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Molecular doping applied to Si nanowires array based solar cells

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ABSTRACT

Solution-based processing is a rapidly growing area in the electronics and photonics field due to the possibility of reducing fabrication costs of materials for solar cells, transistors, memory and many other devices. Moreover thanks to its intrinsic nature it provides the possibility to perform conformal processing on structured surfaces. Most of the solution-processing work has so far been devoted to organic materials, but in this work an approach focused on nanostructured silicon is presented. The idea consists in the immersion of a silicon wafer, with Si nanowires grown on top, in a chemical bath containing dopant precursors molecules diluted in a solvent. The molecules deposit from the liquid all over the exposed surfaces and work as a dopant source for the Si nanowires during successive thermal annealing. Doping levels of $1 \times 10^{19}\,cm^{-3}$ are controllably obtained without structural damage and hetero-interfaces creation. The Si-NWs array used presents density of $2 \times 10^{10}\,cm^{-2}$, average length of 500 nm and diameters up to 70 nm. The doped Si-NWs are then integrated in complete solar cells which have been electrically characterized. It is found that the molecular doping method applied to the SiNW arrays provides higher short circuit current and fill factor than the reference samples.

1. Introduction

Silicon nanowires (Si-NWs) have been largely studied for application in microelectronics because they can be used to realize high mobility transistor channels in next generation of metal oxide semiconductor field effect transistors (MOSFETs) [1–5]. Another rapidly emerging field of application for Si-NWs during recent years is for plasmonic waveguides where they demonstrated very long propagation lengths [6,7]. Si-NWs have been also recognized as promising alternative to the standard planar configuration in photodiodes, like solar cells, because they can be exploited as novel architectures to build radial junctions or as light-trapping layer for the fabrication of efficient devices [8–13]. In all of the above cases the control of the doping protocols is the difficult challenge [14]. Standard doping procedures, such as ion implantation or gaseous-source based methods, present several issues: the use of dangerous gases and high costs facilities, the difficulty to achieve conformal and abrupt junctions, the stochastic spatial distribution of the implanted ions and the severe crystal damage. Other approaches, such as the formation of amorphous doped layers over the NWs, present the drawback of creating hetero-interfaces increasing trapping effects at the junction. An innovative and low cost solution to make controlled and conformal doping at the nanoscale without the generation of structural defects has been recently proposed [15–17]. This method consists in the immersion of the material to be doped in a chemical bath containing the dopant precursor molecules. During the immersion, a molecular layer deposits over the sample surface and works as a dopant source during the successive thermal treatment which releases the dopant atom from the molecule and diffuse it into the substrate. The molecular layer is then a sacrificial layer which is deposited (by dip coating) over the Si surface and, upon annealing, releases the dopant atom inside the Silicon, to form the n layer of the p–n junction.

In this paper a breakthrough in the fabrication of Si-NWs based solar cells is achieved by coupling this chemical doping method and the particular morphology of our Si-NWs array. The Si-NWs have been fabricated by metal-catalized growth [18]. The optical functionality of the Si-NWs array has shown a total reflectance of 10% at the wavelength of 550 nm, corresponding to the peak of the irradiance in the solar spectrum [18], making them particularly attractive as light-trapping layer. The promising optical characteristics of the Si-NWs array are combined with the use of the innovative molecular doping method allowing the formation of a planar junction inside the Si substrate underneath the NWs for an effective charge separation. Silicon solar cells are fabricated with different junction depths and their electrical characterization has been carried out. An important aspect of the proposed approach is

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that, being this an ex-situ doping method, it allows the removal of metallic catalyst, used for the Si-NWs growth, which can be performed as intermediate step between the growth and the doping process. This reduces the defects in the band gap introduced by the catalyst [19–28]. It will be demonstrated that the molecular doping method applied to the Si-NWs array provides higher short circuit current and fill factor than the reference samples, paving the way to more efficient nanostructured solar cells.

2. Material and methods

The substrates used for the Si-NWs deposition were 13 Ω-cm p type 6" Si wafers. After a brief HF dip, Au dots with density of 2×10^{12} cm^{-2} and average radius of 1.6 nm were deposited by sputtering and after a second HF dip they were loaded in the Chemical Vapor Deposition (CVD) chamber for the Si-NWs deposition. The second HF dip was performed to remove the thin oxide shell present on the surface of the gold nanodots and to promote the catalysis [29]. The whole substrate preparation has been performed in sequence. The deposition system used was an Inductively Coupled (ICP) CVD. The substrates were heated at 380 °C for 1 h before the depositions, which were performed at 20 mTorr with a gas ratio of SiH_4/Ar=30 at 380 °C of substrate temperature for 30 min with plasma power of 20 W. In these experimental conditions the Si-NWs array grown present the following structural characteristics: surface density higher than 2×10^{10} cm^{-2}, average lengths of about 500 nm and diameters ranging between 2.5 and 70 nm. Fig. 1 illustrates the main steps sequence of the photodiode fabrication. Fig. 1(a) represents the step of the Si-NWs formation by gold catalyst growth. The gold surface residuals after the Si-NWs growth have been eliminated by means of a two step process which ensures an effective cleaning. It consists in removing the protective oxide shell present on the Si-NWs and on the gold tips and subsequently immersing the samples in a gold etching solution (Fig. 1(b)) [30]. The doping procedures started with a brief HF dip, immediately followed by immersion in a solution of diethyl 1-propylphosphonate and mesitylene (1/4, v/v) at about 160 °C for 2.5 h [17]. The solution was bubbled with nitrogen during the entire reaction to minimize oxygen contamination. This step creates a layer of phosphorus-containing molecules all over the sample surface, on the Si-NWs array and also on the regions of the Si substrate between the NWs (Fig. 1(c)). After the reaction the samples have been immediately capped with 200 nm thick SiO_2 layer by using the spin on glass (SOG) procedure. This process allows to protect the dopant molecules and the sample surface from air exposure and avoids the evaporation of the dopant during the subsequent activation annealing step. This aspect is relevant because, with respect to other methods proposed in literature, it avoids the usage of thermal oxidation which exerts compressive stress and consequent dopant segregation inside the Si-NWs [28].

