Time response in carbon nanotube/Si based photodetectors

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Abstract

We investigated the response of carbon nanotube/Si photodetectors to nanosecond light pulse using two electrode configurations for photovoltaic and photoconductive operations. When operating in photovoltaic mode, the devices show a linear dependence of the photocurrent as a function of the light pulse energy with rise time of 20 ns. In photoconductive mode, an increase of the maximum photocurrent as high as 30 times and a gain in the number of photogenerated charges up to 200% is recorded with a correspondent decrease in the time response below 10 ns. Current voltage characteristics measured as a function of the temperature indicate that the fast response of these devices can be ascribed to the formation of Schottky junctions at carbon nanotube/Si interface. These results make our devices comparable to most commercial photodetectors and pave the way for their use as avalanche photomultipliers.

Keywords:

Carbon nanotubes, Photodetector, Pulsed laser, Junction

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1. Introduction

Photodetectors are widely used in day life as well as in research activities [1]. Their use is becoming more frequent with the developments of the control of smart systems for day life applications [2] as well as in medical [3] and scientific facilities [4] where they play the role of low signal detectors for radiation sources of different kinds. Examples are distance detectors, alarm systems, medical diagnostic facilities, quality controls, thermal and high energy detectors [5]. In all the cases, the most important requirements remain a fast response, a high responsivity and a low noise [6]. Although most of the commercial available photodetectors are based on Si technology, new fields are becoming to be investigated pressed by the necessity to reduce costs and sizes of the devices. From this point of view, nanomaterials present characteristics which are unique especially if one considers the possibility of their use in Si based hybrids [7]. Carbon nanotubes (CNTs) with their nanometric size and their compatibility with Si, represent one of the most promising nanomaterials for Si technology integration [8]. Moreover, due to their good electrical conductivity and optical transparency [9], CNTs are good candidates for photodetector applications. Thanks to their properties to give rise to the formation of a rectified junction when deposited on Si surface, they were used with the double purpose of transparent window and photocharge collectors when deposited in form of thin film on the surface of a doped Si substrate (see ref. [10] and references therein). Following this insight, we recently demonstrated responsivity higher than 1 A/W when single walled CNT (SWCNT)/n-Si junctions were used in photovoltaic (PV) mode using a two terminal configuration as in the case of non-polarized photodiodes [11]. This result was well above that observed for the similar hybrid systems and comparable to the commercial photodiodes [5]. Moreover, an increase of responsivity up to 150% with respect to the non-polarized configuration was observed when the same devices were used in photoconductive (PC) mode using a three terminal configuration [12]. However, in these cases, the junctions were illuminated by using light emitter diodes (LED) which did not allow us to make accurate measurements of the time response due to the limited bandwidth of the light source. In the present work we report a detailed study of the photocurrent response when the SWCNT/n-Si junction is illuminated by a nanosecond pulsed laser emitting in the visible range. Since the photocurrent depends on the contact configuration, we investigated the effect of using a two terminal or a three terminal configuration on the time response. Beside the improvement in the rise time and responsivity, to our knowledge never observed for similar junctions, the experimental results give indications on the charge diffusion mechanism after light absorption and allow to better understand the role played by the SWCNT thin film in collecting the photo generated charges.

