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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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Keywords: black silicon; surface passivatoin; 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 Al_2O_3/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 Ωcm, 400 µm, 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 400-430°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 ($S_{eff,max}$) 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].

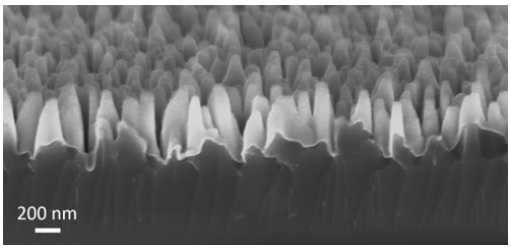

Fig. 1. Scanning electron microscope image of the black silicon structure.

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 ~12 cm/s on planar and ~22-24 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 ~21 cm/s and 43 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].