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Phosphorous Doping of Nanostructured Crystalline Silicon

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ABSTRACT

Nano-textured silicon, known as black silicon (bSi), is attractive as an excellent photon trapping properties. bSi can be produced using simple one-step fabrication reactive ion etching (RIE) technique. In this study, we present recent results of doping of nano-structured crystalline silicon surfaces and compared their properties to planar silicon. We doped planar, KOH-etched random pyramid and RIE nano-structured silicon surfaces with phosphorous oxychloride ($POCl_3$) in the temperature range 850-1000ºC for 15 and 20 min, respectively. Sheet resistance measurements show slight differences in doping density between planar, KOH pyramidal and bSi structures. bSi samples have lower sheet resistance, pointing to higher doping density presumably due to the higher surface area. These results can be used to optimize doping processes for industrial production of bSi solar cells.

INTRODUCTION

Reducing surface reflectance to enhance photon absorption allows increasing conversion efficiency of silicon solar cell. Nanostructured silicon has already attracted attention in photovoltaic research and industry with impressive efficiencies reported [1], [2]. It is an attractive alternative to conventional silicon texturing methods, such as KOH [3] and acidic texturing for Si [4], respectively, or deposited anti-reflective coatings (ARC) [5]. On one hand, KOH is currently widely used in silicon texturing for solar cells, with a reflectance of around 10%. On the other hand, RIE is a scalable, mask-less one-step method for nano-texturing of silicon with low production costs, and resulting reflectance below 1% over a broad range of incident angles [6]. Moreover, the method is suitable for doping processes in diffusion furnaces, unlike metal assisted chemical etching methods, which requires either gold or silver [4], which then poses a severe contamination hazard to the equipment.

The doping process of nano-textured bSi is different from doping of planar and other texture surfaces [7] due to the higher surface area of bSi. bSi to planar area ratio is in the order of 22.25 that potentially leads to higher doping density, faster diffusion and modified p-n junction and emitter properties.

In this work, we aim to investigate phosphorous doping of nanotextured RIE bSi and compare it to doping of planar and KOH textured samples. Experiments were carried out in a Tempress diffusion furnace with $POCl_3$ dopant source. Doping level and recombination properties characterized with sheet resistance and effective carrier lifetime measurements.

EXPERIMENT

We used double side polished boron doped p-type 4 inch crystalline Czochralski silicon wafers with (100) orientation, resistivity of 5.2 Ohm cm, and thickness of 350 µm. Prior to the doping process, we divided the wafers into three categories: planar (no surface modification), KOH-textured and RIE-textured. Planar wafers were only cleaned with standard RCA cleaning procedure. KOH wafers were immersed into buffered HF (bHF) solution to remove native oxide and then textured in 2% KOH solution with 7% IPA. They were then cleaned in a piranha solution to remove traces of the KOH solution. RIE-textured wafers were dry etched (Pegasus SPS) in sulfur hexafluoride (SF_6) and oxygen (O_2) plasma with flow rates of 70 sccm and 100 sccm, respectively. The coil power was 3000 W and the platen power was set at 10 W. The etching time was 16 min. After optional texturing all wafers were RCA cleaned, divided in ten groups for 850ºC, 875ºC, 900ºC, 950ºC, 1000ºC doping temperature 15 and 20 min doping time in combination. The wafers were loaded in a predep phosphorous diffusion furnace and doped using $POCl_3$ as the dopant source. Afterwards all the wafers were subjected to bHF etching and removal of phosphor-silicate glass (PSG) grown during the doping process. For surface passivation, an aluminum oxide layer was grown by atomic layer deposition (ALD) and annealed at 400ºC for 30 min in N_2.

RESULTS AND ANALYSIS

Since doping of the semiconductor in the pre-deposition process is a diffusion process, it is important to note the strong temperature dependency of the diffusivity [8]:

$$D = D_0 \exp\left(-\frac{E_A}{k_B T}\right) \quad (1)$$

where D_0 is the material's diffusion coefficient, E_A is the activation energy, k_B is the Boltzman's constant and T is the temperature in Kelvin. A linear pre-deposition process results in a complementary error-function doping profile [8] with the expected dose Q obtained from

$$Q = C_s \frac{2}{\sqrt{\pi}} \sqrt{Dt} \propto \exp\left(-\frac{E_A}{2k_B T}\right) \quad (2)$$

where C_s is the surface doping concentration (usually the solid solubility), and t is time. The sheet resistance of the doped layer is approximately

$$R_{\square} = \frac{1}{qQ\mu_n} \quad (3)$$

where q is the unit charge and μ_n the average electron mobility. It follows that the sheet resistance is expected to be strongly dependent on the temperature used in the doping process

$$R_{\square} \propto \exp\left(\frac{E_A}{2k_B T}\right) \quad (4)$$

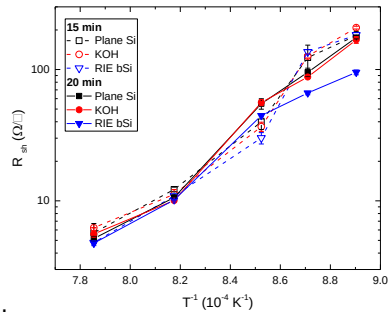

Figure 1: Sheet resistance of planar, KOH-textured and bSi samples for 15 and 20 min doping time

