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Published in:

Proceedings of the 6th International Conference on Crystalline Silicon Photovoltaics (SiliconPV 2016)

DOI:

[10.1016/j.egypro.2016.07.116](https://doi.org/10.1016/j.egypro.2016.07.116)

Published: 01/01/2016

Document Version

Publisher's PDF, also known as Version of record

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Please cite the original version:

Repo, P., & Savin, H. (2016). Effect of different ALD Al₂O₃ oxidants on the surface passivation of black silicon. In P.-J. Ribeyron, A. Cuevas, A. Weeber, C. Ballif, S. Glunz, J. Poortmans, R. Brendel, A. Aberle, R. Sinton, P. Verlinden, & G. Hahn (Eds.), *Proceedings of the 6th International Conference on Crystalline Silicon Photovoltaics (SiliconPV 2016)* (pp. 381-385). (Energy procedia; Vol. 92). Elsevier. <https://doi.org/10.1016/j.egypro.2016.07.116>

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6th International Conference on Silicon Photovoltaics, SiliconPV 2016

Effect of different ALD Al_2O_3 oxidants on the surface passivation of black silicon

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Abstract

We study how different oxidants in atomic layer deposition of aluminium oxide (ALD Al_2O_3) affect the surface passivation of black silicon. Here we show that processes using ozone cause higher fixed charge but surprisingly lead to lower lifetimes in black silicon samples as compared to water-based samples. In planar samples however, the best surface passivation is reached with O_3 -based processes. In case of water as oxidant, the planar wafers suffer from severe blistering and poorer surface passivation, while this seems to be the best process for black silicon. To find a reason for the lifetime differences we also study different Al_2O_3 stacks where both H_2O and O_3 are used as oxidants. In conclusion, surface texture seems to affect the optimal oxidant in the ALD process.

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Peer review by the scientific conference committee of SiliconPV 2016 under responsibility of PSE AG.

Keywords: black silicon; surface passivation; aluminum oxide

1. Introduction

Black silicon (b-Si) is a subject of great interest in the field of photovoltaics due to its low surface reflectance and light trapping properties. Recent progress in passivation of b-Si surfaces, especially with aluminium oxide (ALD Al_2O_3), has finally resulted in reasonable efficiencies of the actual b-Si solar cells [1]. However, the target being even higher efficiencies, the properties of ALD films and $\text{Al}_2\text{O}_3/\text{Si}$ interface need to be further optimized for b-Si surfaces.

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While water is the most common oxidant in thermal ALD, in planar wafers ozone has shown enhancement in the passivation and especially in the field effect due to higher negative oxide charge [2-4]. Therefore, we expect that higher negative charge is beneficial also for the passivation of b-Si surfaces where the effect of charge is more pronounced [5]. In addition to pure O_3 , the combination of O_3 and H_2O have shown even lower surface recombination velocities [2,3]. Here we study if this is also the case in b-Si and if it is possible to optimize the passivation of b-Si surfaces by properly tuning the oxidants.

2. Experimental details

Black silicon was fabricated using a maskless cryogenic deep reactive ion etching process (ICP-RIE) at a temperature of -120°C with a mixture of SF_6 and O_2 gases. A scanning electron microscope (SEM) image of the resulting black silicon structure is presented in Figure 1. Both sides of each 4 inch p-type magnetic CZ wafer ($3\ \Omega\text{cm}$, $400\ \mu\text{m}$, oxygen level 8-9 ppma) were etched to produce symmetric samples for minority carrier lifetime measurements. Approximately 25 nm (200 cycles) of Al_2O_3 was deposited on both sides of the wafers with thermal atomic layer deposition (ALD) at 200°C . Trimethylaluminum (TMA) was used as the aluminum source in all the processes but the oxidant was varied: i) H_2O , ii) O_3 and iii) $H_2O + O_3$. Passivation was activated by annealing at $400\text{-}430^\circ\text{C}$ for 30 minutes in nitrogen. Injection dependent carrier lifetime was measured with quasi-steady state photoconductance (QSSPC, WTC-120 Sinton Instruments) and the maximum effective surface recombination velocity ($S_{\text{eff,max}}$) was calculated from the measured values assuming infinite bulk lifetime. To study more thoroughly the passivation properties interface defect density (D_{it}) and total interface charge density (Q_{tot}) were measured with contactless CV method (COCOS) using Semilab PV-2000 tool [6].

