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# Silicon doped by molecular doping technique: Role of the surface layers of doped Si on the electrical characteristics

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ABSTRACT

We present results on an investigation about the chemical–physical properties of the Si surface after molecular doping (MD) method and successive annealing. The purpose of this work is to study the atomic structure of the first layers of silicon after the doping procedure in order to evaluate the possible intermixing between the carbon atoms constituting the precursor molecule and the Si atoms of the substrate. Moreover the role of this intermixed layer on the electrical characteristics of the semiconductor is also examined. The chemical characteristics of the samples after the doping procedure are obtained by performing X-ray spectroscopy, while the electrical characteristics are studied by four probe point and spreading resistance profiling. In order to clean the Si from the presence of the surface intermixed layer a wet chemical etch based on $HNO_3$ is proposed. Four probe point measurements have been performed also after the etching to demonstrate that it is possible to modulate the sample sheet resistance as a function of the post-doping chemical treatment of the surface.



## 1. Introduction

Shallow junctions formation in silicon is one of the most important steps in the fabrication of microelectronic (IC's) and photovoltaic (PV) devices. As for the fabrication of nanostructured features, also for the doping, two approaches can be envisaged: the top–down and bottom–up methods. In the top–down methods, the doping is realized directly onto the substrate, for example, by Molecular Beam Epitaxy or Single Ion implantation. In the bottom–up approach, the idea is to use molecular precursors which self-assembles in one monolayer directly on Si with controlled density and with designed properties. The monolayer doping (MD) recently proposed in literature [1–7] can be categorized as one of the bottom–up approaches. It is based on solution processing, which is a rapidly growing area in the electronics and photonics field due to the possibility of reducing fabrication costs of materials for transistors, memory, solar cells and many other devices. The process is based on the immersion of the sample in a solution of specific molecular precursors dissolved in a suitable solvent and brought at their boiling temperature. In this way the precursor molecules are anchored to the surface forming a monolayer. The sample is then finished with the deposition of a $SiO_2$ cap layer and a subsequent annealing step is used to release the dopant atoms from the molecular monolayer and diffuse them into the substrate. This method presents many advantages: it does not introduce structural defects inside the substrate, it can be used for the formation of n- and p-type doping, it provides conformality, it does not use dangerous and expensive sources or gases and it allows to control and to modulate the junction depth at a nanometer level [2,7].

During the last years, recent studies have been addressed on one hand to design the molecule characteristics to increase the doping efficiency and on the other hand to investigate the chemical properties of the surface [1,8,9]. In a previous paper we have shown the characteristics of the bonds between the as deposited molecule and the Si substrate, by demonstrating that the P is bonded to Si through oxygen atoms and that after the deposition a part of the molecules transform into propionates [6]. In this work the Si surface after the molecule deposition and after the annealing step, necessary to diffuse the dopant, is studied. The purpose is to understand the chemical nature of the first surface layers of doped Si after the MD procedures and its role on the electrical properties. X-ray photoelectron spectroscopy (XPS) has been combined with Spreading Resistance profiling (SRP) and four point probe (4PP) analysis. A chemical wet etch has also been

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performed on some samples after the doping procedure to investigate the electrical properties after the removal of a portion of surface layer [10–11].

## 2. Experimental

The substrates used were p-type $<111>$ Si samples of $1 \times 1$ cm$^2$ in size, with a $R=1$–$10\ \Omega$ cm. The MD doping procedures started with a brief HF dip, immediately followed by immersion in a solution of diethyl 1-propylphosphonate and mesitylene (20% v/v) at the solution boiling temperature, about 160 °C, for 2.5 h. This step creates a layer of phosphorus-containing molecules all over the sample surface. A furnace annealing at 1050 °C for 500 s in $N_2$ is then performed to diffuse and activate the dopant. In order to investigate the surface properties no capping layer has been deposited over the molecular monolayer before the annealing process. A chemical wet etch is then performed in order to remove a portion of the surface doped layer after the diffusion step. The wet oxidation/etching process consists of 3 steps: (1) native oxide removal by HF (16% v/v) etch; (2) chemical oxidation by immersion in pure $HNO_3$ (63% v/v) at its boiling temperature for 10 min [10–11]; (3) HF (16% v/v) dip for 120 s to remove the $SiO_2$ layer formed during the chemical oxidation. The literature indicates that with this process the total Si etched depth corresponds to 1.6 nm. In the experiments reported in the paper, some samples have been subjected to two cycles of the oxidation/etching process to reach a nominal total etched depth of 3.2 nm.

