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Avoiding blistering in Al₂O₃ deposited on planar and black Si

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Abstract

Aluminum oxide (Al₂O₃) fabricated by atomic layer deposition (ALD) has during the last decade emerged as an excellent surface passivation material for both planar and micro/nanostructured silicon. The post-ALD thermal treatment required to activate the surface passivation of Al₂O₃ results often in blistering and film delamination. Here, we studied how several fabrication steps affect blistering and the quality of surface passivation by Al₂O₃. Decreasing the fraction of blistered area on planar Si surfaces results in lower surface recombination velocity, in agreement with previous reports. By using simple analytical expressions, we estimated that surface recombination is at least 20 times faster at the blister than at the non-blistered areas. Exposing the Si surface to a reactive ion etch (RIE) treatment as short as 30 s is enough to suppress blistering. Anti-reflective nanostructured Si (black Si) fabricated using the same RIE process by increasing the RIE time does not suffer from blistering either. Finally, we investigated the effective lifetime of black Si textured surfaces and we implemented a pre-ALD conditioning routine that dramatically improves the quality of passivation by Al₂O₃ on black Si.

Key Words: surface passivation, Al₂O₃, blistering, black silicon

1. Introduction

The power conversion efficiency of silicon (Si) solar cells is severely affected by charge recombination at the surface of Si wafers, which mainly results in a less-than-ideal open circuit voltage [1,2]. Surface passivation is the act of decreasing surface recombination, typically performed by growing or depositing a thin dielectric layer on the surface of Si [3]. Aluminum oxide (Al_2O_3) has emerged as excellent material for passivation of Si, with performance comparable to or higher than that of thermally grown Si oxide (SiO_2) [4]. Low surface recombination velocity has been achieved by depositing Al_2O_3 by sputtering [5,6], plasma-enhanced chemical vapor deposition (PECVD) [7–9], and atomic layer deposition (ALD) [10–13]. Al_2O_3 and $\text{Al}_2\text{O}_3/\text{SiN}_x\text{:H}$ stacks are already industrially relevant for: (i) rear side passivation of cells based on p-type substrates [14], thus replacing the traditional Al back surface field, and (ii) passivation of p^+ emitters in cells based on n-type substrates [15,16]. Al_2O_3 has also demonstrated outstanding passivation performance when deposited on nanostructured, naturally antireflective Si (usually referred to as black Si [17], hereinafter bSi) [18,19]. The characteristic dimension of nanostructures in bSi leads to suppression of optical reflectance at the air-Si interface [20]. This in turn relaxes requirements on the antireflective properties of passivation films. If leading to enhanced photon absorption as compared to conventional texturing, higher short circuit current may also be obtained [21]. In addition, it has been shown that reflection off cells based on bSi surfaces is less affected by the increase in incidence angle, which is particularly relevant for building-integrated applications [22,23]. bSi suffers from higher surface recombination given the increased surface area and the sub-surface damage originated by the texturing process (the latter when fabricated by reactive ion etch – RIE) [24], leading to losses in terms of open circuit voltage and fill factor. However, the gap between efficiency of bSi based cells and that of conventionally textured cells under same fabrication conditions is progressively closing [16], and the best passivation of bSi has been achieved so far by ALD coating with Al_2O_3 [25].

A post-ALD thermal treatment in inert or slightly reducing atmosphere is mandatory to activate the passivation by Al_2O_3 [4]. After such treatments, blistering is very often observed at the Si- Al_2O_3 interface, sometimes leading to partial delamination of the Al_2O_3 film [26–28]. Possible explanations put forward to explaining formation of blisters are cavitation of the substrate caused by the surface diffusion of Si atoms, followed by buckling of the Al_2O_3 after a critical internal pressure is reached [29–31] and mechanical shear stress due to thermal mismatch between Si and Al_2O_3 during annealing [32]. The presence of $\text{SiN}_x\text{:H}$ as capping