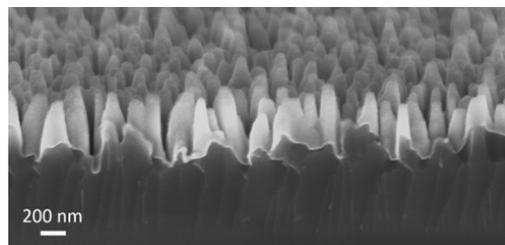


Fig. 1. Scanning electron microscope image of the black silicon structure.

3. Results and discussion

Figure 2 shows the injection level dependent minority carrier lifetime for both black silicon and their planar counterparts after three different ALD processes and post-deposition anneal. With processes using O_3 as the oxidant (O_3 or $H_2O + O_3$) lifetime in planar wafers is higher than in the corresponding b-Si samples. This is not surprising taking into account the larger surface area of b-Si. These processes provide surface recombination velocity of $\sim 12\ \text{cm/s}$ on planar and $\sim 22\text{-}24\ \text{cm/s}$ on black silicon. In the process where pure H_2O is used the result is opposite: lifetime in b-Si sample is a bit higher than in the corresponding planar reference having surface recombination velocities of $\sim 21\ \text{cm/s}$ and $43\ \text{cm/s}$, respectively. Our hypothesis is that this difference is at least partly caused by blistering: We observed severe blistering in the planar H_2O sample whereas in b-Si it was not observed. It is also worth mentioning that there is no blistering in the planar samples processed with pure O_3 . Surprisingly, the lifetime in the H_2O b-Si sample is higher than in the b-Si samples where O_3 is used, especially in the case of pure O_3 . This is unexpected because higher Q_{tot} values have been reported for O_3 processes [2] which should be even more beneficial for b-Si surface passivation [5].

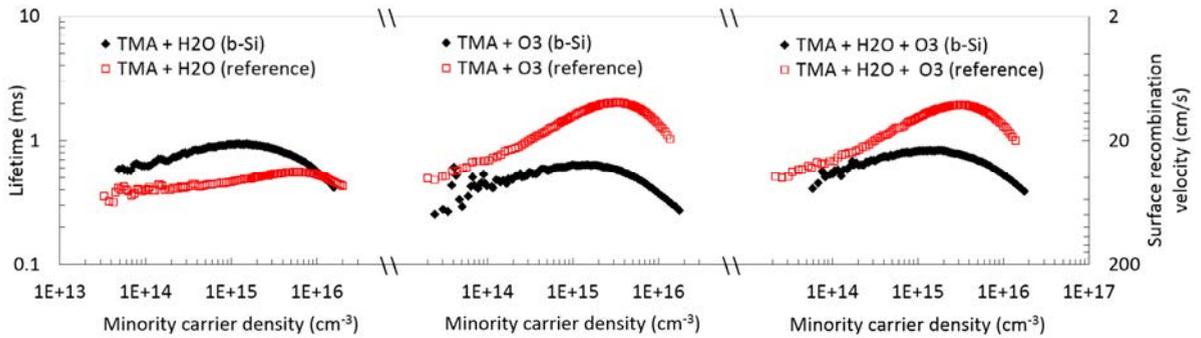


Fig. 2. Injection level dependent carrier lifetime and surface recombination velocity of both black silicon and planar counterparts after three different ALD processes: i) TMA + H₂O, ii) TMA + O₃ and iii) TMA + H₂O + O₃. Samples were measured after annealing at 400-430°C for 30 minutes.

