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Effects of HNO_3 molecular doping in graphene/Si Schottky barrier solar cells

L. Lancellotti*, E. Bobeico*, A. Capasso**, M. Della Noce*, T. Dikonimos**, N. Lisi**, P. Delli Veneri*
*UTTP-MDB, Materials and devices-ENEA – Portici Research Center- Portici (Italy)
**UTTMAT-SUP, Materials-ENEA – Casaccia Research Center- Rome (Italy)
laura.lancellotti@enea.it

***Abstract*— Schottky barrier solar cells based on graphene/n-silicon heterojunction have been fabricated and characterized and the effect of graphene molecular doping by HNO_3 on the solar cells performances have been analyzed. Different doping conditions and thermal annealing processes have been tested to asses and optimize the stability of the devices. The PCE of the cells increases after the treatment by HNO_3 and reaches 5% in devices treated at 200 °C immediately before the exposition to the oxidant. Up to now our devices retain about 80% of efficiency over a period of two weeks, which represents a good stability result for similar devices.**

Keywords—graphene; solar cell; Schottky barrier; chemical doping

I. Introduction

Graphene films, grown by chemical vapor deposition (CVD) and transferred onto crystalline silicon wafers, form graphene/silicon (G/Si) Schottky barrier solar cells. A full understanding of the nature of the behavior and performance potentiality of G/Si heterojunction is of great interest, since its structure is the simplest among the graphene based solar cells. In G/Si heterojunction, graphene serves not only as transparent conductive electrode but also for producing a built-in field and inducing charge separation [1]. The optimization processes of a basic G/Si heterojunction solar cell are essentially based on the adjustment of graphene layer number [2], the introduction of antireflection layers [3] and the material doping [4]. Doping of graphene films can be obtained through atom doping (e.g. boron doping) and molecular doping (e.g. HNO_3 doping). In all the cases of molecular doping, performance stability is a problem: after few days storage in the air only a little percentage of PCE enhancement is retained since the molecular dopants tend to gradually evaporate from the surface of graphene. In the present work, G/Si Schottky junction solar cells have been assembled and electrically characterized under illumination conditions. The effects of graphene molecular doping by HNO_3 on the G/Si heterojunction solar cells performances have been investigated. The pristine devices, not intentionally doped, showed a PCE less than 1%. After the treatment by HNO_3 the PCE enhanced to 5%. We have devoted particular attention to the influence of the doping process conditions on the stability of the devices performance. We have reached an 80% PCE retainment over two weeks which, at the moment, represents a good stability result for similar devices.

II. Experimental

A. Material and device preparation

The G/Si heterojunction devices have been fabricated on commercially purchased lightly n-doped (resistivity of 1Ω-cm) Si wafers with 300 nm SiO_2 layer. The silicon substrates have been patterned by photolithography and wet-etching of oxide (by hydrofluoric acid solution) to prepare square windows. The device active area is 0.09 cm^2. The front and back contacts have been, respectively, realized evaporating Ti/Au on the SiO_2 and a Ti/Pd/Ag trilayer on the back side of the n-Si. Graphene films have been grown on copper foil substrates by a non toxic and low-cost ethanol based CVD [5]. The growth processes have been performed near 1000°C. A system for the fast cooling of the samples, to stop the growth of further graphene layers, allows to bring the sample temperature below 500°C in few seconds. The thermal CVD reactor consists of a vacuum fitted, 40mm diameter quartz tube, placed horizontally into an oven furnace. After removing the graphene grown on the back surface, the Copper foils have been left floating on the top of a $HNO_3(70\%):H_2O=1:3$ solution for a complete etching of the copper. The films have been then scooped using a thermally oxidized silicon wafer and transferred into a clean distilled water bath to remove the acid residues. Finally the films have been transferred onto the cell substrates, taking care to fully cover with the film the patterned active area and the gold contacts. During the process the graphene film were protected using a novel type of supporting material, specifically designed for wet processing. The scheme of the cell substrate is shown in Fig. 1. In Fig. 2 it is shown a photograph of the frontal part of the final device. Doping treatment of the assembled G/Si solar cells have been carried out by placing the assembled cells downward, on the graphene side, exposed to the vapor of nitric acid for 3 minutes.

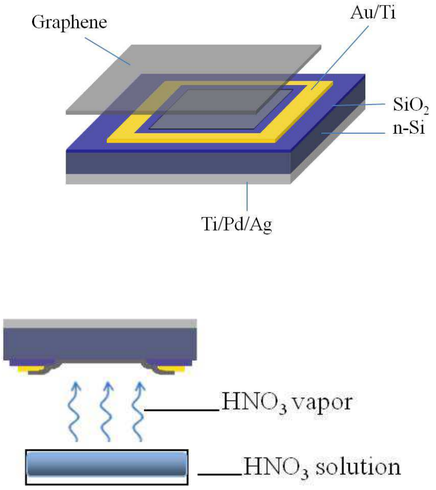

Fig. 1. Schematic diagrams of the G/Si solar cell and HNO$_3$ doping.

Fig. 2. Photograph of the frontal part of the final device. The shadow visible on the gold contact is graphene film, the central grey zone is the active area of the device where graphene contacts silicon and the dark zone is SiO$_2$/Si.