layer does not seem to avoid blistering [33], which is also found on surfaces textured by KOH (i.e. pyramid textured surfaces) [32]. While Vermang *et al.* showed that it is possible to exploit the presence of blisters to create local openings at the rear of a cell during contact firing [34], it is generally believed that blistering should be avoided if possible, in order to have a better control of the rear passivation. In addition, the quality of passivation of Al_2O_3 is likely to be affected by the presence of blisters. A few studies reported variations of effective surface recombination velocity (S_{eff}) with varying amount of blistering [32,35], based on effective lifetime (τ_{eff}) measurements using by quasi-steady state photoconductance method, and therefore averaged on full size wafers. In addition, experimental direct evidence that the *local* quality of the passivation is degraded at the blisters is difficult to obtain, although such an effect is expected. Several strategies have been employed to reduce blistering at the Si/ Al_2O_3 interface, including: decreasing the Al_2O_3 thickness [33]; depositing the Al_2O_3 at higher temperature, or letting the temperature rise during ALD (*i.e.* thermal drift ALD) [36]; using O_3 as oxygen precursor instead of H_2O [27]; depositing Al_2O_3 on a hydrophilic surface such as a chemically grown SiO_2 layer [26]; varying the post-ALD thermal treatment temperature [27]. In all these cases, decreased blistering was attributed to the lower content of hydrogen in the films and/or the facilitated effusion of hydrogen from the films. However, hydrogen is also known as an excellent passivation agent for both bulk and surface defects in Si, and treatment in atmospheres containing hydrogen are routinely used to reduce recombination in Si solar cells. It follows that the gain in surface passivation by avoiding blistering should not be counteracted by any decrease in passivation due to lower content of hydrogen.

Here, we investigated the effect of several fabrication steps (pre-ALD cleaning, ALD temperature, post-ALD thermal treatment) on blistering and on the quality of surface passivation offered by Al_2O_3 films. Based on electron microscopy images to determine the surface coverage of blisters and on a simple analytical model, we estimated the *local* recombination velocity at the blisters S_b , and we found that it is at least 20 times higher than that of the non-blistered areas. We found that exposing the Si surface to a 30 s reactive ion etch (RIE) treatment is enough to suppress blistering completely. Importantly, such a process does not increase S_{eff} within experimental deviations, and can be used as an alternative to the modifications to ALD and post-ALD processing that result in a lower content of hydrogen as side effect. We used the same RIE process to fabricate bSi textured surfaces, by increasing the RIE time, and we found that no bSi surfaces suffered from blistering either. Finally, we

investigated the effective lifetime of bSi surfaces and the effect of pre-conditioning of the ALD chamber on the quality of the passivation by Al_2O_3 on bSi.

2. Experimental Section

2.1 Fabrication

100 mm diameter Czochralski (CZ) mono-crystalline (100) p-type boron-doped Si wafers with thickness $525 \pm 25 \mu\text{m}$ or $350 \pm 25 \mu\text{m}$ and resistivity of $5 \Omega \text{ cm}$ were used as substrates. Some wafers were textured on one side using mask-less reactive ion etch (RIE) at -20°C in a Pegasus system (SPTS) using the following parameters: 3000 W coil power, 10 W platen power (both operating at 13.56 MHz), gas flow ratio $\text{O}_2 : \text{SF}_6 \approx 10:7$, chamber pressure of 34 mTorr. The etching time varied from 30 s to 16 min depending on the wafer. All wafers were then RCA (Radio Corporation of America) cleaned (RCA1: 1:1:5 mixture of H_2O_2 , NH_4OH solution and de-ionized water; RCA2: 1:1:5 mixture of H_2O_2 , HCl solution and de-ionized water; both solutions were heated to 70°C). For some wafers, the final oxide strip in 5 % diluted hydrofluoric acid (HF) was omitted, in order to keep the SiO_2 from the second part of the cleaning on the surface. The surfaces were passivated with 380 cycles of Al_2O_3 synthesized at 200 or 250°C in an atomic layer deposition (ALD) process (R200, Picosun). Trimethyl-aluminum (TMA) and H_2O were used as precursors for aluminum and oxygen, respectively. In some cases, a chamber preconditioning procedure was employed where 50 cycles were deposited on the wafer holder without any wafer in the chamber. The Al_2O_3 layers were activated by post-deposition treatment. Some wafers were annealed in a N_2 atmosphere using a Tempress furnace. Annealing temperature was either 400°C or 500°C , and the annealing time was either 10 or 30 min. The other wafers received a rapid thermal annealing at 400°C or 500°C in a Jipelec RTP tool. The ramp-up time, annealing time and ramp-down time were 1 min, 5 min and 1 min, respectively.

