



## Boron doping of silicon rich carbides: Electrical properties

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### ABSTRACT

Boron doped multilayers based on silicon carbide/silicon rich carbide, aimed at the formation of silicon nanodots for photovoltaic applications, are studied. X-ray diffraction confirms the formation of crystallized Si and 3C-SiC nanodomains. Fourier Transform Infrared spectroscopy indicates the occurrence of remarkable interdiffusion between adjacent layers. However, the investigated material retains memory of the initial dopant distribution. Electrical measurements suggest the presence of an unintentional dopant impurity in the intrinsic SiC matrix. The overall volume concentration of nanodots is determined by optical simulation and is shown not to contribute to lateral conduction. Remarkable higher room temperature dark conductivity is obtained in the multilayer that includes a boron doped well, rather than boron doped barrier, indicating efficient doping in the former case. Room temperature lateral dark conductivity up to  $10^{-3}$  S/cm is measured on the multilayer with boron doped barrier and well. The result compares favorably with silicon dioxide and makes SiC encouraging for application in photovoltaic devices.

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### 1. Introduction

Silicon nanocrystals (Si-NC) embedded in a dielectric matrix showing tunable band gap properties are presently considered as attracting top absorbers in silicon based high efficiency multijunction devices [1,2]. The nanocrystals are formed by fabricating an overstoichiometric silicon compound, on which phase separation into silicon and the wide band-gap stoichiometric compound is induced by annealing. The wide band gap matrix has the role of spatially separating the nanocrystals, thus giving rise to size related quantum effects [3–5]. The multilayer approach is used to introduce separate control of the Si-NC size and density, and was indeed proven to be effective in the case of silicon dioxide as a dielectric matrix [6]. The use of silicon carbide as a dielectric matrix was introduced later, because of the lower band gap and therefore the anticipated better conduction properties of SiC with respect to SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>, more favorable in view of applications to electronic devices [2].

In a photovoltaic device, n and p doped layers are required to create the internal electric field that separates the photogenerated carriers and drives them to the electrical contacts, thus

preventing recombination. If Si-NC are used as absorber material in the device, the bandgap of doped layers should be large enough, not to squander the energy of carrier photogenerated in the nanodots. Doped Si nanodots will in principle meet the requirement, and a proof of concept on the topic has been reported for the case of SiO<sub>2</sub> matrix [7,8]. For Si-NC in SiC matrix, the B doped Si-NC:SiC material has shown to form a heterojunction with n-type c-Si [9], although it is hard to distinguish whether the acceptor level involved in the observed built-in voltage formation is located within the Si-NC, the SiC matrix, or at the interface.

If doping is introduced in the Si-NC based absorber, this will alter the carrier collection properties, through modification of the electric field across the device; introduction, or possibly passivation, of electronic defects; modification of the resistive losses and so on. Prediction of such effects implies information on the electronic properties of the composite (Si-NC and dielectric matrix) material. Effective B doping of Si-NC was already observed [10,11], although in SiO<sub>2</sub> matrix it suffers from segregation at the Si/SiO<sub>2</sub> interface and in the bulk of the Si-NC, with electrically active configuration only in the latter case [12]. The role of boron was also demonstrated to depend on the nanodot size [13]. Less attention has been paid to the electrical properties of the matrix, and to its contribution to the overall electrical performance. In the case of Si-NC in SiO<sub>2</sub>, the insulating matrix allows assuming that transport takes place through silicon related subdomains – in fact, it becomes detectable only for sufficiently close Si-NC spacing [14]. In the case of the

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Si-NC:SiC system, due to the lower band gap and less marked phase separation, a parallel of conducting paths is to be expected, and the different contributions are less evident to separate. This further complicates the analysis of doped materials. The situation is also affected by possible diffusion of the dopant within the matrix and among sublayers during thermal treatments [9]. In summary, further investigation seems highly significant due to the limited literature existing in the case of SiC matrix [9,15], particularly if obtained by PECVD [16–19].

In this paper, we investigate the electrical behavior of the Si-NC:SiC system with B doping, where B doping is introduced either in the SRC or in the SiC sublayers, or both (modulated doping), in order to shed light on the physics of the system, and identify the most favorable doping scheme. The comparison with reference single layers will allow to evidence the effect of the presence of Si-NC embedded in the matrix, and the role of interfacial states; the electrical results will be discussed also basing on the different crystallization occurring in a massive SRC [16] compared to the nanosized sublayer, as a consequence of the fact that small silicon clusters tend to remain amorphous [20,21].