To investigate the reason why H₂O processes provide better passivation for b-Si than pure O₃ process, contactless CV measurements were performed both on planar and b-Si samples. H₂O samples show lowest Q_{tot} value (see Figure 3a) while the value is the highest when pure O₃ is used, which is in agreement with literature [2,4]. This applies both for planar and b-Si samples. According to previous results [5], the measured charge value in b-Si is effective and could be scaled to a local value that corresponds the value measured from planar wafers. This is done by dividing the charge by the increase in surface area. In our case the charge in b-Si samples is approximately three times higher than in the planar references. This corresponds quite well the area enhancement of the black silicon structure used in this study (see Figure 1). However, the field-effect passivation cannot explain the lifetime behavior in b-Si as the pure H₂O process with the lowest charge provides the best passivation.

As the measured charge does not explain the lifetime behavior in black silicon the reason could be in the chemical passivation. Midgap D_{it} values measured from planar reference wafers are presented in Figure 3b. The D_{it} value is slightly higher in the ozone process than in the H₂O-based process. This is in agreement with previously published results and may be related to the higher interface carbon density and lower interface hydrogen density in the pure O₃ process at this concentration [2]. We measured D_{it} also from b-Si samples and they were roughly ten times higher than in the corresponding planar references in all processes. Although it is reasonable to expect larger effective D_{it} for b-Si due to increased surface area, the estimation of D_{it} from COCOS measurements in the case of b-Si needs to be addressed further in order to explain any differences reliably with the measured D_{it} .

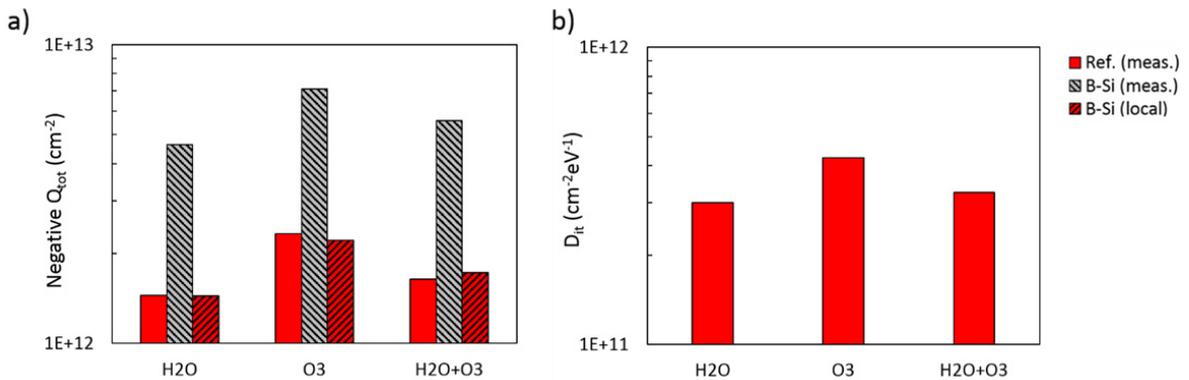


Fig. 3. In a) total negative fixed charge density and b) interface defect density after three different ALD processes. Local fixed charge values were rescaled by three from the measured values according to [5]. Samples were measured after annealing at 400-430°C for 30 minutes.

As mentioned, Q_{tot} values do not explain the lifetime differences in b-Si when different ALD Al_2O_3 processes are applied. The most likely reason for the variation in lifetime are the differences e.g. in the thickness and uniformity of the interfacial SiO_x layer caused by the use of different oxidants [7]. Another possible reason can be the lack of O_3 that can cause non-uniformity of the Al_2O_3 film. O_3 is rather stable but it can decompose at elevated temperatures of $>200^\circ\text{C}$ [8]. O_3 decomposition rate depends e.g. on the pressure and ambient [9-10] as well as on the surface condition [11]. Liu et al. have reported non-uniformities on HfO_2 films on high aspect ratio structures when O_3 is used at 200°C process temperature [12]. Another possibility is that the growth of Al_2O_3 on b-Si can prevent the reactants reaching the grooves of black silicon. High-resolution TEM imaging of the Si/ Al_2O_3 interface could help us see the possible non-uniformity of the film and differences in the interfacial SiO_x layer. Hence, we are currently performing these studies.