2.2 Characterization

The thickness of the Al_2O_3 layer was measured using ellipsometry (VASE J. A. Woollam Co.). Scanning electron microscopy (SEM) images were acquired using a Carl Zeiss Supra 40VP microscope at an acceleration voltage of 5 kV. Size and surface coverage of the blisters were calculated from top-view SEM images using the image analysis software ImageJ. Optical reflectance R and transmittance T were measured using a UV spectrophotometer (UV-2600, Shimadzu Co.). The absorptance A was then determined using the relation $A = 1 - R - T$. Effective lifetime measurements were performed using the microwave-detected

photoconductivity (MDP) method in transient single point and mapping mode, at an injection level Δn of $\sim 10^{15} \text{ cm}^{-3}$, using a MDP mapper (Freiberg Instruments). For symmetrical, non-textured wafers, the effective surface recombination was calculated using the relation $S_{\text{eff}} = W/(2\tau_{\text{eff}})$, where W is the wafer thickness and τ_{eff} is the effective lifetime. S_{eff} was then used to calculate the surface recombination velocity of the textured surface according to the relation: $S_{\text{textured}} = W/\tau_{\text{eff}} - S_{\text{planar}}$.

3. Results and Discussion

3.1 Blistering in Al_2O_3 on flat Si

We fabricated a first set of wafers to test the effect of ALD deposition temperature and furnace annealing on formation of blisters on surfaces which have been cleaned following the complete RCA procedure, including the final oxide strip using 5% diluted HF. The Al_2O_3 thickness was fixed to 30 nm. Previous work using our ALD reactor, as well as by other groups [18,37], indicated that such thickness is required to passivate bSi well. We chose ALD deposition temperatures of 200 and 250 °C, since these temperatures usually define the window resulting in higher quality of passivation [4]. We followed the same reasoning for the post-ALD annealing temperature, 400 °C or 500 °C. We annealed the wafers for 30 min and 5 min at 400 °C and 500 °C, respectively, so that all wafers would remain in the furnace for approximately the same time. This is because the idle temperature of the furnace is 400 °C and the ramp-up and ramp-down time for the process is of 10 °C min^{-1} . Figure 1 shows top-view low magnification SEM images of 4 wafers with different combinations of T_{ALD} and annealing conditions. All surfaces suffer from severe blistering, with blister diameter of up to 100 μm . It appears that the wafer with $T_{\text{ALD}} = 200 \text{ °C}$ and $T_{\text{ann}} = 400 \text{ °C}$ suffers from slightly less pronounced blistering. This in contrast with previous reports where it was found that higher ALD and post-ALD processing temperatures lead to less severe blistering thanks to the lower content of hydrogen in the Al_2O_3 [27,36]. Nonetheless, significant amount of blistering such the one observed here is to be avoided when using Al_2O_3 as e.g. rear passivation layer. In addition, we measured effective lifetime values between 52.7 and 74.1 μs , which is more than an order of magnitude lower than what routinely achieved with Al_2O_3 .

Figure 1. Top-view, small magnification SEM images of flat wafers after RCA cleaning (including last HF dip), Al₂O₃ deposition and annealing in a tube furnace. Blistering is critical on these wafers, with diameter up to around 100 μm . The scale bar represents 200 μm .

