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Diffusion of phosphorous in black silicon

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Abstract — **Black silicon is a promising texturing method for solar cells since it suppresses optical reflection in a broad spectral range. This relaxes the usual antireflection requirements on the coatings used for surface passivation of silicon. Fabrication of n-type emitters requires diffusion of phosphorous through the nanostructures of black silicon, which may need different optimal conditions as compared to diffusion through *e.g.* pyramidal wet-etched structures due to the different characteristic dimensions. In addition, the diffusion process should ideally not deteriorate the antireflective properties of black silicon. Here, we have investigated the effect of temperature and time during the doping process on optical reflectance and sheet resistance of black silicon. Doping temperatures of 875 °C and lower result in negligible increase of reflectance as compared to pristine black silicon. In addition, the sheet resistance of black silicon emitters is confirmed to be lower than that of planar Si under identical annealing conditions.**

Index Terms —**black silicon, phosphorous emitter, diffusion**

I. Introduction

Black silicon (bSi) [1,2] has great potential as texturing method for Si-based photovoltaics thanks to its intrinsic antireflective properties both at normal and at high angle of incidence of light [3]. Power conversion efficiencies between 18 and 22% have been achieved in the lab on bSi solar cells using laser-doped selective emitters [4], interdigitated back contact (IBC) [5], and on multicrystalline substrates [6]. These results were obtained by texturing Si using maskless reactive ion etch (RIE). Maskless RIE is of commercial interest because: (i) it is a single-step process and therefore potentially industrially scalable, (ii) it works indifferently mono-, quasi-mono- and multicrystalline Si, and (iii) can be used on diamond-wire cut wafers. Diffusion of phosphorous (P) in p-type Si substrates is the *de facto* industrial standard for fabrication of emitters in back-surface field Si solar cells [7]. Diffusion of P through the nanostructures of bSi is likely to require different optimal conditions as compared to diffusion through *e.g.* pyramidal wet-etched structures due to the different characteristic dimensions. In addition, the diffusion process should ideally not increase the reflectance of bSi. Here, we have investigated the effect of temperature and time during the doping process on optical reflectance, morphology and sheet resistance of bSi.

II. Methods

All wafers were 100 mm, 350 μm thick CZ p-type (100) Si. BSi was obtained by non-cryogenic RIE using a SPTS Pegasus system using the following process parameters: temperature of -20 °C, SF_6 and O_2 plasma with 7:10 gas flow ratio, total chamber pressure of 38 mTorr, 3000 W coil power, 10 W platen power and 14 min process time. The wafers where then cleaned using the standard RCA procedure. Doping with P was performed in a Tempress furnace with a pre-deposition step (with $POCl_3$ vapors as a source of P) followed by a drive-in step in N_2 atmosphere. For each wafer, the temperature and time were the same for pre-deposition and drive-in. For different wafers, the temperature was varied between 850 °C and 1050 °C, while the time was either 15 or 30 min. Planar Si samples were doped along with textured wafers for reference purposes. P-doped glass layers were removed by etching in buffered hydrofluoric acid (bHF).

Scanning electron microscopy was performed in a VP 40 SEM (Zeiss) at an accelerating voltage of 10 kV. Reflectance measurements were carried out using a UV-2600 spectrophotometer (Shimadzu Co.) equipped with an integrating sphere. The sheet resistance was measured 10 times for each wafer using a FPP-500 (Veeco).

III. Results

Reflectance measurements in the wavelength range 280 - 1100 nm are shown in Fig. 1 for pristine bSi and for bSi surfaces after doping, as well as for a reference Si surface. The pristine bSi is characterized by reflectance lower than 5% in the range 300-1000 nm. Doping at temperature between 850 °C and 865 °C has a very similar effect on the reflectance, which increases to 10 % or higher between 280 and 400 nm while remaining around 7% or lower throughout the visible and up to 1000 nm. Doping temperatures between 875 °C and 950 °C also results in rather similar reflectance spectra, with values larger than 15% in the UV and between 15% and 8% in the visible and NIR. Doping at 1050 °C results in a further, considerable increase in reflectance (30% or higher in the UV and at least 17% in the visible and NIR. These differences in reflectance can also be appreciated by the naked eye, as photographs of selected surfaces after doping show Figure 2. It is worth to note that these values of reflectance are most likely to drop further with

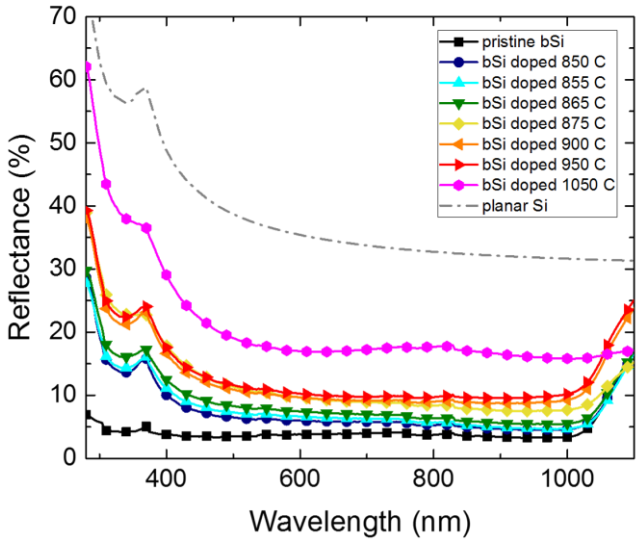

Fig.1. Optical reflectance in the wavelength range 280-1100 nm for pristine bSi before and after doping at different temperature, as well as for a planar reference Si surface.

