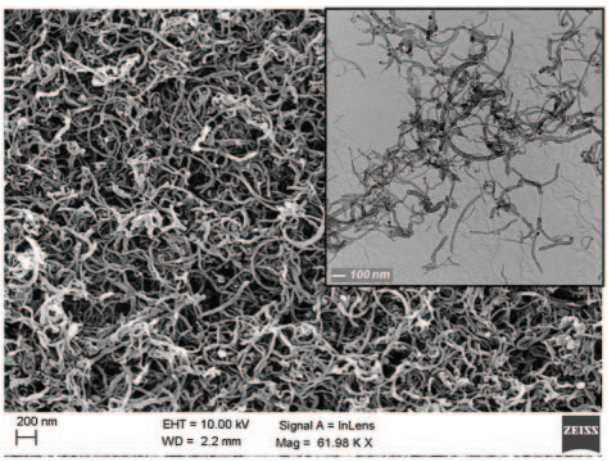

Fig. 2. – SEM image of a CNTs film on silicon substrate. In the inset the TEM micrograph of four shots of the dispersion is shown, with a white scale bar of 100 nm.

After the spray deposition, CNTs were covered by Indium Tin Oxide film 50 nm thick by means of Ion Beam Sputtering (IBS) technique in photodetector applications.

The detectors were connected to an Agilent B1500A Semiconductor Device Analyzer to apply voltages and measure currents, to carry out the photoconductive characterizations. A Thorlabs OSL1 white light source with optical fiber and a focusing lens was used to obtain a light spot on the device. Thorlabs PM100D Optical power/energy meter was used to characterize the light source.

3. – Result and discussion

The dispersion degree in film was observed by means of TEM (fig. 2), preparing CNTs very thin layer performing few number of spray on TEM grids.

The film quality was influenced by the duration of each shot (single spray), the time between two consecutives shot and finally the substrate temperature. The shot duration was set at 15 ms, the time between two shots at two second and temperature substrate at 120 °C. This temperature help the solvent to evaporate and the dispersion has no time to reorganize into large droplets.

On MWCNT deposited on Si/SiO_2 was performed an XPS characterization as a function of the shot number. In fig. 3 was showed the wide scan spectra. At low number silicon and oxygen coming from the substrate are detected. When shot number was increased a better coverage was obtained and was confirmed by the marked reduction of these peaks.

To test the in-plane film homogeneity, for all samples was determined elemental surface chemical composition measuring at least three points on each. In table I are reported the results expressed as mean value with one standard deviation. The data evidence the higher coverage of substrate with the MWCNTs film and the reduction of the standard deviation when the numbers of the shot increase, as a consequence of the film in-plane homogeneity improvement.

The analysis of the details carbon spectral region provide information on the oxidation state of CNTs. Figure 4 reports the overlay of C1s peaks at different shot number. It

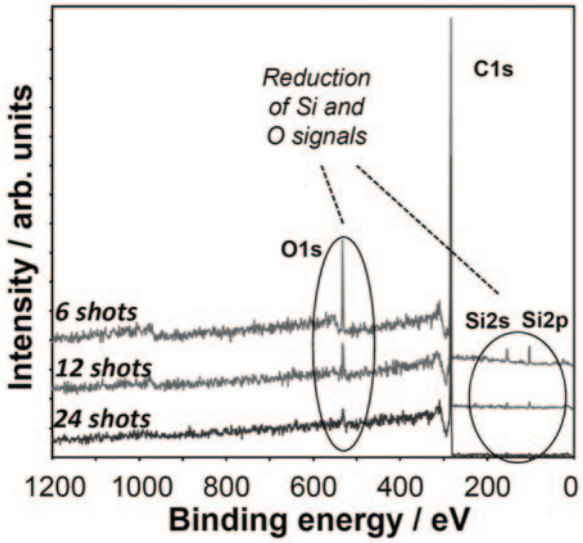

Fig. 3. – XPS wide scan spectra relative to MWCNTs deposited on Si/SiO_2 substrate acquired as a function of shot number.

is possible to observe that they are perfectly overlapped and the shape of each signal resembles a fully non-oxidized carbon. The BE position (284.4 ± 0.2 eV) and the shake up features due to $\pi \rightarrow \pi^*$ transitions in sp^2 orbital confirmed the almost exclusive presence of unsaturated carbon atoms.

The atomic percentages have been recalculated, removing the silicon oxide contribution from the substrate and the results are reported in the right side of table I. The oxygen percentages are very low, and they do not change increasing the number of shot, confirming no oxidation of CNTs. The aging results confirms that there is no oxidation of CNTs even after four months, as can be observed looking at the complete overlap of C1s signal relative to an as-deposited sample an aged one.

In order to obtain the final devices, CNTs were deposited on Silicon substrates provided by Fondazione Bruno Kessler. The final layout is reported in fig. 5.

