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6th International Conference on Silicon Photovoltaics, SiliconPV 2016

## Effect of different ALD $\text{Al}_2\text{O}_3$ 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  $\text{Al}_2\text{O}_3$ ) 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  $\text{O}_3$ -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  $\text{Al}_2\text{O}_3$  stacks where both  $\text{H}_2\text{O}$  and  $\text{O}_3$  are used as oxidants. In conclusion, surface texture seems to affect the optimal oxidant in the ALD process.

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*Keywords:* black silicon; surface passivation; aluminum oxide

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### 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  $\text{Al}_2\text{O}_3$ ), 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  $-120^\circ\text{C}$  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  $25\ \text{nm}$  (200 cycles) of  $Al_2O_3$  was deposited on both sides of the wafers with thermal atomic layer deposition (ALD) at  $200^\circ\text{C}$ . 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 ( $D_{\text{it}}$ ) and total interface charge density ( $Q_{\text{tot}}$ ) were measured with contactless CV method (COCOS) using Semilab PV-2000 tool [6].

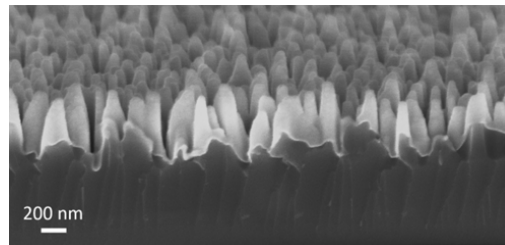


Fig. 1. Scanning electron microscope image of the black silicon structure.

## 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  $Q_{\text{tot}}$  values have been reported for  $O_3$  processes [2] which should be even more beneficial for b-Si surface passivation [5].

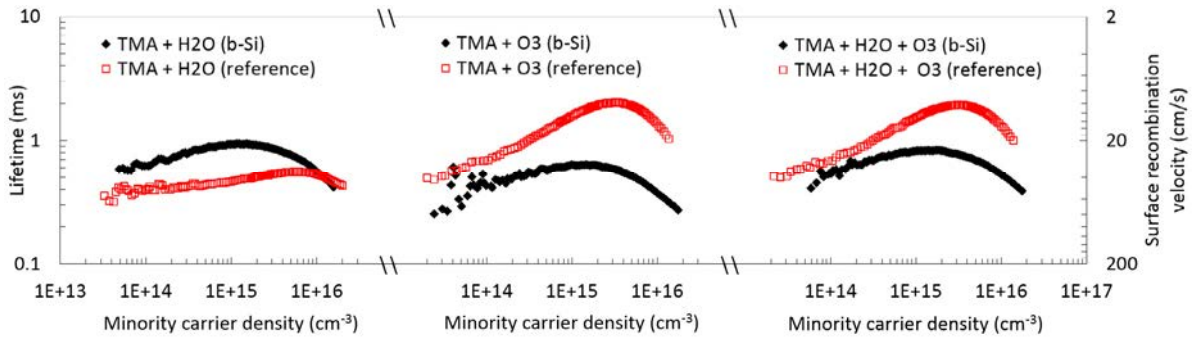


Fig. 2. Injection level dependent carrier lifetime and surface recombination velocity of both black silicon and planar counterparts after three different ALD processes: i) TMA + H<sub>2</sub>O, ii) TMA + O<sub>3</sub> and iii) TMA + H<sub>2</sub>O + O<sub>3</sub>. Samples were measured after annealing at 400-430°C for 30 minutes.

To investigate the reason why H<sub>2</sub>O processes provide better passivation for b-Si than pure O<sub>3</sub> process, contactless CV measurements were performed both on planar and b-Si samples. H<sub>2</sub>O samples show lowest Q<sub>tot</sub> value (see Figure 3a) while the value is the highest when pure O<sub>3</sub> 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 H<sub>2</sub>O 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<sub>it</sub> values measured from planar reference wafers are presented in Figure 3b. The D<sub>it</sub> value is slightly higher in the ozone process than in the H<sub>2</sub>O-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 O<sub>3</sub> process at this concentration [2]. We measured D<sub>it</sub> 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<sub>it</sub> for b-Si due to increased surface area, the estimation of D<sub>it</sub> 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<sub>it</sub>.