We fabricated a second set of samples with $T_{\text{ALD}} = 200\text{ }^{\circ}\text{C}$, and with the following modifications. First, we omitted the last dip in 5% HF during RCA cleaning of all wafers. Second, we annealed two wafers using RTP instead of the tube furnace. RTP allows for much higher ramp-up rates than tube furnaces and therefore for faster processing times per wafer. However, the RTP system available for this study allowed for loading of one full sized wafer at the time, which results in lower throughput. SEM imaging of these wafer reveal much smaller blister size as compared to the surfaces with complete RCA cleaning, as shown in Figure 2. This is in agreement with previous work demonstrating that leaving a hydrophilic surface before ALD lead to smaller blister size [26]. Interestingly, RTP annealed samples appear to have higher number density of blisters and smaller blister diameter as compared with the tube furnace annealed samples. Table 1 summarizes our analysis of blistering on these wafers, as well as measurements of minority carrier effective lifetime τ_{eff} . An upper bound for the effective surface recombination velocity S_{eff} is calculated from τ_{eff} under the assumption of negligible bulk recombination using the relation $S_{\text{eff}} = W/(2\tau_{\text{eff}})$, where W is

the wafer thickness. Increasing T_{ann} from 400 °C to 500 °C and replacing furnace annealing with RTP annealing has two effects: (i) the average diameter of blisters decreases, and (ii) the number density of blisters increases. The resulting surface coverage of blisters is between 0.71% and 1.77%. It is worth mentioning that the wafer with lowest S_{eff} is also the one with lowest surface coverage of blisters f . Combining data on the surface coverage of blisters with S_{eff} , we can estimate the effect of blistering on the quality of the surface passivation. As a first approximation, we can divide S_{eff} in the sum of the contributions from blistered areas and non-blistered areas:

$$S_{\text{eff}} = f \times S_b + (1 - f) \times S_0 \quad (1)$$

where S_b is the recombination velocity on the blisters and S_0 is the recombination velocity away from the blisters. Here no spatial variation in the values of S_b and S_0 is assumed. In addition, we note that S_0 is a constant regardless of the surface, which may not necessarily be the case given the different annealing conditions, while S_b is sample dependent. Plotting S_{eff} as function of f and fitting linearly yields a value of S_0 of $36.7 \pm 5.5 \text{ cm s}^{-1}$. Then we can substitute S_0 and obtain S_b for each surface. This results in values of S_b between 726 cm s^{-1} and 1043 cm s^{-1} , at least 20 times higher than S_0 , and similar to those of Si surfaces before passivation. This confirms that the quality of passivation at the blisters is severely degraded, regardless of whether delamination of the Al_2O_3 is present or not. In fact, even such low surface coverage of blisters results in an increase of S_{eff} of at least 17%. A more rigorous treatment that takes into account diffusion of minority carriers to the blistered areas leads to a modification of the expression for S_{eff} . The treatment is presented in the Supporting Information. Here, we assume $S_b \gg S_0$, and S_0 is sample dependent. For each surface, S_{eff} can then be written as

$$S_{\text{eff}} = (1 - \sqrt{f})^2 \times S_0 + \frac{4D}{\sqrt{\pi}} \sqrt{Nf} \quad (2)$$

Where D is the diffusivity of minority carriers in Si and N is the number density of blisters. The values of S_0 are between 35.5 cm s^{-1} and 43.7 cm s^{-1} for the different surfaces, which are at least an order of magnitude lower than those of S_b estimated with the cruder model, thus ensuring self-consistency of the procedure. We also note that these values are close to the number for S_0 extracted from the $S_{\text{eff}}(f)$ linear fit. In general, we note that the combination of Equations (1) and (2) can be used to extract quantitative information on the local variation of the surface recombination velocity at damaged areas, *e.g.*, blisters, provided that the surface recombination velocity of the damaged areas is much larger than that of the non-damaged areas. This can be useful to quantify the effect of local failure of passivation films when

measuring effective lifetime with *e.g.* the quasi-steady state photoconductance method, where the whole surface is illuminated at the same time, or when using the microwave detected photoconductance method and the spatial resolution of the equipment is not sufficient to resolve local variations on the sub- μm scale, such as in this case.

Figure 2. Top-view, small magnification SEM images of flat wafers after RCA cleaning (without last HF dip), Al_2O_3 deposition and annealing in a tube furnace. Post-ALD treatment at 500 °C results in a higher number density of smaller blisters as compared to treatment at 400 °C. The scale bar represents 200 μm .