To study further the possible non-uniformity of Al_2O_3 on b-Si in the case of O_3 as the oxidant we employed two different processes: 1) deposition of 2 nm of Al_2O_3 with pure H_2O process followed by 18 nm of Al_2O_3 with pure O_3 process, 2) deposition of 10 nm of Al_2O_3 with pure H_2O process followed by 10 nm of Al_2O_3 with pure O_3 process. These experiments were done on p-type $1\ \Omega\text{cm}$ FZ material with wafer thickness of $250\ \mu\text{m}$. Other process parameters and post-deposition anneal were kept the same as described in the Experimental details. On b-Si samples both of these processes lead to maximum surface recombination velocities close to the ones reached with pure H_2O process, the 10+10 process having slightly lower $S_{\text{eff,max}}$ than the 2+18 process (see Figure 4). This is not surprising as the 10+10 process can be considered nearly identical as the pure H_2O process the only difference being smaller hydrogen content due to the top layer deposited with the pure O_3 process. Measured Q_{tot} values also correspond to the ones measured from pure H_2O samples on b-Si. These results also indicate that there should not be any conformality issues in the O_3 process. 2 nm of Al_2O_3 does not provide proper surface passivation which indicates that in the 2+18 process the film is deposited into the black silicon grooves also by the subsequent O_3 process. This leads to the more likely reason behind the lifetime differences i.e. the differences in the interfacial SiO_x properties that could be studied with HRTEM as suggested before. It is worth noticing that extremely low $S_{\text{eff,max}}$ was reached on planar samples with both Al_2O_3 stacks, 2+18 reaching values as low as $\sim 5\ \text{cm/s}$. In addition, 2+18 process exhibited clearly less blistering on planar wafers as compared to the 10+10 and pure H_2O processes as can be expected as pure O_3 process has no blisters.

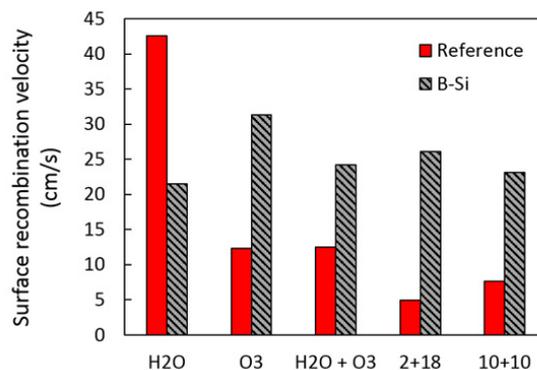


Fig. 4. Calculated maximum surface recombination velocity $S_{\text{eff,max}}$ at an injection level of $1 \cdot 10^{15}\ \text{cm}^{-3}$ on black silicon and planar references after five different ALD processes and annealing. 2+18 and 10+10 refer to the processes where pure H_2O process was used before the pure O_3 process having 20 nm thick film as the target.

4. Conclusions

In this work we have shown that the choice of oxidant in ALD Al_2O_3 process can affect the passivation quality of black silicon surfaces. Processes using O_3 lead to the highest lifetimes in planar samples whereas using pure H_2O leads to highest lifetime in the b-Si sample. Also, pure H_2O process provides better passivation for b-Si than for the

planar reference. The low lifetime after pure H₂O process in the planar sample is probably caused by severe blistering that we observe only in water-based processes whereas no blistering is seen in the pure O₃ case.

Acknowledgements

The authors acknowledge Aalto University Micronova Nanofabrication Centre for providing facilities. This work was partly funded through the European Metrology Research Programme (EMRP) Project ENG53 ThinErgy. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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