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Single and double side textured black silicon require different annealing conditions for optimal passivation with ALD Al_2O_3

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Abstract — **Black silicon is an attractive surface for solar cells thanks to its intrinsic antireflective properties, however progress in surface passivation is required to exploit its full potential. Here, we present effective minority carrier lifetime measurements on single side textured, double side textured, and flat reference Si surfaces, passivated by Al_2O_3 with subsequent thermal activation. Effective lifetime measurements revealed that the annealing time resulting in highest effective lifetime, and therefore in the lowest surface recombination velocity of the textured surface, is depending on whether the wafers are single or double side textured. It follows that optimization of passivation of black silicon lifetime samples needs to be carried out on samples with texturing on one or both sides, depending on the solar cell architecture of interest.**

Index Terms —**black silicon, ALD, Al_2O_3, surface recombination velocity.**

I. Introduction

Black silicon (hereinafter bSi) [1,2] has demonstrated great potential as texturing method for Si photovoltaics thanks to its excellent antireflective properties both at normal and at high angle of incidence of light [3]. Promising power conversion efficiencies between 18 and 22% have been achieved in the lab using laser-doped selective emitters [4], interdigitated back contact (IBC) [5], and on multicrystalline Si substrates [6]. These results were obtained using maskless reactive ion etch (RIE) for the Si texturing. Maskless RIE is of commercial interest because: (i) it is a potentially scalable single-step process, (ii) it works indifferently on any type of Si surface regardless its degree of crystallinity, and (iii) can be used directly on diamond-wire cut wafers. The increased surface recombination due to increased surface area and process-induced damage currently limits the open circuit voltage (V_{oc}) and therefore the efficiency of RIE textured solar cells. Al_2O_3 is known to efficiently reduce surface recombination on Si, thanks to its excellent chemical and physical passivation [7,8]. Al_2O_3 deposited by atomic layer deposition (ALD) is ideal for passivation of nanostructured surfaces such as bSi thanks to the excellent conformity of the ALD processing. Surface recombination velocities of 7 cm s^{-1} have been calculated from minority carrier effective lifetime of Al_2O_3 passivated bSi fabricated by cryogenic RIE [9], and passivation stacks consisting of a few nm Al_2O_3 and a thicker SiN_x layer are already of industrial interest. A thermal activation step, normally a furnace or rapid thermal annealing, is needed to activate the Al_2O_3 passivation, with optimal conditions that vary from equipment to equipment and between different types of bSi. Since bSi is also considered for bifacial architectures where both sides are textured, it is of interest to investigate whether the optimal annealing conditions may depend on whether bSi is present on one or both sides of the wafer, which is the focus of the present study. To this end, we fabricated and characterized wafers with either one or both sides textured, in contrast to lifetime studies in the literature which normally employ symmetrical wafers.

II. Methods

All wafers were 100 mm, 350 µm thick CZ n-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, 38 mTtorr chamber pressure, 3000 W coil power, 10 W platen power, 14 min process time. The wafers were then cleaned using the standard RCA cleaning, except for the last HF dip which was omitted thus leaving the chemically grown SiO_2 layer on the surface. Passivation was achieved by coating the wafers with Al_2O_3 deposited by thermal ALD in a R200 tool (Picosun), using TMA and H_2O as precursors for Al and O, respectively. The process temperature was 200 °C and number of ALD cycles was 380, resulting in 32 nm thick films. The Al_2O_3 layers were activated by annealing at 400 °C in N_2 in a Tempress furnace. The annealing time was varied between 5 and 30 min.

Scanning electron microscopy was performed in a VP 40 SEM (Zeiss) at an accelerating voltage of 5 kV. Reflectance measurements were carried out using a UV spectrophotometer (UV-2600, Shimadzu Co.) equipped with an integrating sphere. Effective minority carrier lifetime was measured with the contactless microwave-detected photoconductance method using an MDPmap tool (Freiberg Instruments). Lifetime values were extracted at an injection level of 10^{15} cm^{-3} and averaged over full or half 4'' wafers.