XPS analysis was performed on a K-Alpha system from Thermo Scientific, equipped with a monochromatic Al Kα source (1486.6 eV), and operating in constant analyzer energy (CAE) mode with a pass energy of 200 and 50 eV for survey and high resolution spectra, respectively. A spot size diameter of about 400 μm was adopted. The binding energy was calibrated by the elemental Si 2p peak centered at 99.3 eV for silicon substrate. Measurements were carried out at 90° take-off angles between the sample surface and the direction of photoelectrons detected by the analyzer. Curve fitting of the core-level XPS lines was carried out using XPSpeak41 software with a Gaussian–Lorentzian product function and linear Shirley background subtraction. A Gaussian–Lorentzian mixing ratio was taken as 0.15 for all lines.

SRP measurements have been performed on a SSM150 tool in order to analyze the carrier concentration profiles in the doped samples and after the chemical processes. During SRP measurements, two metallic probes, between which a small potential of 5 mV is applied, are used to quantify the resistance profile, which is computed and converted into resistivity and carrier concentration by means of both calibration curves and additional software procedures and corrections. Depth information is obtained by stepping down the probes along a bevelled surface of the sample. The analyses have been conducted in the high resolution configuration, to guarantee the best accuracy for the extraction of the electrically active dopant profiles from the acquired raw data. The samples have been prepared with very small bevel angles and depth resolutions of about 3 nm have been achieved.

4PP were carried out to obtain the sheet resistance. The experimental set up is: a 6 in. Wentworth's metal chuck on which is placed the sample under test; four metal probes with micromanipulators, the outer probes externally connected to a current generator (Source Measure Unit K236) and the inner probes to a voltage meter (electrometer K6512), either driven by PC using Labview's software for data acquisition. The raw data ($V$–$I$) were subsequently analyzed by Matlab's macro data analysis to extract the sheet resistance, $R_s$, values.

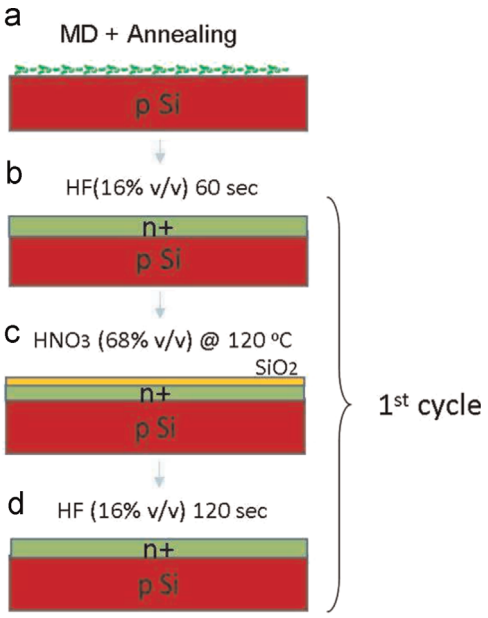


**Fig. 1.** Schematic diagram of the process: (a) Si p-type sample is doped by MD and annealed at 1050 °C for 500 s, (b) HF etching is performed for 60 s, (c) then the sample is immersed in $HNO_3$ at 120 °C for 10 min, (d) HF 16% for 60 s. On some samples two cycles of oxidation/etching have been performed.

## 3. Results and discussion

In Fig. 1 we report a schematic diagram showing the main processing steps of the chemical treatment after the MD doping, as described in the Experimental paragraph.

In Fig. 2 we show the XPS spectra executed on the sample after both the MD and the annealing processes. Differences in surface composition between the silicon substrate and the sample are better evidenced by normalized elemental Si 2p spectra (see inset in Fig. 2). How it is possible to notice, both an enhancement and a shift at lower binding energy of the oxidized component were recorded in the annealed sample. While an almost single component of the native silicon oxide is evident in the silicon substrate at the binding energy of 103.5 eV, the annealed sample is characterized by a multi-component band in the range 101–104 eV, sign of the presence of different silicon oxidation states. This indicates that during the annealing process the sample undergoes to a small oxidation process despite the process is carried out in a stream of $N_2$.

By making an appropriate deconvolution of the XPS spectrum it

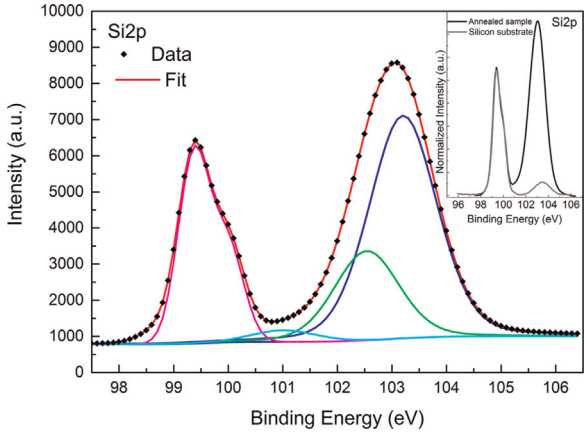


**Fig. 2.** XPS spectra of Si 2p after the MD doping and annealing process. In the inset, normalized Si 2p spectra of silicon substrate and of the sample are also shown.