## 2. Experimental procedure

The Si nanodot fabrication was based on the multilayer approach. Silicon rich carbides (SRC)/stoichiometric SiC multilayers were fabricated by Plasma Enhanced Chemical Vapour Deposition (PECVD), on quartz, and bare and oxidized Si substrates, at 13.56 MHz, 24 mW/cm<sup>2</sup>, 0.95 mbar pressure, and 160 °C substrate temperature  $T_s$ , using SiH<sub>4</sub>, CH<sub>4</sub>, and H<sub>2</sub> as gas precursors. The nominal Si atomic fraction  $x$  in the SRC was 0.65, obtained with gas ratio  $R_g = \text{SiH}_4:\text{CH}_4:\text{H}_2 = 6.1:70:10$  (flow rates in sccm).  $R_g$  was 2:70:10 for SiC. Boron doping was achieved by introducing B<sub>2</sub>H<sub>6</sub> in the gas mixture, 0.8% and 1%, in SRC and SiC respectively, with respect to SiH<sub>4</sub>. Three multilayers, M1, M2, M3, were fabricated, in which Boron was introduced either within the SRC (M1) or within the SiC (M2) or in both layers (M3). An intrinsic multilayer (M0) was also fabricated, using 1.0 mbar pressure, and  $T_s = 350$  °C,  $R_g = 11.4:70:10$  and 2.6:70:10 for SRC ( $x = 0.75$ ) and SiC respectively. The multilayers were fabricated by starting with a 20 nm SiC layer that shrinks to 10 nm after annealing in correlation with hydrogen evolution, see Ref. [22] for details. Then we deposited 30 SRC + SiC double layers with thicknesses regulated in order to obtain 3 nm after annealing for both, by taking into account the specific shrinkage of SiC and SRC upon annealing. An a-Si:H sacrificial layer, 20 nm thick, was then deposited on the top of the samples. The reason for this is given below. After multilayer deposition and prior to the a-Si:H sacrificial layer deposition, the doped samples underwent an in situ 350 °C, 4 h annealing, to avoid sample blistering during subsequent thermal treatments, mainly because the available annealing furnace can be controlled only above that temperature. Test samples of SiC and SRC, either doped or undoped, about 200 nm thick single layers samples, and undoped multilayers, were also fabricated on similar substrates with the same procedure. The optical gap  $E_{04}$  for the annealed SiC material is 2.3 eV. The Tauc plot procedure could not be applied, due to the strong non-linearity of the Tauc plot. Reference a-Si and a-SiC layers were obtained after dehydrogenation (600 °C, 4 h) of the corresponding PECVD deposited material.

Subsequently, all samples underwent a two step annealing (600 °C, 4 h + 1100 °C, 30' plus ramps) in fluent N<sub>2</sub>:O<sub>2</sub> = 10:1 atmosphere. The low temperature step is required to produce hydrogen evolution, while the high temperature step results in SiC and Si crystallization. Due to the presence of oxygen during the annealing process the silicon sacrificial layer partially oxidizes. This surface oxide is then removed in HF, and the residual unoxidized Si layer is removed in a 2% TMAH solution at 40 °C. This procedure is needed to

avoid formation of a surface SiC<sub>y</sub>O<sub>z</sub> compound, with stoichiometry depending on the composition of the underlying material, that consumes part of the initial double-layers, and that cannot be removed with standard microelectronics wet etching (either HF, TMAH, or CP4). Details on the identification and elimination of the SiC<sub>y</sub>O<sub>z</sub> compound can be found in [23], where the effect of such unwanted capping layer on electrical measurements is also illustrated.

The lateral conductance as a function of temperature was measured using parallel plane Ni evaporated contacts spaced 1 mm. A two terminal configuration was used in a K20A vacuum cryostat by MMR Technologies. The current was measured using a Keithley 219 amperometer. The ohmicity of the contacts was checked in the range  $-30\text{ V}/+30\text{ V}$ .

The reflectance and transmittance (R&T) spectra were measured using an Avantes UV-vis fiber optics spectrophotometer and a HP8542A diode array spectrophotometer. The spectral data were elaborated by means of the computer code Optical that treats the multilayer structure using the Jones matrix – Fresnel coefficient approach, and allows the introduction of the Bruggeman effective medium approximation (EMA) model in the description of the spectral refractive index of the layers. The materials used in the EMA mixture were amorphous and microcrystalline silicon, with n-k spectra taken from Refs. [24,25] respectively, and nominally microcrystalline SiC [22]. In this last case, the n-k spectra were deduced from R&T measurement taken on a single SiC sample deposited on quartz and annealed at 1100 °C as described above, and fitted using the modified Tauc-Lorentz model proposed by [26] further modified to finely account for defect excess absorption [Allegrezza, to be published]. The simulation also revealed the presence of a low density surface layer, that was taken into account while obtaining the n-k spectra of  $\mu\text{c-SiC}$ .

Infrared transmittance was measured using a Thermo Nicolet 5700 Fourier Transform Infrared spectrometer (FTIR). The IR transmittance data were simulated using Optical (see above), in which the spectral n-k of silicon was simulated using a combination of 17 Lorentz oscillators, to account for the vibrational spectrum of c-Si. The doped surface region of the wafer was simulated using the same set of oscillators with the introduction of a free carrier absorption Drude component. A measurement of the Drude component in the Si wafer substrate was achieved by removing the deposited Si-NC layers via dry etching in an SF<sub>6</sub>:O<sub>2</sub> plasma with 64:22 (flows in sccm) gas flow ratio, at 75 mTorr, 80 W. The etch rate showed a marked dependency on composition and was determined to be 23 nm/min for stoichiometric SiC, 40 nm/min for Si<sub>0.65</sub>C<sub>0.35</sub>, and around 700 nm/min for c-Si [27]. The etching duration was chosen in order to uncover the c-Si substrate surface.

XRD patterns were collected in out-of plane grazing incidence geometry, where the incident angle, i.e. the angle between the incoming beam and the sample surface, was kept constant and at a small value (0.8°) while the detector moved (2 $\theta$  scan) in the plane normal to the surface. The measurements were performed using the SmartLab diffractometer (Rigaku), equipped with a rotating anode (Cu K $\alpha$   $\lambda = 1.54180$  Å) followed by a parabolic mirror, to collimate the incident beam and Soller slits (divergence of 0.114°) in front of the detector to collimate the diffracted beam.

High Resolution Transmission Electron Microscopy (HRTEM) was performed by means of cross-section energy-filtered TEM (EFTEM) images, taken using a JEOL 2010 instrument, operating at 200 keV FEG, equipped with a Gatan image filter (0.8 eV resolution).

## 3. Results and discussion

### 3.1. Structural results

Si-NC formation was observed by TEM. Fig. 1(a) shows the HRTEM image of a multilayer with intrinsic SiC barrier and SRC

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