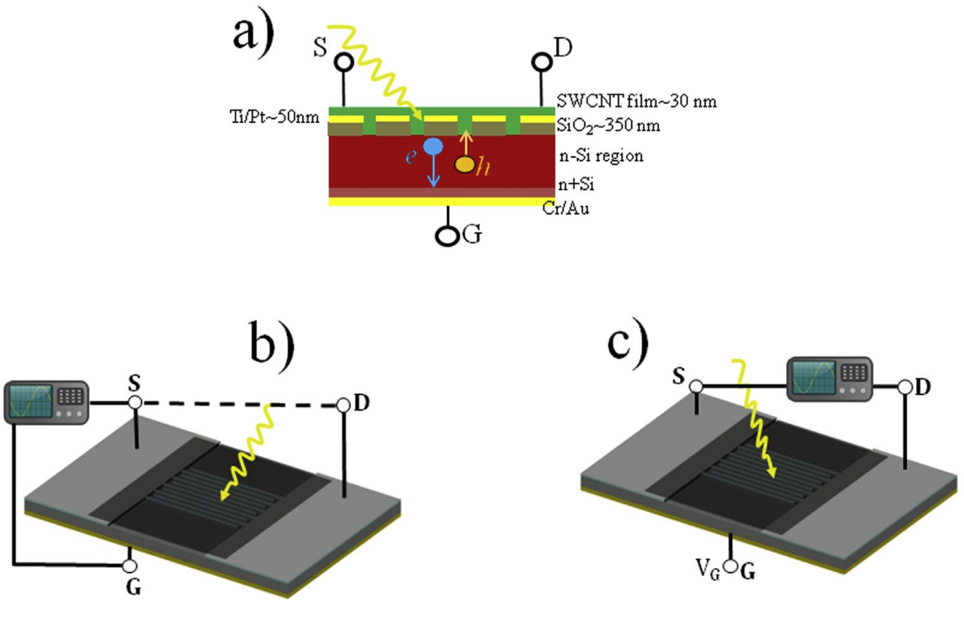

Fig. 1. **(a)** Schematic section of the SWCNT/Si photodetector with the photocharges drifted towards the opposite electrodes by the interface built-in potential; **(b)** three dimensional view of the photodetector with the terminals connected for photovoltaic and **(c)** photoconductive measurements.

2. Experimental

SWCNT thin films were obtained by vacuum filtration method following a well-established process developed for solar cells production as detailed elsewhere [13]. The films consist of a mixture of metallic (10%) and semiconducting (90%) SWCNTs fully characterized by transmission and reflection optical spectroscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and electron microscopy [13,14]. They are semitransparent with optical transmission depending on their thickness. For the present experiment, SWCNT thin films with optical transmission of 63%, thickness of 30 nm and sheet resistance of 500 Ω/sq were synthesized. The substrates were fabricated by the Fondazione Bruno Kessler [15] and consist of *n* doped Si wafers, 150 μm thick, with donor concentration atoms of 10^{16} cm^{-3} corresponding to an electrical resistivity of 0.53 $\Omega \cdot$cm. The top surface of the Si substrates, cut in rectangular shapes of 3x6 mm^2, is provided with two interdigitated Ti/Pt electrodes consisting of ten fingers (five per electrodes) separated by a distance of 250 μm and deposited on a template of SiO$_2$ structure which works as insulator between the top electrodes and the Si surface [16]. A third Cr/Au metallic electrode is deposited on the bottom surface of the Si substrate which is heavily n-doped to allow the formation of an Ohmic contact. A schematic drawing of the substrate is shown in Fig. 1. The SWCNT film is deposited on the top surface of the substrate by printing method and results to be in contact with the interdigitated electrodes and with the Si surface left free by the SiO$_2$/electrode structure [11,12,16]. The SWCNT/Si junction is formed at the interface between the SWCNT film and the Si surface which represents the active area of the detector and, for the case studied here, results to be A = 7.8 mm^2. Photocharges are generated by the absorption of the light penetrating the Si substrate through the semitransparent SWCNT thin film. Since Si is *n*-doped, electrons and holes are drifted towards the bottom metallic electrode and the top SWCNT film, respectively [12].