III. Results

Fig.1 shows SEM images of bSi samples after coating with Al_2O_3 (top-view and cross-section in the top and bottom panels, respectively). The surface is characterized by hillock-like structures with height between 300 and 400 nm, and separated
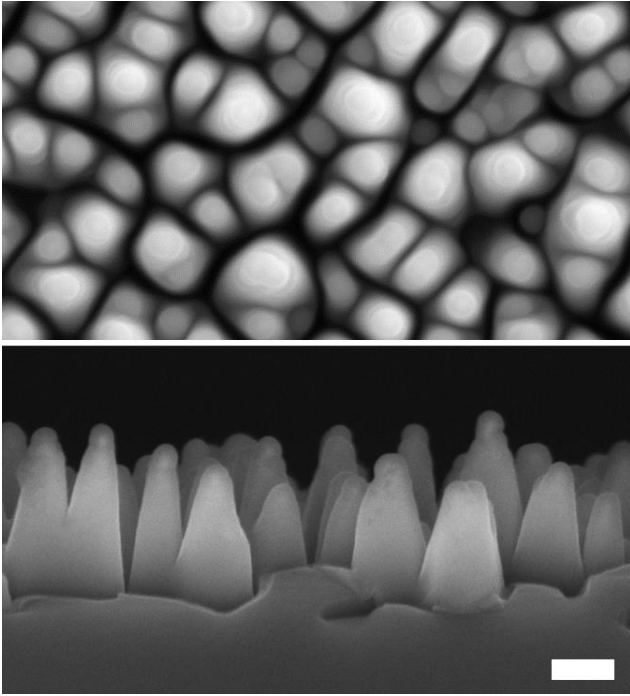
Fig. 1. Top-view and cross-section of bSi coated with Al_2O_3 for surface passivation. The scale bar represents 200 nm for both images.

100 nm or less from one another. The cross-section also reveals that the Al_2O_3 is fully conformal on the nanostructures, as expected by ALD.

Reflectance measurements in the wavelength range 280-1100 nm are shown in Fig. 2 for both single side and double side textured surfaces, as well as for a planar Si surface. The reflectance of the bSi surface is around 5% or lower between 300 and 1000 nm. Interestingly, the reflectance of the double side textured surface is almost half of that of the single textured surface between 1000 and 1100 nm. This may be explained by the fact that photons that arrive at the textured back surface of the double textured sample are not reflected as efficiently as off the planar back surface in the single side textured sample. In general, these measurements confirm the good intrinsic antireflective properties of our bSi.

Fig. 3 summarizes the results from the mapping of effective lifetime, τ_{eff}, on double-side textured, single-side textured and planar surfaces, as function of annealing time at 400 °C. Similar trends are observed for non-textured and single-side textured samples, where τ_{eff} reaches a maximum at 15 min annealing and then decreases at 30 min annealing. Even though the decrease is not dramatic (average τ_{eff} from 3.39 ± 0.33 ms to 3.21 ± 0.55 ms for the non-textured wafers and from 1.82 ± 0.31 ms to 1.66 ± 0.32 ms for single-side texturing), it appears that the optimal annealing time is somewhere between 15 and 30 min. In contrast, τ_{eff} is highest after 30 min annealing for the double-side texturing, a value of 1.62 ± 0.37 ms that is very close to that of the single-side texturing after the same annealing time. In order to determine the surface recombination velocity (SRV) of each surface, we start from the generic expression
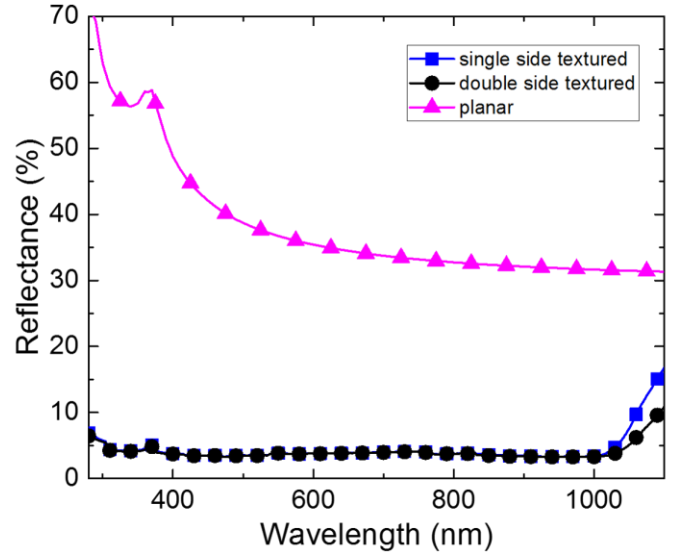

Fig. 2. Optical reflectance of single side textured, double side textured bSi and planar Si, measured using a spectrophotometer with an integrating sphere.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{(SRV_f + SRV_r)}{W} \quad (1)$$

where τ_b is the bulk lifetime, W is the sample thickness and SRV_f and SRV_r are the SRV of the front and rear surfaces, respectively.