Post-ALD treatment	Average blister diameter (μm)	Blister number density (10^3 mm^{-2})	Blister surface coverage (%)	S_{eff} (cm s^{-1})	S_0 (cm s^{-1})
30 min @ 400 °C (furnace)	25.0	2.0	0.71	43.0 ± 11.9	35.9 ± 11.5
5 min @ 500 °C (furnace)	14.3	6.2	1.77	51.5 ± 14.3	41.6 ± 14.7
5 min @ 400 °C (RTP)	9.3	14.6	1.54	52.5 ± 12.2	43.7 ± 11.9
5 min @ 500 °C (RTP)	4.8	54.7	1.45	47.0 ± 6.2	37 ± 7.1

Table 1. Quantitative analysis of blistering on wafers with different annealing conditions. The right-most columns shows average values of effective surface recombination velocity on 100 mm diameter wafers (S_{eff}), and of surface recombination velocity away from the blistered areas (S_0).

3.2 Effect of annealing time and of short RIE on blistering

We observed a further slight decrease in number density of blisters by decreasing t_{ann} from 30 min to 10 min, as shown in Figure 3(a). However, this does not lead to a decrease in S_{eff} , which actually increases from 43 to 47.9 cm s^{-1} . If we accept the hypothesis that blistering occurs by cavitation followed by delamination and buckling, a rougher Si surface might impede delamination and result in lower blistering. In order to obtain a rougher Si surface, we employed a mask-less RIE process as described in Methods, with a short t_{RIE} (30 s). Such a RIE process is designed to produce black silicon texturing consisting of conical-like hillocks approximately 200-400 nm in height and width (for $t_{\text{RIE}} > 10$ min) yielding ultra-low optical reflectance. Indeed, we observed no blistering when the wafers were exposed to a 30 s RIE treatment before ALD coating and annealing (see Figure 3(b)). Higher magnification top-view SEM images reveal that the short RIE treatment results in a grainy surface due to the formation of initial etching pits. The quality of the subsequent passivation is only slightly affected by the RIE treatment, as shown in Figure 3(d). We speculate that the increased roughness reduces shear stress at the interface as a driving force for blistering/delamination. In perspective, this finding could make a short RIE treatment before deposition of passivation stacks that include Al_2O_3 interesting to inhibit blistering and film delamination. RIE is a single side processing which makes it possible to use different processes on each side of the cell, e.g. a process resulting in bSi on the front for low reflectance of incident light and a shorter process on the back resulting in high internal reflectance. To this extent, it may be of interest to reduce t_{RIE} further to find the minimum time required to eliminate blistering.

Figure 3. (a) Top-view SEM image of a wafer annealed for 10 min at 400 °C. (b) Top-view SEM image of a wafer with surface etched for 30 s by RIE, and annealed for 10 min at 400 °C. Blistering is absent on this surface. (c). Higher magnification image of the same sample as in (b). Grains with approximate diameter between 20 and 50 nm are visible. (d) S_{eff} comparison between wafer with no RIE and wafer with 30 s RIE. The S_{eff} of the etched wafer is slightly higher; however, the average values are not separated by one standard deviation.

3.5 Al₂O₃ on black Si – effect of RIE time and of chamber preconditioning

The RIE process used for the sample textured earlier can lead to formation of bSi by increasing t_{RIE} . The presence of nanostructures with characteristic dimensions comparable to the wavelength of UV-vis-NIR photons leads to suppression of optical reflectance at the air-Si interface. Figure 4 summarizes our SEM characterization of Si surfaces textured for t_{RIE}