The junctions have been characterized by current voltage (I–V) measurements in dark conditions using a Keythley 2400 source/meter plunging the samples in a dewar containing liquid nitrogen for temperature measurements. For the optical measurements the samples were mounted in a metallic box with the top surface positioned under a circular pinhole of diameter of 1 mm used for the light input. The light source was a frequency doubled Q-switched Nd:YAG pulsed laser (Quantel Brilliant) emitting light at wavelength λ = 532 nm at a repetition rate of 10 Hz. Before to start with the measurement session, the width of the laser pulse and its maximum intensity were measured by a Si-PIN PhDiode photodetector (Antel Optronics AR-S2, nominal response time of 35 ps) positioned in the place of the sample and connected to a 30 Ghz Tektronix oscilloscope. The measured laser pulse showed 5 ns at full width half maximum (FWHM) with a rise time of 2 ns, and an energy of 560 nJ which we assume to be the same delivered to the sample. In order to study the response of our samples to the incident pulse energy, the laser beam intensity was regulated by using optical attenuators which allow to obtain energy values at the sample surface in the range ε = 56 pJ ÷ 560 nJ for each pulse. The particular geometry of the electrodes allows to polarize the samples using a two-terminal or a three-terminal configuration. In the former case, hereafter also called photovoltaic (PV) mode, the top (S, D or both) and the bottom (G) electrodes (see Fig. 1b) are connected to the source/meter facility. In the latter case, hereafter also called photoconductive (PC) mode and shown in Fig. 1c, the two top electrodes (S and D) are connected to the source/meter and the bottom electrode (G) is used as a gate electrode (connected to another voltage supply). For both the terminal configurations, the photocurrent generated after the absorption of the laser pulse was recorded by the 30 GHz Tektronix oscilloscope.

3. Results and discussion

Fig. 2 shows the time dependence of the short circuit current I_{PV}, acquired in the PV mode, after the junction is illuminated by the laser pulse at different energy. I_{PV} different from zero is recorded at pulse energy down to 56 pJ (the minimum available) showing a high sensitivity of our photodetectors. Moreover a rise time $r_{PV} \approx 20$ ns is measured as the difference between the 90% and 10% of the peak value for every pulse energy. These results are comparable to those reported for commercial photodetectors [5] confirming the high sensitivity and the fast response of our devices.

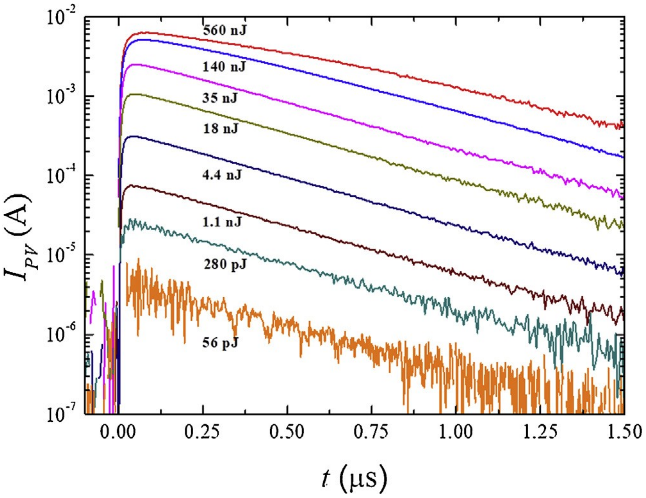

Fig. 2. Photocurrent vs. time collected in the photovoltaic mode at different energies of the nanosecond light pulse.