In Fig. 1 the sheet resistances measured for all doped samples are shown as a function of the reciprocal absolute doping temperature in a semi-log plot, and the expected behaviour (Eq. 4) is to a fair approximation observed, i.e., the sheet resistance decreases rapidly as doping temperature is increased such that data points are almost on a straight line in Fig. 1.

In Fig. 2 sheet resistance differentials between the different surfaces are shown as a function of doping temperature. In particular, for 20 min doping time it appears that the sheet resistance obtained on bSi is lower as those of the other two surfaces, which are very similar in sheet resistance value. Data from the 15 min experiment does not show the same unique tendency, perhaps because of lower total dose, which makes sheet resistance measurements more difficult and more prone to error.

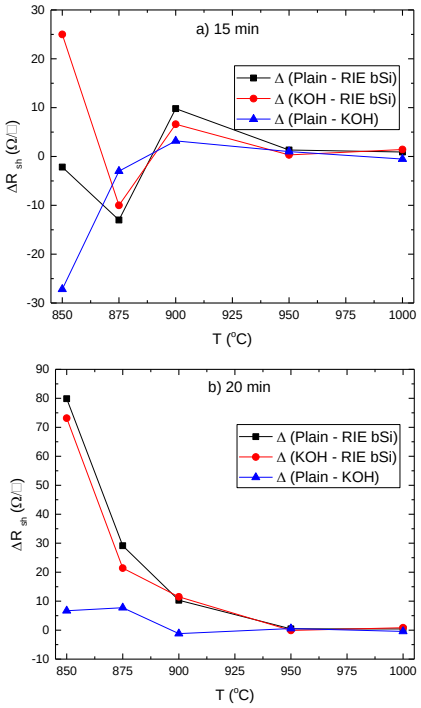

Figure 2: Sheet resistance difference between planar- KOH, planar-bSi and KOH-bSi samples depending on doping temperature and time

Surface morphology of KOH pyramidal microstructures and bSi nanostructures was investigated by scanning electron microscopy in top and cross-section views. *Note: SEM images and geometrical analysis will be available at the conference*. Based on image processing and theoretical geometrical calculations we extracted the surface area ratio as a ratio between the area of the top surfaces and their projected area. The surface area ratio of the KOH-textured samples was 2.84, resulting in almost identical sheet resistance to that of planar silicon. The surface area ratio for bSi was of 22.25. This difference in area ratio may explain the significantly lower sheet resistance of bSi particularly at lower doping temperatures where the diffusion length is short (even on the length scale of the bSi nanostructures) and the effect of the increased surface area is large. At higher doping temperatures (i.e. longer diffusion lengths), the difference in sheet resistance is much smaller.

The Microwave Detected Photoconductivity (MDP) method was used for minority carrier lifetime measurements of reference samples before and after the doping process. The effective lifetime decreases with increasing doping temperature and doping time. The graphic data will be presented at the conference.

Fig.3 shows normal incidence spectral reflectance of the planar, KOH and black silicon samples. Black silicon shows an average reflectance below 1% due to its unique nanohillock surface structure, while the KOH etched sample has average reflectance below 8%.

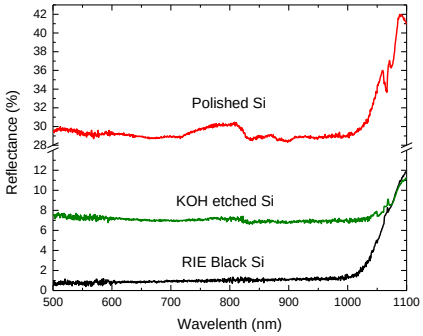

Figure 3: Experimental reflectance spectra of polished, KOH etched and bSi samples before doping processes.

CONCLUSIONS

Micro- and nano-texturing of silicon affects the doping of silicon in a pre-deposition doping process such that the doping level is increased compared to that of planar silicon, particularly at low doping temperature. With increased temperature, this difference almost disappears due to higher diffusion coefficient. The effective lifetime decreases with increased doping time and temperature.

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