Carbon Nanotubes-Based Radiation Detectors
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1. Introduction

Since lots of events in nature are followed by the emission of electromagnetic (e.m.) radiation in certain wavelengths regions, the necessity to observe, measure and analyze such events have driven the development of suitable radiation detectors. Electromagnetic radiation in the visible spectral region and its spectroscopical neighbourhood, Ultraviolet as well as Infrared, are of major interest since produced into a wide range of observable phenomena, from Sun emission to molecules fluorescence. In this field of investigation, for decades, the main detectors have been photomultipliers and silicon based photo-detectors. The firsts are based on the emission of electrons from the photocathode whereas the latter work by exploiting the generation of an electron-hole pair inside silicon junctions. Today the trend in photo-detectors research is twofold. On one hand the increase of sensitivity is constant in the development process. On the other hand, the extension of the photo-detector sensitivity to other spectral regions different from visible has gained increasing interest. The latter is mainly driven by new finding in the space observations of UV (300-400 nm) fluorescence tracks and the Cherenkov reflected bump of the extensive air shower induced by ultrahigh-energy particles traversing the atmosphere (Ebisuzaki et al., 2009).

For space physics and for astroparticle physics envisaged for the next decade it will be indispensable to develop UV sensitive detectors, high pixelled and with high quantum efficiency, as described in the Cosmic Vision 2015-2025 plan for the ESA science program that cites: "The proposed mission will be based on large openings and large field-of-view optics with high throughput, as well as on large area, highly pixelled, fast and high detection efficiency near-UV camera". It is necessary therefore to start the job of developing matrices of detectors, suitable for single photon counting, finely pixelled on great surfaces, with great quantum efficiency and obviously low cost. Detectors that at the moment do not exist.

In accelerators and space physics it is acquiring great importance the identification of particles through Cerenkov detectors like the RICH used in the ALICE experiment at CERN and AMS2 in the space station. Also in this case the Cerenkov light to detect is ultraviolet. In order to reconstruct the intersection ring of the emitted light cone with the sensitive surface of the detector it is necessary a finely pixelled UV detector with high quantum efficiency. Actually the most promising detectors are the SiPM for their fine structure and the ability to achieve amplification factors up to $10^6$. However they introduce severe limitations: the
intrinsic noise due to thermal noise that makes problematic their use above 24 °C; the lowest efficiency in the UV because at such wavelengths the photons are not able to penetrate in the deeper part of the silicon structure; the difficulty to realize matrices with dimensions larger than 5 x 5 mm²; the elevated cost of the device.

Therefore, watching the scenario of the experiments presently discussed for the next quinquennium, the availability of a cheap, wide area, finely pixelled and UV sensitive radiation detector represents a goal of primary importance.

It is a matter of fact, indeed, that recent progress in light detection and photo-generation has been possible thanks to the improvements in nanotechnology. Nano-inprint technology, for example, is already used to produce new generation compact spectrometers and light-sensors.

Among all the new materials employed in nanotechnology applications, in the last twenty years, Carbon Nanotubes has been largely studied due to their characteristics. One of the key features of such nanostructures for electronic and optoelectronic applications is that their metallic or semiconductive character depends on the chirality (for a review about this specific topic, we suggest one of the numerous papers and books available in literature, for example (Saito et al., 1998; Dresselhaus et al., 2001; Jorio at al., 2008)). Furthermore, the presence of a defect in the nanotube walls, e.g. a single atom missing, can result, locally, in the change of the chirality, thus into the variation of the nanotube electronic characteristics (semiconductor-metal junction) within a structure that is only a few nanometers wide (Hartschuh et al., 2003; Anderson et al., 2007). Handling such defects and structures would open the way to a new, unprecedented miniaturization degree.

Recently, a new technique called Density Gradient Ultracentrifugation DGU have allowed sorting nanotubes with respect to their metallic or semiconductive character, opening the way to new experiments and combinations (Arnold et al., 2006; Hersam, 2008). In the same time, high-resolution microscopy techniques have allowed the characterization of nanotubes down to the investigation of a single one (Odom et al., 2002; Lin et al., 2006). Owing to these considerations, it is reasonable that the CNTs exploitation in nano-electronic devices is going to become real.