The effect of the gate voltage is shown in Fig. 3a where the current (I_{PC}) measured in PC mode, corresponding to the current flowing inside the SWCNT film, is reported as a function of the time at different gate voltages V_G when the junction is illuminated by a pulse energy $\varepsilon = 8.9$ nJ. The curves are obtained by subtracting the dark current contribution and represent the response of the photodetector to the light pulse. An increase up to 30 times of I_{PC} with respect to its value at $V_G = 0$ is observed and a reduction of the rise time to $r_{PC} < 10$ ns is measured. This confirms the improvement obtained by using the three terminal configuration which, in addition to increase the photodetector response, gives a reduction of the rise time ($r_{PC} < 10$ ns) with respect to the PV configuration ($r_{PV} \approx 20$ ns). The peak current I_{PCmax} of the curves in Fig. 3a is shown in Fig. 3b as a function of V_G. A double behavior in the photodetector response is observed by the change in the linear slope at $V_G \approx 9$ V. This can be ascribed to the starting of the avalanche regime which causes an increase of the photocurrent independent on the light energy. This effect is well represented by the I–V characteristics shown in the inset of the same figure and acquired for the same sample under dark (black line) and under light (red line) conditions using a d.c. LED as light source. The difference between the linear behaviour observed for $V_G > 9$ V in the main panel of Fig. 3b and the rather exponential dependence of the I–V characteristic in the inset of the same figure is due to the absence of the dark current contribution in the data reported in the main panel. In order to better highlight the difference between the PV and the PC configurations on the photodetector response, we report in Fig. 4a the number of photocharges collected in the two operating modes. These are calculated by the area of the curves in Fig. 2 for the PV mode and by the area of the curves obtained in the PC mode at different laser pulse energy with $V_G = 0$. Therefore, in the figure the black squares represent the charges collected by using the S and G terminals (PV mode) whereas the red circles are the charges collected by the SWCNT film at S and D terminals with $V_G = 0$ (PC mode with $V_G = 0$). For both the electrode configurations the dependence is well approximated by a straight line up to about 30 nJ confirming the possibility to use the device as a linear detector. For $\varepsilon > 30$ nJ the detector saturates and its response is not proportional to the pulse energy anymore. Interestingly, a marked difference of about one order of magnitude at any pulse energy is reported between the number of photocharges collected using the two different operation modes. This can be ascribed to the different mechanism governing the current flow in the two configurations. In the PV mode the photocharges, collected by measuring the current between the S and G terminals, are both electrons and holes produced by the light absorption and separated by the built- in potential at the SWCNT/Si interface.

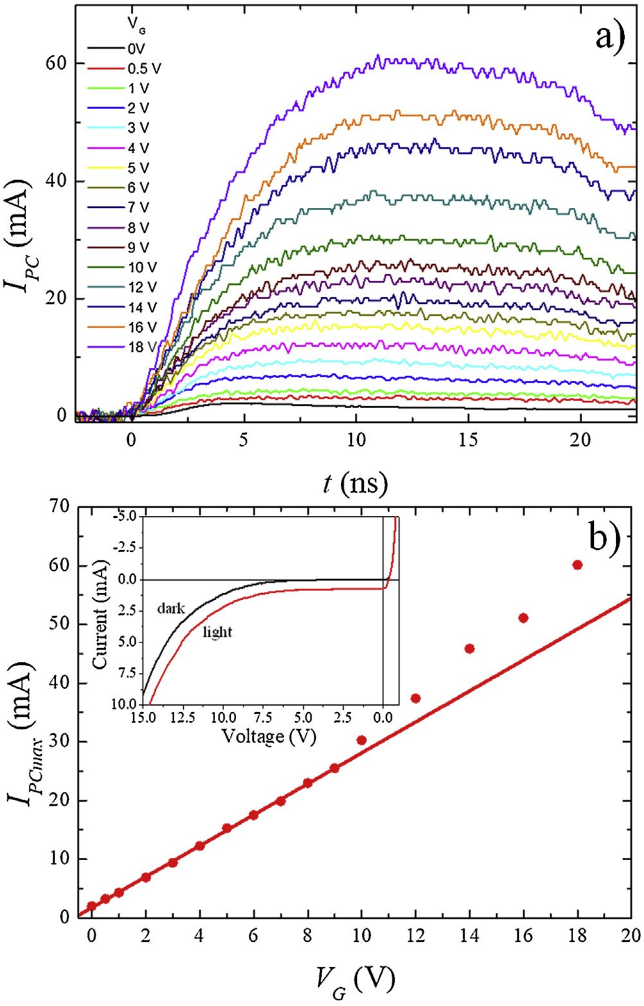

Fig. 3. (a) Photocurrent vs. time collected in the photoconductive mode at different values of the gate voltage V_G; (**b**) maximum of the curves shown in a) as a function of V_G. The straight line is a fit to the data in the range V_G = 0–9 V. **Inset**: Current voltage characteristics of the same device measured in the photovoltaic mode under dark and light condition.