Assuming $\tau_b \gg \tau_{eff}$, the bulk recombination term can be neglected. For the symmetric samples (i.e. double textured and non-textured), $SRV_f = SRV_r$ and (1) simplifies to

$$SRV = \frac{W}{2\tau_{eff}} \quad (2)$$

For the single side textured wafers, $SRV_f \neq SRV_r$, nonetheless SRV_f can be obtained extracting the SRV from the non-textured wafer annealed for the corresponding time and using the following expression

$$SRV_f = \frac{W}{\tau_{eff}} - SRV_r \quad (3)$$

The bottom panel of Fig. 3 shows values of $SRV_f = SRV_r = SRV$ for symmetric samples, as well as of SRV_f for front (i.e. single) side textured wafers. The trend here is even clearer. Both planar and double side textured surfaces reach a minimum in SRV_f for annealing time of 15 min, with values of 5.16 ± 0.5 cm s^{-1} and of 14.1 ± 2.1 cm s^{-1}, respectively. Instead, the SRV of the double-textured wafers decreases further for annealing time of 30 min. Moreover, the lowest SRV for the double side textured wafers (10.8 ± 2.5 cm s^{-1}) is about 30% *lower* than the lowest SRV_f for single textured wafers, and not far from the lowest recorder SRV for RIE textured bSi. While additional work is needed in order to further explore the annealing conditions for e.g. double side textured wafers, since an optimal annealing time could not be found, these results already are significant in
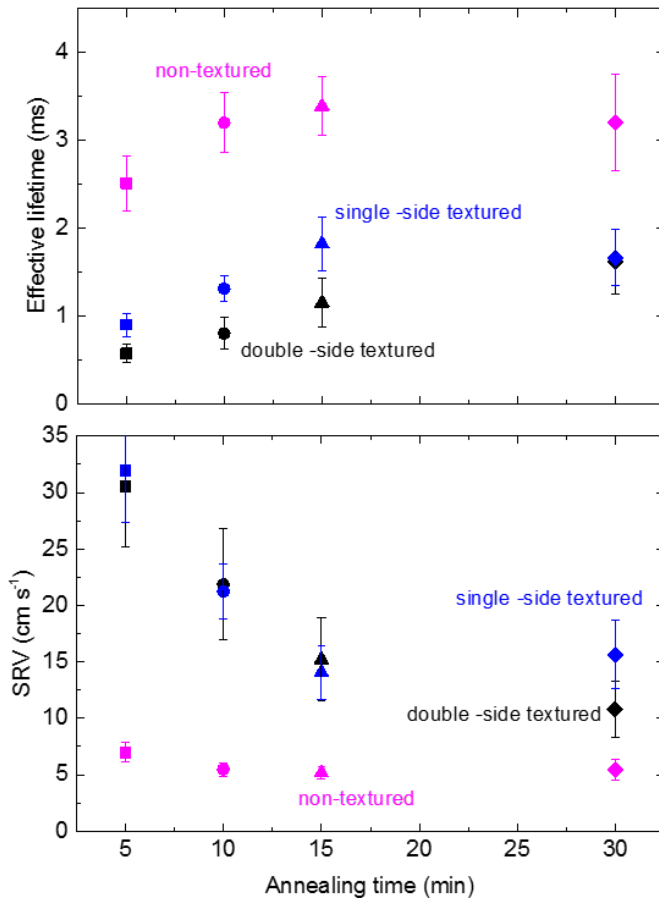
Fig. 3. Top: Effective minority carrier lifetime as function of annealing time. Bottom: Calculated surface recombination velocity (for single side textured surfaces, the SRV of this surface is plotted).

that they indicate that the conditions yielding optimal passivation depend on whether one or both surfaces of the wafers are textured.

IV. CONCLUSIONS

Black silicon was obtained by non-cryogenic RIE and coated by Al_2O_3 using ALD, followed by annealing for thermal activation of the surface passivation. Effective lifetime measurements revealed that the annealing time resulting in highest effective lifetime, and therefore in lowest surface recombination velocity of the textured surface, is depending on whether the wafers were single or double side textured. As a result, the final solar cell architecture needs to be kept in mind already at an early stage of fabricating samples for the purpose

of lifetime measurements, when using RIE for surface texturing.

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