increasing from 30 s to 16 min. As mentioned earlier, 30 s of RIE processing is sufficient to observe the formation of etching pits, however with no long-range order in their position. This is in agreement with the current understanding of the formation of bSi, where the first step consists of removal of the native Si oxide at slightly different etch rates depending on random spatial variation on thickness and density of the oxide [38]. For etching time of 3 min, the etching pits begin to overlap with each other resulting in hillock-shaped structures in the Si. Further etching results in an increase in hillock height and average base area. Surface features become smoother upon coating with Al_2O_3 , as visible from top-view images in the middle row. The cross-section images confirm that the Al_2O_3 coating is conformal, as expected when using ALD. From $t_{\text{RIE}} \geq 4$ min, the hillocks are more easily defined from the bulk Si. The height of the nanostructures then increases from less than 150 nm to about 450 nm for the longest etching time of 16 min. Importantly, no textured sample suffers from blistering, in agreement with results described in the previous section. Increasing t_{RIE} leads to a dramatic decrease in optical reflectance, as shown in Figure 5(a). There is basically no difference between the reflectance of the planar surface and that of $t_{\text{RIE}} = 30$ s, after coating with Al_2O_3 . In both cases, R converges to 30 % for photon wavelength close to the bandgap of Si, a value similar to that of a planar Si surface. Instead, R is lower than that of a Si surface for wavelength shorter than 1000 nm, indicating that the Al_2O_3 coating have already a certain antireflective effect, although not as good as for e.g. $\text{SiN}_x\text{:H}$, which has a better refractive index match with Si. Increasing t_{RIE} to 1 min and 2 min

Figure 4. SEM characterization of wafers with front size texturing by RIE. Top row: top-view SEM images of wafers with different t_{RIE} . Bottom row: cross-section SEM images of the same

wafers. The scale bar represents 100 nm for all images except for $t_{\text{RIE}} = 16$ min, where the scale bar represents 200 nm.

leads to a sizeable decrease in R , down to about 8 % for $t_{\text{RIE}} = 2$ min around 400 nm. The reflectance reaches almost 30 % close to the bandgap of Si for these wafers as well. For $t_{\text{RIE}} \geq 6$ min, the spectra resemble much more closely those measured by others on bSi fabricated by RIE [25,37,39]. R is lower than 5 % for wavelength up to almost 1050 nm, after which R increases steeply reaching 20 % at 1200 nm. The transmittance T in the wavelength range 1000-1200 nm is plotted in Fig. 5(b). T decreases slightly for increasing t_{RIE} , and the largest decrease takes place from $t_{\text{RIE}} = 12$ min to $t_{\text{RIE}} = 16$

Figure 5. Optical properties for surfaces textured for different t_{RIE} . (a) Reflectance. (b) Transmittance. (c) Absorptance. The legend is the same for all plots.

min. For $t_{\text{RIE}} = 16$ min, T approaches values normally obtained using upright KOH textured pyramids, which indicates that the light trapping ability of our bSi can be similar to that of KOH textured samples, if t_{RIE} is sufficiently long. The absorptance can then be calculated using the relation $A = 1 - R - T$, and it is plotted in Fig. 5(c). Clearly, A follows the opposite trend of R and T , with increasing A for increasing t_{RIE} .

The surface recombination velocity of the textured surface S_{textured} is plotted as function of t_{RIE} in Figure 6 for two batches of wafers. In one of them, we introduced an ALD chamber pre-conditioning routine consisting in depositing 50 cycles of Al_2O_3 in the chamber and on the wafer holder *without* wafers, before coating the wafers (4 per ALD run due to restriction in the dimensions of the chamber) and annealing them in the same furnace run. Wafers from the other batch were coated without chamber pre-conditioning. The differences between the two batches of wafers are clear. Wafers coated without pre-conditioning follow a peculiar trend in S_{textured} as function of t_{RIE} . First, the average S_{textured} increases about 30% (from 58.2 to 93.9 cm s^{-1}) increasing t_{RIE} from 30 s to $t_{\text{RIE}} = 2$ min. Then, it reaches a maximum of 222.1 cm s^{-1} for $t_{\text{RIE}} = 4$ min. For further increasing t_{RIE} , S_{textured} decreases until it reaches 68.5 cm s^{-1} for $t_{\text{RIE}} = 16$ min, a value similar to the average measured for $t_{\text{RIE}} = 1$ min. A decrease in τ_{eff} followed by an increase for longer RIE times has been reported by Otto *et al.* [25]. Such a trend seems counterintuitive, given that by increasing t_{RIE} the surface area of the textured wafers increases and so should the total surface recombination. Slight variations in the etching parameters used to fabricate ‘shallow’, ‘intermediate’ and ‘deep’ nanostructures may account for the observed trends in terms of τ_{eff} . We note here that the only parameter we varied in our RIE processing is t_{RIE} . In addition, we note that the standard deviation measured on surfaces with $t_{\text{RIE}} \geq 2$ min is too large to draw solid conclusions about differences in surface recombination velocity.