On the other hand, in the PC mode (with V_G = 0) the photocharges are collected by measuring the current between the S and D electrodes and are essentially holes driven across the junction by the action of the same built-in potential. They are less in number than the electron-hole pairs collected in the PV mode and this explains the difference in the data of Fig. 4a. Nevertheless, the number of holes collected by the SWCNT film in the PC mode can be hugely increased by the action of the gate potential V_G which, driving the junction in the avalanche regime, allows to obtain an amplified response as shown in the inset of the same figure. Here the number of charges collected by the SWCNT film, calculated by the area under the curves reported in Fig. 3a, are shown as a function of the applied voltage V_G. The action of the gate voltage in the three terminal configuration gives an increase on the response of the photodetector by a factor of about 200 when V_G ranges between 0 V and 18 V. This result overcomes that obtained for similar junctions and gives a valuable perspective to these devices to be used in avalanche mode for small signal amplification. Avalanche photodetectors, in fact, work in inverse polarized mode using bias voltage of the order of 100 V which is very high especially if low size photodetectors are designed. The result to obtain such gains by using bias voltage less than 20 V is of a paramount importance in any field of applications for photodetectors and makes our devices a believable alternative to the today's Si technology.

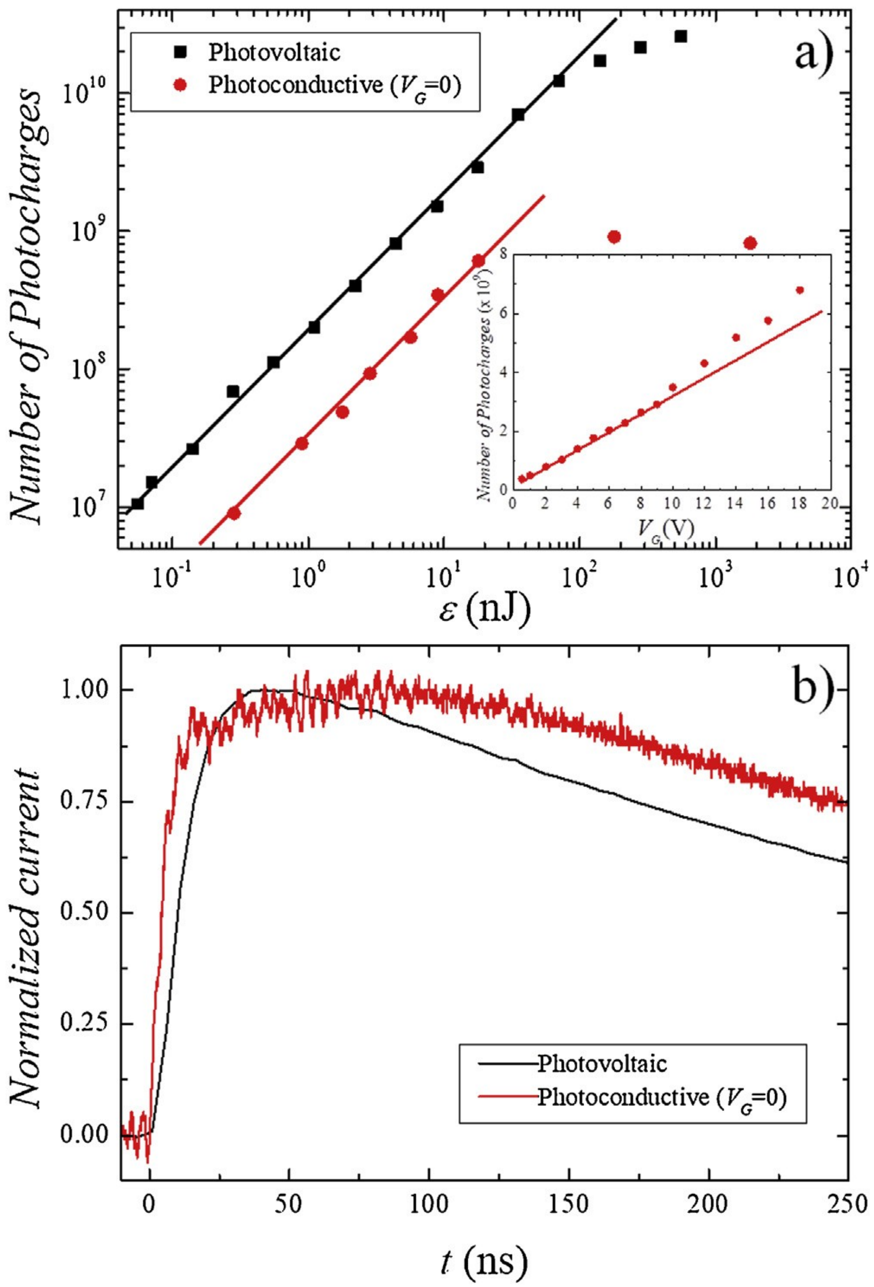

Fig. 4. (a) Number of photocharges collected in photovoltaic (black squares) and photoconductive (red circles) mode as a function of the light pulse energy. The lines are linear fit to the data for ε<30 nJ; **Inset**: number of photocharges collected in pho- toconductive mode as a function of the gate voltage V_G. (**b)** normalized photocurrent with respect to its maximum value as a function of the time in the photovoltaic (black lower curve) and photoconductive (red upper curve) mode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The improvement of the photodetector performances observed in the PC mode is even more emphasized if one is interested to the time response of the device. Fig. 4b shows the photocurrents, normalized with respect to their maximum value, recorded in PV (black line) and in PC (red line, V_G = 0) modes for the same laser excitation pulse (ε = 8.9 nJ). Rise time r_{PV} = 19.6 ns and r_{PC} = 9.6 ns are measured as the difference between 90% and 10% of the maximum of the curves for the PV and the PC mode, respectively. This improvement in the response is observed in all the measured devices when the photocharges are collected between the S and D electrodes and can be ascribed to the same mechanism discussed above for the photocharges collected in the two different terminal configurations. Only holes photogenerated in proximity of the SWCNT/Si junction are collected in the PC mode by the SWCNT thin film giving a faster response with respect to the PV configuration where electrons, in order to be collected, have to reach the