So far, Carbon Nanotubes have already been studied as components for nano-structured gas sensors (Salehi-Khojin, 2010) thanks to their gas absorption-desorption characteristics. A couple of experiments have investigated the possibility to exploit CNTs for the realization of light-sensitive devices (Wei et al., 2006; Itkis et al., 2006; Gabor et al., 2009). However, most of the light-sensitive applications have been proposed in the photovoltaic research field where nanotubes are used together with other molecules or polymers in different steps of the charge carriers production and collection (Peumans et al., 2001; Kymakis et al., 2002; Kymakis et al., 2003; Balasubramanian at al. 2004; Battacharyya et al. 2004; Lee, 2005).

In this chapter, the possibility to use carbon nanotubes in designing new radiation detectors will be discussed. First a proof of the possibility to employ electronic signals produced inside CNTs will be given by discussing the condition where nanotubes are deposited on sapphire that is passive both from the optical and the electronic point of view. Then, the possibility to exploit carbon nanotubes in combination with other materials like silicon, will be presented. In this case, the signals obtained are similar to those obtained with commercially available detectors.
2. Carbon nanotubes detectors

As sketched in figure 1, a possible layout for a CNTs-based prototype detector is that obtained by starting from a suitable substrate (silicon, sapphire or others) whose surface is covered with electrodes. Those electrodes are usually a few microns interdigitated in order to take high the ratio in between the electrodes distance and the electrodes area. This is a well known configuration, also used in other „sensors“, like gas sensors. The electrodes, that are usually made of gold or platinum, are sputtered on the sample surface using masks for area selection.

The substrate with electrodes is then covered with nanotubes. At this step, Carbon nanotubes can be deposited from a solution by drop casting or they can be grown by chemical methods directly on the sample surface. In the first configuration, a web of nanotubes cover the electrodes. This simple preparation allows to use any available CNTs type, commercial, single walled, multi-walled, etc. Instead, in prototypes resulting from the direct growth of CNTs on the sample surface, nanotubes are usually in between the electrodes only. In fact, in this prototype the deposition technique is the Chemical Vapour Deposition (CVD), a procedure where the nanotubes grow from a catalyst particle (a few nanometers in size), usually Nickel or Iron, by expulsion of carbon atoms from the saturated particle. In this process, carbon atoms expelled from the particle come from an hydrocarbon gas that fill the atmosphere of the process. The whole process is usually assisted by substrate heating. The temperature of the substrate can also influence the final CNTs type and distribution. The diffusion of catalyst particles on the metallic electrodes, guarantees the growth of nanotubes in between the electrodes only.

Indeed the linear dimensions of this prototypes are usually a few millimeters in size with micro-strip electrodes (about 100 µm wide and 100 µm interspaced). Carbon Nanotubes are then grown by CVD or by solution casting.

About the detectors characterization, usually a light beam (often from a laser) shine light onto the sample.
In order to collect the charges generated in the CNTs layer, a drain voltage \( V_{\text{drain}} \) is applied to one of the electrodes. The signal from the sample \( V_{\text{out}} \) is then picked up from the other electrode and measured by means of a digital oscilloscope and its internal 50 \( \Omega \) load resistance \( R_{\text{osc}} \). By naming \( I = \frac{V_{\text{out}}}{R_{\text{osc}}} \), the current in the equivalent circuit, an equivalent impedance \( R_{\text{cnt}} \) for the sample can be obtained using the relation \( \frac{V_{\text{drain}}}{R_{\text{cnt}} + R_{\text{osc}}} = \frac{V_{\text{out}}}{R_{\text{osc}}} = I \).

The possibility to obtain signals from a CNTs carpet is not obvious. For this reason it is worth separating the problem by discussing two configurations. A first one where nanotubes are investigated on a light unsensitive material like sapphire and a second one in which light is used in combination with a light sensitive material, like silicon.

### 2.1 CNTs on sapphire substrates

The advantage of using substrates like sapphire, that are inactive both from the electrical and optical point of view, allows one to exclude any possible contribution to the collected signals from other than the carbon nanotubes layer.