B. *Characterization methods*

The pristine and nitric acid treated graphene have been characterized by Raman spectroscopy performed through a Renishaw inVia Reflex Raman spectrometer using 514.5 nm excitation source. The sheet resistance of the graphene has been measured using a four-point probe with a nanovoltmeter (NAPSON Resistest RT-8A) and the Van der Pauw method was applied. The solar cells are characterized by measuring the current density–voltage characteristics under a dual lamp WACOM solar simulator in standard test conditions (25 ^{o}C, AM1.5G, 1000W/m^2).

III. Results and discussion

Fig. 2 shows Raman spectra of pristine and nitric acid treated graphene (after annealing at 200^{o}C) where the characteristic D, G and 2D Raman bands are clearly visible. As can be seen in the comparative Raman spectra the pristine graphene (PG) shows a D band at 1352 cm^{-1}. The G and 2D band positions occurred at 1582 cm^{-1} and 2706 cm^{-1}, respectively, and the corresponding intensity ratio of G and 2D bands (I_G/I_{2D}~0.5) confirms the presence of the few layer graphene structure [6]. There is a blue shift (~9cm^{-1}) in the G band peak of doped graphene (DG) ascribed to conventional fluctuation due to hole doping in graphene [7]. Furthermore, we observed slight blue shift in the 2D band peak of DG (2709 cm^{-1}) samples compared to PG (2706 cm^{-1}), explained in reference [8] through the effect of the functionalization of different functional groups with carbon atoms through sp^3 hybridization.

Upon modifying graphene with molecular doping, the sheet resistance of the samples changes from 597 to 221 ohm square, decreasing by 63% of the original value.

In Fig. 4 and Fig. 5 we show the effect of doping and ageing on the current density–voltage characteristics under illumination. Devices realized with pristine graphene show PCE<1% (Fig. 4, blue curve). The best PCE for a device with no annealing before doping is 3.4% (cell 1, Fig. 4, red curve) and lose a 50% of these value after 15 days of storage in the air (Fig. 4, green curve). In devices annealed at 200 ^{o}C for 20 minutes before the exposition to the dopant, PCE reaches 5% (cell 2, Fig. 5, red curve) and retains an 80% of its value after 15 days (Fig. 5, green curve). This result could be partially explained through the desorption of transfer residues at the interface between graphene and silicon and the removal of trapped water after device fabrication induced by thermal annealing.

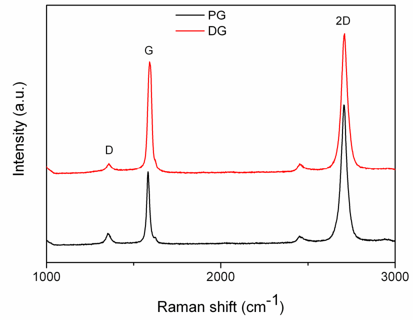

Fig. 3. Comparative Raman spectra of pristine and nitric acid doped graphene.

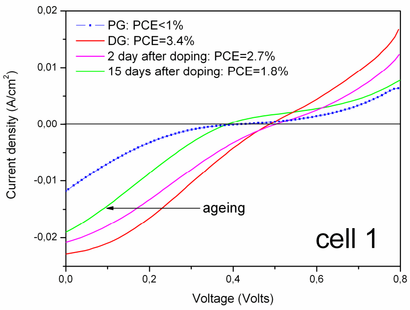

Fig. 4. Doping and ageing effect on the J-V illuminated curve of a solar cell with no annealing before doping. The characteristic of device with pristine graphene (blue curve) is compared to the ones acquired immediately after doping (red curve) and after 2 days (violet curve) and 15 days (green curve) of ageing.

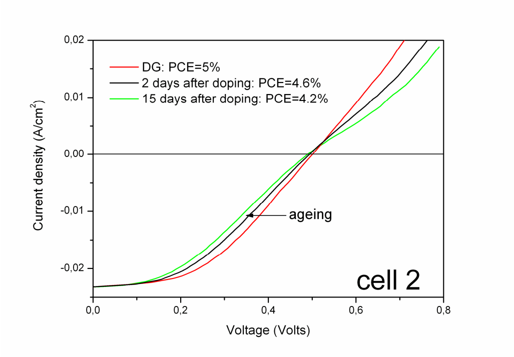

Fig. 5. Doping and ageing effect on the J-V illuminated curve of a solar cell annealed at 200°C before doping process. The characteristic of the device with doped graphene (red curve) is compared with the ones acquired after 2 days (violet curve) and 15 days (green curve) of ageing.

In Table I we show the ageing effect on the electrical parameters extracted from the curves shown in Fig. 4 (cell 1, grey rows) and Fig. 5 (cell 2, white rows).

I. Conclusions

The PCE of the G/Si solar cells results greatly enhanced after molecular doping by nitric acid. In all the cases of molecular doping, performance stability is a problem: generally, after few days storage in the air, only a little percentage of PCE enhancement is retained since the molecular dopants tend to gradually evaporate from the surface of graphene. In our devices, the power conversion efficiency reaches 5% in devices annealed at 200 °C immediately before the exposition to nitric acid and shows an 80% stability after 2 weeks.

TABLE I.

		Short circuit current density (A/cm^2)	***Open circuit voltage (mV)***	***Fill Factor (%)***	***PCE (%)***
Cell 1	Doped device	***23***	***487***	***31***	***3.4***
	2 days ageing	***21***	***502***	***26***	***2.7***
	15 days ageing	***19***	***386***	***24***	***1.8***
Cell 2	Doped device	***23***	***501***	***43***	***5***
	2 days ageing	***23***	***494***	***40***	***4.6***
	15 days ageing	***23***	***489***	***37***	***4.2***

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