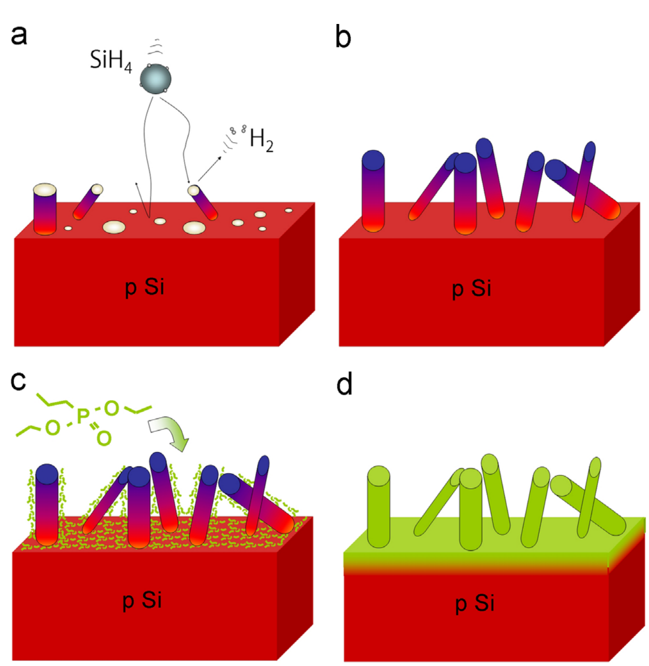

Fig. 1. Schematic of the main fabrication processes of the Si-NWs array based solar cell. (a) Nanowires formation by metal catalyzed CVD on p-doped Si substrate; (b) metallic catalyst removal; (c) deposition of phosphorus containing molecules monolayer; and (d) dopant release and diffusion.

A furnace annealing at 900 °C or 950 °C for 500 s, with a ramp temperature of 10 °C/min, starting from 600 °C, is then performed to diffuse and activate the dopant (Fig. 1(d)). Due to the presence of the molecules on the NWs array and on the Si substrate surface between them, the dopant diffusion is expected not only in the array but also in the substrate. The target for the whole architecture is then a 'substrate junction', i.e. a planar junction deep below the surface of the Si substrate. Because of the very small size of the Si-NWs and the high expected depletion width, the dopant diffusion has been tuned to obtain a susbtrate-junction architecture, rather than a radial- or an interface-junction geometry. The n^+ doped Si-NWs array is then used as top light-trapping layer, and together with n^+ doped portion of the Si substrate underneath, it represents the cell emitter (Fig. 1(d), green portions. For black and white figure: top part of the device). So the top metallic layer deposited over the emitter makes an electrical contact only with the n^+region, without short-circuiting the p type substrate.

Identical doping procedures have been performed on planar samples. The back contact has been realized by 200 nm aluminum deposited by sputtering and heated in furnace at 500 °C, after removal of the parasitic junction formed on the rear due to the doping process. The top SOG layer has been removed by HF etch, before the top contact realization with silver paste of 1 mm diameter by drop casting. The diodes have not been subjected to any passivation process. A further improvement of the diode realization would be to deposit on the top a conformal layer of transparent conductive layer. The samples were analyzed by using a ZEISS SUPRA35 Scanning Electron Microscope (SEM) with a field emission electron gun and by Transmission Electron Microscopy (TEM) equipped with a system for Energy Filtering (EFTEM). The carrier concentration has been measured by Spreading Resistance Profiling (SRP) on the flat samples after the thermal annealing. The current–voltage (*IV*) characteristics have been acquired in dark and controlled light conditions, by using a Keithley 237 source-measure unit. The light irradiation has been performed by using a solar simulator based on a 150 W Xenon lamp, with a light spot of 3.5 cm and equipped with an ASTM filter which produces the AM1.5G solar spectrum. The collimated beam of the lamp has been directed normally to the surface of the sample, fully covering the whole sample area in all the cases. The light intensity measurement has been performed by using a calibrated Si photodiode.

3. Results and discussion

Fig. 2 shows the SEM micrographs of a Si-NWs sample observed in cross view (a) and planar view (b). The average length of the Si-NWs is 500 nm, with some Si-NWs presenting a length up to 1 μm. The surfacial density measured from the SEM in planar view is 2×10^{10} cm^{-2}. Due to the very high density and to the 'forest-like' morphology of the sample the Si-NWs are not all visible and the density value could be underestimated. The Si-NWs