Figure 2 shows the transmittance, in the visible and near-infrared spectral region, of a Multi-Walled CNTs carpet grown by CVD at 500 °C on a sapphire substrate. The same figure also shows the transmittance of the sapphire substrate only. In accordance with what expected, the contribution to the light absorption from the substrate is negligible with respect to that of the CNTs.
from the CNTs. It is evident that the values and shape of the two curves plotted in Figure 2 are quite different especially towards small wavelengths where the spectrum of MWCNTs goes approximately to zero. Sapphire instead appears to be mostly transparent in the wide range investigated, according to reference literature and commercial data sheets. Absorbance values can then be calculated, by definition, as the logarithm of the inverse transmittance. The absorbance spectrum of MWCNTs obtained by subtracting the sapphire absorbance values from the total absorbance values of the sample is shown in Figure 3. The trend of the curve clearly shows higher absorbance for shorter wavelengths, thus for higher photons energy. If the light absorption is thought to be due to charges photo-generation, a similar trend should result also for the dependence of the collected electrical signal from the light wavelength.

![Absorbance of a CNTs layer, grown by means of CVD technique, together with the detection efficiency of the same layer under a 25V drain voltage.](image)

In the case of reference (Ambrosio A., et al., 2008), for example, a pulsed laser beam is generated by means of a Nd:YAG laser, > 10 ns pulse duration, 10 Hz repetition rate. For their study, authors use optical harmonic separators and dielectric mirrors mounted outside of the laser in order to have, time by time, three different beams of adjustable energy and at three different wavelengths, 1064 nm (1.6 mJ energy\(^1\)), 532 nm (0.46 energy\(^1\)) and 355 nm (0.19 mJ energy\(^1\)) (respectively fundamental, second and third harmonic of the neodymium laser). The light pulses hit the sample into a central circular area of about 3 mm in diameter.

\(^1\) average energy per light pulse
This area is selected by means of an adjustable iris so that the exposed sample area is fixed for all the three light wavelengths employed. When laser light is sent onto the sample, a part of the laser beam is also sent to an amplified photodiode producing a trigger signal for the measurement. By integrating the signals, as visualized on the oscilloscope, on the time interval monitored and dividing by the value of the load resistance, it is possible to estimate the amount of charge involved in the photo-generation process.

By measuring the photo-generated charge amount in experimental configurations like those described above and knowing the energy of the light used to illuminate the sample, it is possible to calculate the detection efficiency as the ratio between the number of collected charges divided by the number of incident photons. In Figure 3 the detection efficiency of the device in the case of drain voltage of 25V in between the electrode are reported. As it is easy to see, illumination at 355 nm, thus towards UV light, results into higher efficiency values, with respect to other wavelengths.

This result is largely desirable due to the low efficiency of commercial detectors to the UV electromagnetic radiation. Furthermore, as it is evident from what reported in figure 3, the trend of the device efficiency is in agreement with the absorbance characteristics of MWCNTs constituting the sensitive material in the device. Other experiments have confirmed this behaviour by employing both coherent and non-coherent light sources in pulsed as well as continuous illumination regimes (Passacantando et al., 2008; Coscia et al., 2009).

In these experiments, the absence of any photo-electrical response from the substrate guarantees that the signals observed are only due to the nanotube layer.

2.2 CNTs on silicon substrates

The previous device cannot be used as radiation detector due to the dark current of the order of milliamperes. In order to minimize the dark current a different readout configuration has been tested. A sketch of the device is reported in Figure 4a (Ambrosio M., et al., 2010). Both the surfaces of a Si wafer (resistivity 4Ωcm) were covered with a few nanometers thick silicon nitride (Si₃N₄). Two platinum/gold squared electrodes and an extensive Pt/Au back contact were sputtered on the front and rear side of the sample, respectively. Then, carbon nanostructures were grown directly on the front surface by CVD. A 3 nm nickel (Ni) film was thermally evaporated on the substrate. Ni-deposited substrates were introduced into a CVD reactor (base pressure: 10⁻⁶ Torr) and heated at either 500 or 750°C for 20 min in NH₃ gas at a flow rate of 100sccm. During this period, Si₃N₄ layer prevented nickel diffusion into the silicon wafer so avoiding nickel silicides formation. CNTs were obtained by adding C₂H₂ at a flow rate of 20sccm for 10min at the same temperature of the NH₃ thermal treatment (500 or 750°C). During both the annealing and the CNTs growth, the pressure inside the CVD reactor was kept fixed at 5.5 Torr. Figure 4b and Figure 4c show scanning electron microscopy (SEM) images of the samples synthesized at 500°C and 750°C, respectively. Figure 4b exhibits CNTs very short, bended and characterized by different diameter along the structure.