bottom electrode which is about 150 μm away from the SWCNT/Si junction [17]. Other minor mechanisms as charge recombination and difference between the charge mobility in SWCNT film and Si can be invoked to explain the observed difference in the response time between the two configurations. A slight decrease of r_{PC} is recorded when V_G is increased in the PC configuration. This is expected because the action of the external potential is to increase the photocharge velocity towards the SWCNT film and, as a consequence, to decrease the drift time. Due to the limited rise time of the laser pulse, which is of the same order of the measured time response of our devices, the measured value of r_{PC} is probably overestimated and a better response in terms of rise time should be obtained by using a faster laser pulse. The high sensitivity and the fast response of our devices can be understood by investigating the kind of junction that is established at SWCNT/n-Si interface. Considering that the SWCNT film is a mixture of metallic (10%) and semiconducting (90%) SWCNTs, the type of junction that is expected to be established at the interface should be semiconducting-semiconducting (S-S) [18], semiconducting-metallic (S-M) [19] or a mixture of both. It is well known that S-M junctions, although more noisy than their counterpart S-S junctions, are faster because of the formation of a Schottky barrier which shows reduced switching times with respect to *p*-*n* junctions [20]. I–V characteristics at different temperature were performed on our devices in PV configuration in dark conditions and they are shown in Fig. 5 in a semi-logarithmic scale. In this contact configuration, the I–V dependence follows the diode characteristics given by $I = I_0 (e^{qv/k_BT} - 1)$ where k_B is the Boltzmann constant, q the elementary charge and T the temperature [21]. I_0 represents the saturation current and its temperature dependence univocally determines the kind of junction. In particular, in the case of Schottky junctions this dependence is given by I_0 $A^* T^2 e^{(-q\varphi_{Bn}/k_BT)}$ were A^* is the Richardson constant that for free electrons is $A^* = 120$ A/cm^2 K^2 and φ_{Bn} is the S-M contact barrier [21]. The inset of Fig. 5 shows the temperature dependence of I_0 measured by linear extrapolation at zero voltage of the low current part of the I–V curves corresponding to voltage less than 100 mV. The data, reported as I_0/T^2 vs T^{-1} in a semilogarithmic scale, are well approximated by a liner dependence down to $T =$ 140 K confirming that the junction behaves as a Schottky type well below room temperature. The result of the fitting procedure gives $_{Bn}$ = 0.28 eV. Such a low value of the interface potential barrier is in agreement with the low time response observed in our devices. The deviation from the linear dependence at $T < 140$ K is due to tunnel effects which become predominant at low temperature [22]. The formation of a Schottky-like junction at the SWCNT/Si interface can be ascribed to the metallic component of the SWCNT film and it is responsible for the fast component of the time response of our devices [21]. This suggests that