TABLE I. – *On the left, elemental atomic percentages for MWCNTs deposited on* Si/SiO_2 *substrate as a function of the number of shot. On the right, carbon and oxygen atomic percentages without the silicon oxide contribution of the substrate. Data averaged out of three different analysis points are reported as mean value ± standard deviation.*

	Total atomic %			Atomic % without the silicon oxide contribution	
Shots	% C	% O	% Si	% C	% O
6	88 ± 4	9 ± 2	3 ± 1	97.1 ± 0.5	2.9 ± 0.5
12	94.5 ± 1.2	4.4 ± 0.9	1.1 ± 0.5	97.6 ± 0.5	2.4 ± 0.5
24	95.5 ± 0.5	3.9 ± 0.5	0.6 ± 0.5	97.2 ± 0.5	2.8 ± 0.7

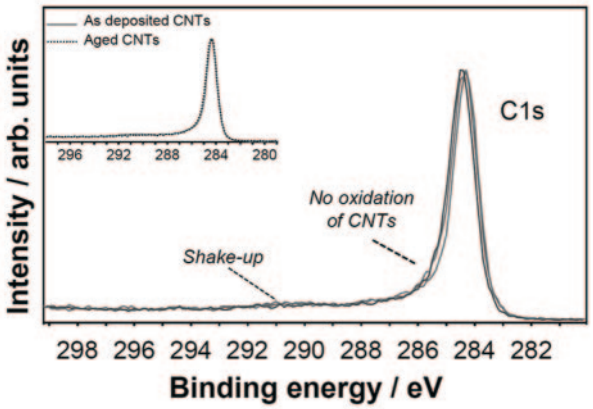

Fig. 4. – C1*s* XP spectra relative to MWCNTs at different shot number. In the inset C1*s* XP spectra of an as-deposited sample and an aged one (solid and dotted lines, respectively).

In order to perform the electrical characterization of the devices, CNTs and one of the front contacts were covered by 50 nm thick ITO layer and the back side was glued on aluminium disks using silver paste.

The terminals of the Agilent Source/Monitor Unit were connected to the sample under measurement by means of two point probes. By convention, the ground was connected to the back and the apply voltage to the ITO. The current-voltage characterization was performed by applying a linear voltage sweep from 0 to +15 V and reading the currents, both in dark condition and under illumination of CNTs with the white light spot. The net photocurrents, obtained by subtracting the dark currents, are reported in fig. 6.

Current-voltage measurements on substrates without MWCNTs were not reported because, as expected, they did not return any signal.

The results show that the devices are characterized by very low dark signals and currents up to 1,15 mA under light illumination, and the photocurrent saturation at about 12 V.

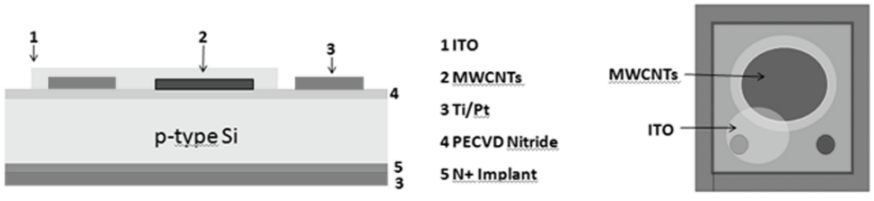

Fig. 5. – Photodetector layout (on the left) and an overview (on right).

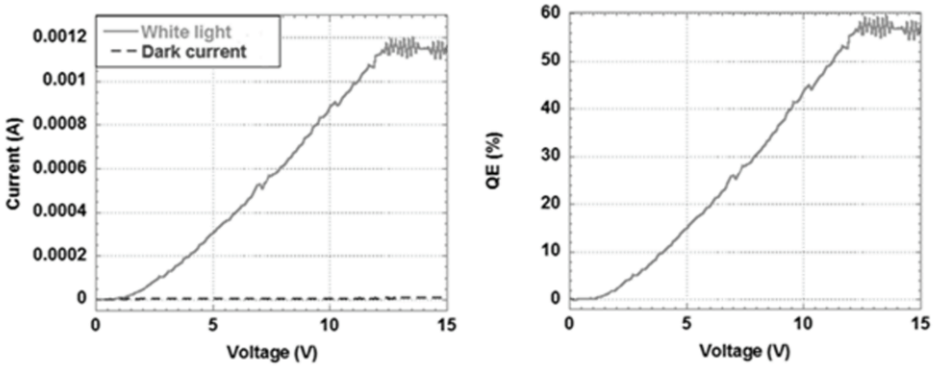

Fig. 6. – Current-voltage characteristics of the devices (on the left) and quantum efficiency as a function of the voltage (on the right).

The measured current values were used to obtain the photoconductive absolute Quantum Efficiency (QE) of the devices by means of the following formula:

$$\mathrm{QE}(\%) = [R \cdot h \cdot c/(\lambda \cdot e)] \cdot (I_{\mathrm{sam}}/I_{\mathrm{ref}}) \cdot 100 = \eta \cdot (I_{\mathrm{sam}}/I_{\mathrm{ref}}) \cdot 100,$$

where

R [A/W] = responsivity,

$\lambda = 550\,\mathrm{nm}$,

I_{sam} [A] = sample current,

I_{ref} [A] = calibrated photodiode current,

η = calibrated photodiode internal quantum efficiency = $[R \cdot h \cdot c/(\lambda \cdot e)]$,

P [W] = radiation power.

The light source responsivity was calculated with the optical power/energy meter as $R = I_{\mathrm{ref}}/P$. The highest QE obtained at saturation point is 59%.

4. – Conclusion

In this paper a spray technique is used to obtain MWCNTs films on silicon-based photodetectors.

The devices are characterized by the presence of a continuous nitride layer between the CNTs and the silicon substrate.

The CNTs surface chemical analysis show the absence of oxidation and that film uniformity increase with the spray number.

The current-voltage characterization show good net photocurrents of the devices and quantum efficiency values up to 59%.

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