The average diameter of these nanostructures was of 48±9nm. In Figure 4c, entangled carbon nanotubes (18±7nm in mean diameter), grown as a vertical carpet (Figure 4c, inset), are easily recognizable. High resolution TEM images, not reported here, were also recorded confirming for the former sample the presence of carbon nanofibers and for the latter the formation of MWCNTs.
Current-voltage measurements were performed at room temperature for the sample at 500 °C. The back contact was grounded, while a potential sweep from negative to positive values of the voltage was applied to one of the Au/Pt front electrodes (see Figure 4a). If the drain voltage is applied to one electrode, and the signal is read on the other a large amount of dark current is drained. When the drain voltage is applied in between the two electrodes in the top side and the electrode on the back of substrate (Figure 4a), no current is expected to be drained due to the insulator layer of Si3N4. The I-V characteristic measured in absence of light (dark current) is reported in Figure 5. Instead the I-V plot, reported in Figure 6, appears similar to that obtained in a metallic-semiconductor junction. Moreover in this configuration the device becomes photosensitive: illuminating CNTs between electrodes, a photocurrent is drained through the silicon substrate proportionally to the intensity of light, and as reported in Figure 7, the photodetection efficiency is about 50% at any beam intensity increasing at lower wavelengths.

The light source is a continuous laser beam, 650 nm wavelength, at different power. It can be seen as the generated signal is typical of a detector: the drained current increases with the drain voltage, up to a voltage value from which the current becomes constant. This nearly constant current means that all photo-generated carriers have been collected at the electrodes. In the saturation region our device works as an ideal photodetector, in which the output signal depends only on the radiation intensity. Moreover, the proportionality between photocurrent (averaged in the plateau) and light power is linear. This means that the responsivity of our system, i.e. the slope of the straight fitting lines, is a constant quantity and does not depend on any other parameter, not even the intensity of the incident light. The active role of CNT in the creation of the junction is demonstrated.
by the complete absence of signals lighting areas where no CNTs have been grown. Moreover complete absence of photo-signals has been observed in substrates without CNTs. The junction effect becomes evident only after the growth of nanotubes on the silicon substrate.

Fig. 5. The I-V dark current in the configuration reported in Fig. 4a.

Fig. 6. The I-V plot related a continuous laser beam, 650 nm wavelength, at different power.
2.3 Nanolithography and patternization

In order to grow the carbon-nanotubes with a definite pattern, a procedure based on a lift-off process has been developed (Ambrosio M., et al., 2009). "Lift-off" is a method for making metallic patterns on a substrate, especially for those noble metal thin films such as platinum, tantalum, nickel or iron which are difficult to be etched by conventional methods. The general lift-off process is as follow: first a pattern is defined on a substrate using photoresist. A film, usually metallic, is deposited all over the substrate, covering the photoresist and areas in which the photoresist has been cleared. During the actual lifting-off, the photoresist under the film is removed with a solvent, taking the film with it, and leaving only the film which was deposited directly on the substrate. In this way the assisting material layer is exposed (Figure 8a). This layer is then wet-etched so as to undercut the resist (Figure 8b). The metal is subsequently deposited on the wafer, by a thermal evaporation process (Figure 8c). The resist is removed taking away the unwanted metal with it. The assisting layer is then stripped off too, leaving the metal pattern alone (Figure 6d). The dimension of the pattern spread from 10 \( \mu \text{m} \) down to 100 nm. This is obtained with an Electron Beam Lithography system.