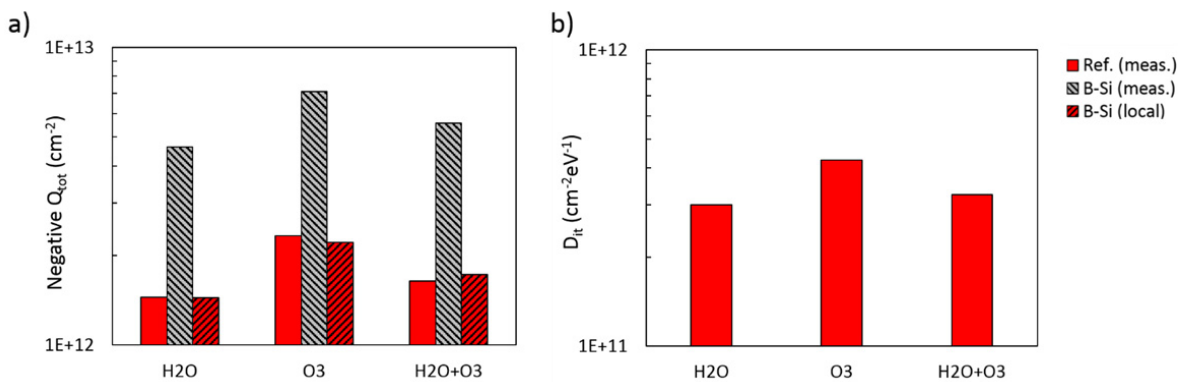


Fig. 3. In a) total negative fixed charge density and b) interface defect density after three different ALD processes. Local fixed charge values were rescaled by three from the measured values according to [5]. Samples were measured after annealing at 400-430°C for 30 minutes.

As mentioned,  $Q_{\text{tot}}$  values do not explain the lifetime differences in b-Si when different ALD  $\text{Al}_2\text{O}_3$  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  $\text{SiO}_x$  layer caused by the use of different oxidants [7]. Another possible reason can be the lack of  $\text{O}_3$  that can cause non-uniformity of the  $\text{Al}_2\text{O}_3$  film.  $\text{O}_3$  is rather stable but it can decompose at elevated temperatures of  $>200^\circ\text{C}$  [8].  $\text{O}_3$  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  $\text{HfO}_2$  films on high aspect ratio structures when  $\text{O}_3$  is used at  $200^\circ\text{C}$  process temperature [12]. Another possibility is that the growth of  $\text{Al}_2\text{O}_3$  on b-Si can prevent the reactants reaching the grooves of black silicon. High-resolution TEM imaging of the Si/ $\text{Al}_2\text{O}_3$  interface could help us see the possible non-uniformity of the film and differences in the interfacial  $\text{SiO}_x$  layer. Hence, we are currently performing these studies.

To study further the possible non-uniformity of  $\text{Al}_2\text{O}_3$  on b-Si in the case of  $\text{O}_3$  as the oxidant we employed two different processes: 1) deposition of 2 nm of  $\text{Al}_2\text{O}_3$  with pure  $\text{H}_2\text{O}$  process followed by 18 nm of  $\text{Al}_2\text{O}_3$  with pure  $\text{O}_3$  process, 2) deposition of 10 nm of  $\text{Al}_2\text{O}_3$  with pure  $\text{H}_2\text{O}$  process followed by 10 nm of  $\text{Al}_2\text{O}_3$  with pure  $\text{O}_3$  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  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  process the only difference being smaller hydrogen content due to the top layer deposited with the pure  $\text{O}_3$  process. Measured  $Q_{\text{tot}}$  values also correspond to the ones measured from pure  $\text{H}_2\text{O}$  samples on b-Si. These results also indicate that there should not be any conformality issues in the  $\text{O}_3$  process. 2 nm of  $\text{Al}_2\text{O}_3$  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  $\text{O}_3$  process. This leads to the more likely reason behind the lifetime differences i.e. the differences in the interfacial  $\text{SiO}_x$  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  $\text{Al}_2\text{O}_3$  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  $\text{H}_2\text{O}$  processes as can be expected as pure  $\text{O}_3$  process has no blisters.

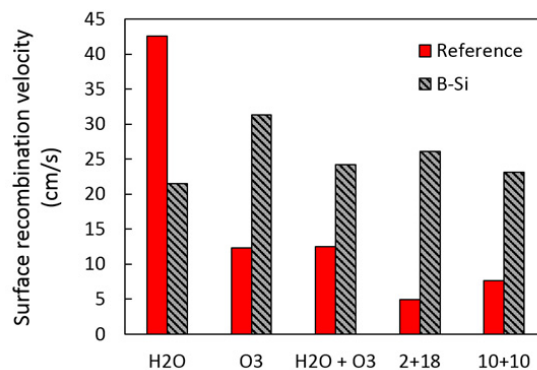


Fig. 4. Calculated maximum surface recombination velocity  $S_{\text{eff,max}}$  at an injection level of  $1 \cdot 10^{15}\ \text{cm}^{-3}$  on black silicon and planar references after five different ALD processes and annealing. 2+18 and 10+10 refer to the processes where pure  $\text{H}_2\text{O}$  process was used before the pure  $\text{O}_3$  process having 20 nm thick film as the target.

#### 4. Conclusions

In this work we have shown that the choice of oxidant in ALD  $\text{Al}_2\text{O}_3$  process can affect the passivation quality of black silicon surfaces. Processes using  $\text{O}_3$  lead to the highest lifetimes in planar samples whereas using pure  $\text{H}_2\text{O}$  leads to highest lifetime in the b-Si sample. Also, pure  $\text{H}_2\text{O}$  process provides better passivation for b-Si than for the

planar reference. The low lifetime after pure H<sub>2</sub>O 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 O<sub>3</sub> case.

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