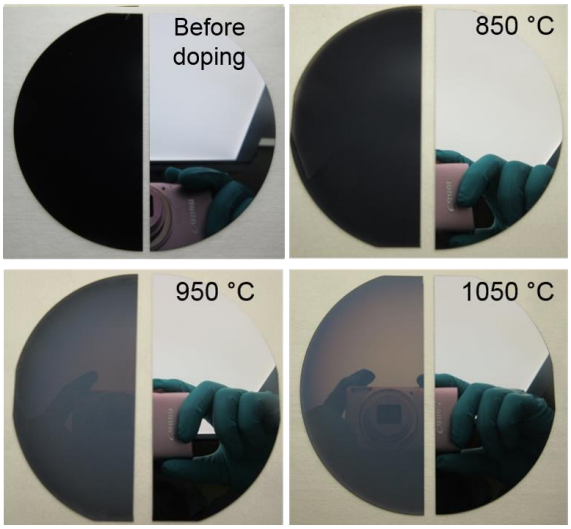

Fig.2. Photographs of bSi and planar reference Si before doping and after doping at different temperatures for 15 min.

deposition of relevant coatings for passivation of bSi (SiN_x:H, Al_2O_3, or a stack of these two).

During the doping process, a layer of P doped glass is grown into the Si, and subsequently removed by wet etch. This processing may lead to appreciable modifications of the nanostructures in the textured surface, depending on the process parameters. Indeed, cross-section SEM inspection reveals alterations in the morphology of all the textured surfaces following the doping process. Figure 3 shows a comparison between representative cross-section images of bSi before doping and after doping for 15 min at temperatures increasing from 850 °C to 1050 °C (from top to bottom). The texturing of the 850 °C samples is almost unaffected by the processing and

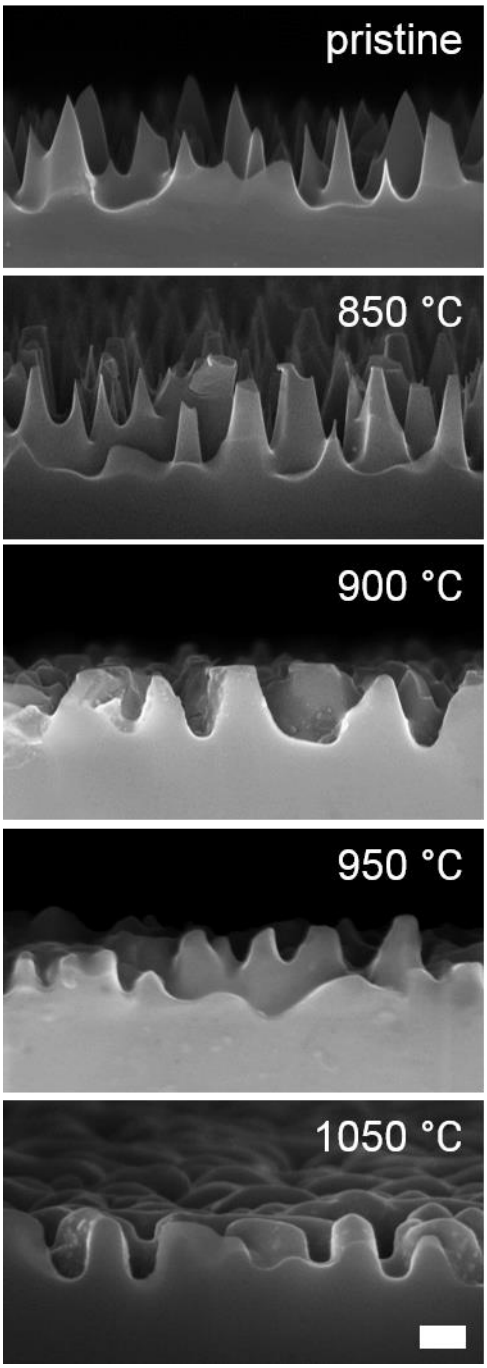

Fig. 3. Cross-section SEM images of pristine bSi and of bSi after doping at temperature increasing from 850 °C to 1050 °C. The scale bar represents 200 nm.

presents typical conical-like hillocks of height between 300 and 400 nm. Only the tips of these hillocks seem to have been oxidized and subsequently etched in bHF, leaving slightly truncated features. Such a process is slightly more pronounced for the surface doped at 900 °C, however the average height of the truncated hillock remains rather uniform. Doping at 950 °C results in smoothening of a considerable amount of features. Finally, doping at 1050 °C results in uniformly smoothed