Figure 9 reports some results obtained with the combined use of nanolithography and Lift-off process. A square matrix of 10x10 pixels \( 4 \times 4 \mu \text{m}^2 \) each is shown in Figure 9a; pixels are made of a dense layer of nanotubes, as shown in Figure 9b, and can assume the desired form, for example the INFN logo shown in Figure 9c. The nanotubes grow only where the Lift-off process left the catalyst: no carbon compounds appear to be present outside the pixel, as shown in Figure 9c.

The possibility to grow CNTs on Silicon substrate according to a defined geometry is very important. As discuss in the previous paragraph, the simple in figure 4a is sensitive to light only where Silicon is covered by CNTs. Outside this area no signal can be detected. This
means that the sample in figure 9a can be considered as a 10 x 10 pixels array. Each pixel is 4 x 4 \( \mu m^2 \). In this structure, it is similar to a SiPM, in which pixel can be at minimum 40 x 40 \( \mu m^2 \) sized. The pixellization process of CNT on Silicon is very cheap and easy to be obtained, also in complex geometry (figure 9a) permitting the detector to be perfectly coupled with the emitting surface. In particular, the CNT distribution can reproduce the complex structure of an optical fibre calorimeter.

Fig. 8. The Lift-off process used for CNT growth patternization.
Fig. 9. a) a square CNT matrix of 10x10 pixels 4x4 mm² obtained with a lift-off process on lithographed mask; b) individual 2x2 μm² CNT pixel; c) the INFN logo made of CNT in micrometric scale; d) Raman image of CNT and silicon substrate
3. Electrical analysis of carbon-nanotubes/silicon heterojunctions

A preliminary study of the electrical behavior at varying temperature of the MWCNTs/silicon junctions has been developed (A. Tinti 2010). The device used for this investigation is shown in Fig. 8. The substrate was a 500 µm Si, covered on both its faces by means of a thin silicon nitride (Si$_3$N$_4$) layer.

Two platinum/gold squared electrodes were sputtered on the front side of the sample and a similar back contact in the form of a serpentine was realized on the other side. A very thin nickel or iron film was then thermally evaporated on a surface selected area far from the electrodes and turned in cluster by means of thermal heating at two different temperatures of 500 and 740 °C into an ammonia rich chamber. Finally, MWCNTs were deposited by means of the CVD technique.

![Multilayer structure constituting the samples](https://example.com/multilayer_structure.png)

**Fig. 10.** Section and top views of the multilayer structure constituting the samples. Measurements layout is also depicted.

The last operation in order to make the device suitable to electrical measurements was to accomplish the front contact acting as a bonding among the insulated electrodes and the carpet of CNTs. This was done by sputtering on the sample, through a proper mask, a thin film (100 nm) of indium tin oxide (ITO) which contacted both the Au/Pt pads and the nanotubes (see Fig. 10). ITO is a transparent conductive oxide (TCO) with a direct band gap generally greater than 3.75 eV in energy, depending on the exact composition, and then is an almost completely non-absorbing material in the visible spectral range. An average optical transmittance of 80% was in fact obtained between 400 and 800 nm for such a coating when deposited onto a glass substrate and then analyzed by means of a spectrophotometer. Moreover, Van der Paw technique provided an average electrical resistivity of $8 \times 10^{-4}$ Ωcm, a sufficiently low value to create a near-ideal ohmic contact at the interface with CNTs.
The experimental layout is also sketched in Fig. 10. A bias voltage ranging from $-1$ to $+1$ V in 100 mV steps was applied to the back contact, while the outgoing current signal (in the absence of light) from the sample was picked up from one of the two front electrodes, which are at the same electric potential thanks to the ITO coating, and hence measured. The semimetallic nature of nanotubes and the p-character of the silicon suggest that the forward polarization of the CNTs/Si heterojunction occurs when a positive voltage is applied to the semiconductor with respect to the tubes. Moreover, by imagining that CNTs grow perpendicular to the substrate with a length in the 10 µm range, we can state that the applied electrical field is parallel to their axis direction. In this way, it can be exploited the ballistic conduction of charge along the tube, a completely quantum-mechanical mechanism rather than a classical electromagnetic one, in order to optimize the drifting process through the junction and then the carrier collection yield by avoiding the signal attenuation. This is also the reason why the Au/Pt electrodes were made externally in respect to the layer of CNTs and a front rather than a lateral contact of ITO was then used as a bridge between them.