The batch of wafers coated following chamber pre-conditioning shows rather different results. First, S_{textured} increased monotonically with increasing t_{RIE} , from 15.5 cm s^{-1} of the planar reference to 33.1 cm s^{-1} for $t_{\text{RIE}} = 16$ min. Second, the magnitude of S_{textured} is more than half of that of the corresponding wafer from the other batch. Third, the uniformity of the passivation over the full wafers is much higher, since the standard deviation of S_{textured} has decreased by up to an order of magnitude. The S_{textured} values measured on our bSi is similar to that achieved by Plakhotnyuk *et al.* on the same type of substrates and using the same fabrication parameters, and the relative difference in S_{textured} between planar and bSi samples is about 30% higher than the data reported by Otto *et al.* on double-side textured, p-type substrates. Current work focuses on improving the RIE recipe to further decrease sub-surface

damage and thus recombination at the textured surfaces. Nonetheless, the results presented here indicate that an appropriate pre-conditioning of the ALD chamber *in our cleanroom facility* is necessary to ensure: (i) the highest possible quality of passivation when using Al_2O_3 ; and (ii) the batch-to-batch reproducibility of the passivation, which is necessary in order to be able to compare data from wafers coated in different ALD runs. In addition, we note that such chamber pre-conditioning is likely to be required in similar academic facilities characterized by a very broad spectrum of process flows, substrate and materials, whereas it is probably not necessary in industrial facilities dedicated to *e.g.* production of solar cells.

Figure 6. Surface recombination velocity S_{textured} of textured Si surfaces as function of etching time t_{RIE} . Wafers coated without ALD chamber pre-conditioning (circles) show a peculiar trend with a minimum in τ_{eff} for $t_{\text{RIE}} = 4$ min, and relative standard deviations of up to 40%. Wafers coated with ALD chamber pre-conditioning (squares) display monotonically increasing S_{textured} for increasing t_{RIE} and a much smaller relative standard deviation.

4. Conclusions

In this work, we investigated formation of blisters on Al_2O_3 films deposited on planar and nanostructured Si (black Si) surfaces. We found that the ALD deposition temperature and the choice of equipment for the post-ALD thermal treatment result in considerable variations in size and number density of blisters. In particular, lower T_{ALD} and lower T_{ann} in a tube furnace

results in the lowest blister size. The area fraction covered by the blisters remained lower than 2%. Nonetheless, effective lifetime mapping revealed that the surface recombination velocity at the blisters is at least 20 times larger than at the non-blistered surface, with absolute values similar to those of non-passivated Si surfaces. The much larger S_{eff} at the blisters and potential contacting problems from film delamination justify the efforts in minimizing blistering. We found that a short RIE process is able to inhibit formation of blisters, likely thanks to a reduction of shear as driving force for delamination. We found that such a treatment does not increase S_{eff} within experimental deviations, and therefore is an interesting alternative to the other modifications to ALD and post-ALD processing that result in a lower content of hydrogen as side effect. The same RIE process was used to fabricate nanostructured black Si surfaces showing excellent antireflective properties and good IR light trapping for the longest etching time of 16 min. An ALD chamber pre-conditioned routine was found to be necessary to decrease surface recombination velocity of the bSi surface, as well as to improve reproducibility of lifetime data between wafers coated in different batches. These results provide guidelines on avoiding blistering at the Si/Al₂O₃ interface without affecting significantly the surface recombination velocity. In particular, a short RIE treatment before deposition of passivation stacks including Al₂O₃ may be of interest to inhibit blistering and film delamination.

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Notes

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