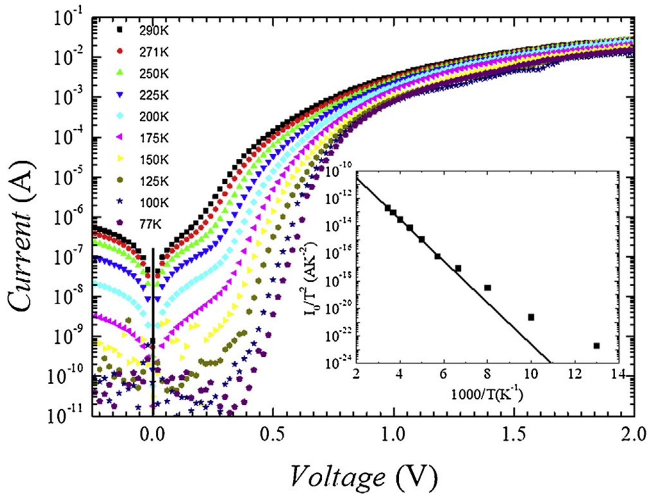

Fig. 5. Current-voltage characteristics for the SWCNT/Si junctions in dark conditions at different temperature. **Inset**: saturation current I_0 vs. temperature for the same sample of the main panel. The values of I_0 are obtained by linear extrapolation to zero voltage of the low current data (V<100 mV) of the main panel. The straight line is a fit to the data which well approximates the experimental points in the range T = 300 K-140 K.

using a higher metallic concentration in the SWCNT mixture would decrease the response time, improving the detector performance as fast light sensor. Nevertheless, it is expected that an increase of the metallic component affects the noise and therefore the right balance between the metallic and the semiconducting SWCNT components should be carefully considered for a better and proper use of the presented photodetector.

5 Conclusions

Fast photodetectors with rise time in the range of nanoseconds can be obtained by depositing SWCNT thin films on *n*-Si substrates. The experimental data show that the response of the devices is comparable to the commercial photodetectors based on Si technology with great advantages in time-consuming and costs. Operating in the photoconductive mode, the SWCNT/Si photodetectors can be used in avalanche regime with gains as high as 200 paving the way to their use for weak signal detection. From the temperature measurements we argue that Schottky barriers are the responsible of the fast response and high gains. Further developments are still possible with an optimization of the

SWCNT/Si interface with a change in the metallic component of the SWCNT mixture forming the thin film. Moreover, better time resolution using femtosecond laser source could give a more accurate determination of the detector response time.

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