During the registration of the dark $I-V$ characteristics, the sample was mounted on the cold finger of a closed cycle helium cryostat (CCHC), in order to analyze the device electrical behavior as a function of the temperature, ranging from 150 to 300 K in about 25 K steps and well controlled and measured by a thermistor in contact with the specimen. Figure 11 shows the sets of the current $I$ versus voltage $V$ plots with varying temperature $T$ in dark conditions (no light on the CNTs). The $I-V$ characteristics are neither typically ohmic nor semiconductive in shape. They are rather semimetallic curves probably due to the presence of semiconductive tubes and metallic ones at once.

Fig. 11. Set of experimental $I-V$ curves as a function of the temperature for the samples investigated. The gradient in the color scale suggests that the higher the temperature (red), the higher the current; on the contrary, the lower the temperature (blue), the lower the current.
The experimental data are not consistent with any activated Arrhenius-type model, in which the current as a function of the temperature for constant voltages would be proportional to the factor $\exp(-E/kT)$, with $E$ the activation energy measured with respect to the valence band. They are instead better fitted by an equation of the form $I_F = I_0 \exp(AV_F)$, the subscript $F$ standing for forward, which is typical for currents controlled by tunneling through the energy barrier at the junction. It must be emphasized that different transport processes may be occurring at the barrier of heterojunction, whereas the measured current will usually be dominated by only one of the transport mechanisms. In any case dark current measurements are well explained by assuming that the charge transport is controlled by tunneling at the presumably high defective interface. In particular, among the various tunnel processes, the best results in the fitting of experimental data are obtained by using an equation that describes a multistep crossing of the depletion region by carriers rather than a band-to-band transition. The agreement of the measured values to the theoretical model is very good.

4. Conclusion

Future experiment will impose severe constraints to new detectors for light sensing and photodetection. In particular finely pixelled, large area, cheap and UV sensitive detectors will be necessary for future space and high energy physics experiments. Up to day Silicon detectors play a fundamental role in photodetection, allowing pixellization of the order of ten microns.

The final product is obtained by means of the so called “top-down” process: starting from macroscopic material the matter is manipulated in such a way to obtain many microscopic elements. This process is very critical and expensive, and the final product is a result of a long and sophisticated process.

The modern silicon technology is actually at the border of nanotechnology and quantum effects begin to assume a strong relevance in the new generation of very high integration scale. Nanotechnology instead is based on a reverse approach: nano and micro materials are built by grouping individual atoms and molecules, in a so called “bottom-up” process. The final object dimensions depend on the duration of building process. This new approach is very cheap and relatively easy to do, being mostly a chemical process. This opens a door on the future allowing the extension of the Moore’s law in the nanoscale world.

Among the new nanostructured materials, carbon nanotubes appear to be the most promising because of their unique physical and electrical properties. It has been demonstrated that they are characterized by an enhanced sensitivity to the radiation on a wide wavelength range, particularly important in the UV region. This opens the possibility to use this new material to build large area photocathodes sensitive in the fluorescence-Cerenkov light emission region (300 – 400 nm). In addition they can be growth on a surface according to a finely pixelled mask obtained by means of nanolithography processes. Commonly people refer to them claiming to be at the beginning of the post silicon era.

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6. References


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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. In the past decades, although carbon nanotubes have undergone massive research, considering the success of silicon, it has, nonetheless, been difficult to appreciate the potential influence of carbon nanotubes in current technology. The main objective of this book is therefore to give a wide variety of possible applications of carbon nanotubes in many industries related to electron device technology. This should allow the user to better appreciate the potential of these innovating nanometer sized materials. Readers of this book should have a good background on electron devices and semiconductor device physics as this book presents excellent results on possible device applications of carbon nanotubes. This book begins with an analysis on fabrication techniques, followed by a study on current models, and it presents a significant amount of work on different devices and applications available to current technology.

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