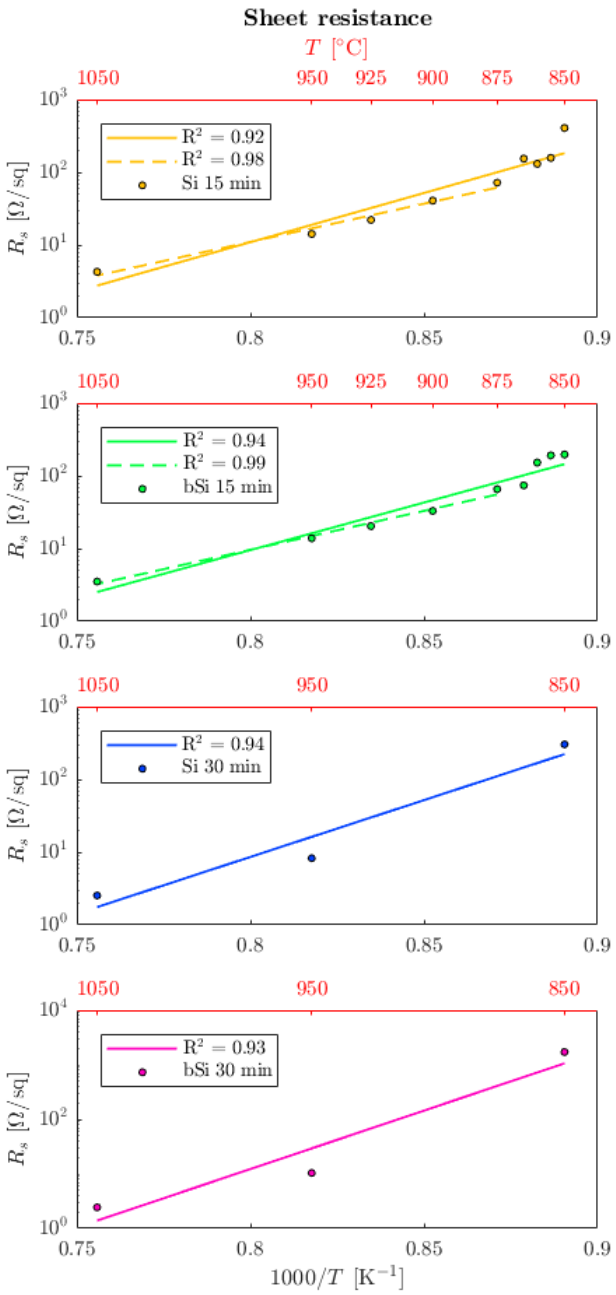

Fig. 4. Sheet resistance as function of inverse temperature for: 15 min doped flat Si, 15 min doped bSi, 30 min flat Si, 30 min bSi (from top to bottom).

cylinder-like featured about half as high as the original hillocks. We conclude that the microscopic modification of the surface texturing due to the doping processing explain the increase in optical reflectance observed after higher doping process temperatures.

We performed macroscopic four point probes measurements in order to determine the sheet resistance of the fabricated P emitters. Decreasing values of sheet resistance were recorded for increasing temperatures, and for increasing time at the same temperature. Results are summarized in Figure 4, where the sheet resistance is plotted as function of inverse temperature. Data for both bSi and flat Si can be fit well by a straight line, which indicates that the diffusion coefficient has a temperature dependency that does not differ much from the behavior predicted by Arrhenius law. In addition, the sheet resistance of bSi is consistently lower than that measured on the corresponding planar Si reference by a factor between 10% and 20%, depending on the process conditions. This is an experimental confirmation that diffusion of P is faster in bSi than in planar Si doped under the same conditions. Furthermore, we note that the bSi emitter doped at 865 °C for 15 min shows a sheet resistance of 74 Ω sq^{-1}, which is very promising for device fabrication. We conclude that such process conditions result in surface with respectable antireflective properties and appropriate emitter sheet resistance. Ideally, in order to obtain further quantitative information on the properties of the p-n junctions fabricated here, the dopant profile in bSi should be directly measured. This is a rather challenging task for routine techniques such as secondary ion mass spectroscopy (SIMS), which is most reliable on polished surfaces. Scanning non-linear dielectric microscopy (SNDM) or electron holography may be more useful in this context. Electrochemical Capacitance-Voltage (ECV) measurements that account for the higher surface area of bSi by using a geometrical correction factor (as previously done for KOH etched pyramid surfaces) may also give useful information.

IV. Conclusions

We have investigated the effect of temperature and time during the phosphorous doping process, leading to the formation of n-type emitters, on optical reflectance, morphology and sheet resistance of black silicon. Doping for 15 min at temperature between 850 °C and 865 °C result in bSi surfaces with respectable antireflective properties (lower than 7% between 400 and 1000 nm). The sheet resistance measured on bSi emitters is consistently lower (between 10% and 20%) than that of planar Si doped under the same conditions. In particular, doping at 865 °C results in a sheet resistance of 73.9 ± 0.2 Ω sq^{-1} suitable for device fabrication.

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