Passivation of optically black silicon by atomic layer deposited Al$_2$O$_3$

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Abstract

Optically black silicon nanostructures show excellent anti-reflection and light trapping properties minimizing reflection losses to less than 1.6 % between 300 – 1100 nm. Our light-trapping scheme enables an absorption enhancement factor of ~10 at the band edge of silicon (1150 nm) as compared to a simulated perfect ARC, where the Yablonovitch limit corresponds to a factor of 15. Just recently it was shown that similar wet-chemically black etched silicon surfaces can be exploited to fabricate high efficiency solar cells [1]. Towards the integration of our structures into a solar cell device, the passivation performance of atomic layer deposited thin Al$_2$O$_3$ films is investigated on a variety of black etched structures. The coatings lead to measured surface recombination velocities of less than 13 cm/s on bifacially black structured as well as 12 cm/s on polished 15 cm p-type Si CZ wafers. Thinner layers promise to be even more effective. This technology will enable high efficiencies on various solar cell concepts.

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1. Introduction

Optically black silicon (b-Si) shows lower reflection losses than conventionally textured Si surfaces combined with simple antireflection coatings (ARC) [2,3]. The enhanced light trapping in such nanostructured b-Si may improve cell efficiency, i.e. higher open circuit voltage and short circuit current, only when it is not compensated by an increase of surface recombination [1]. Therefore, efficiencies of b-

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Si solar cells can not yet compete with state-of-the-art solar cells [1,4]. However, to lower the costs a reduction of the crystalline absorber thickness demands enhanced light trapping concepts [5]. The presented light trapping scheme based on b-Si is a promising route towards thinner cells. Usually, nano-structuring silicon surfaces leads to enhanced minority carrier recombination due to defects in the near surface region, introduced during black-etching as well as due to augmentation of the surface area [6]. Besides optimization of the texturing process towards lower surface defect densities, an effective passivation of the surface is crucial to improve the critical interfacial electronic properties. Thin Al₂O₃ films deposited by atomic layer deposition (ALD) are the best choice for b-Si passivation, because of their conformal growth on surfaces with high aspect ratio features and their capability to passivate silicon [7-10]. After annealing around 400 °C the Al₂O₃ layer enables excellent chemical passivation due to strong coordination of Si and O [11] and selective hydrogenation leading to a low defect state density at the interface [12]. Additionally, a high concentration of fixed negative charges has been measured in these layers, providing a strong field effect passivation [9]. Both mechanisms allow decent passivation of b-Si. In this work we present effective minority carrier lifetimes in the millisecond range of b-Si samples. The samples were fabricated by a plasma etching process and passivated with thin Al₂O₃ layers deposited by an optimized thermal ALD process.

2. Sample preparation

Polished p-type (1-5 Ωcm) CZ Si 6” wafers with thicknesses of 450 μm were structured by an inductive coupled plasma (ICP) dry reactive ion etching (RIE) process with SF₆ and O₂ [3,7]. By varying etching time and process pressure three different surfaces with shallow, intermediate and deep morphologies are produced. The randomly emerging sharp Si needles have characteristic heights of 500 nm, 600 nm and 1700 nm with aspect ratios of 3, 4 and 10, respectively. Before coating, the bifacially textured samples received a standard RCA clean. Al₂O₃ was deposited by thermal ALD from trimethylaluminium (TMA) and H₂O. The passivation was activated by post deposition annealing at temperatures between 350 °C and 500 °C for 30 min in a low pressure Ar ambience or in normal pressure air. Charge carrier lifetimes were measured after annealing via the quasi-steady state photo conductance (QSSPC) method. Hemispherical reflectance and transmittance were measured using an integrating sphere to calculate the spectral absorption of the samples.

3. Results and discussion

The spectral absorption of the passivated b-Si samples with shallow, intermediate and deep surface morphologies are plotted in Fig. 1a. The deep structure shows a slightly higher absorption near the optical band edge of silicon than the shallow and intermediate structures. In comparison to the theoretical absorption of a flat Si wafer without any front reflection losses (dash-dotted black line) both samples show clearly a better light trapping in the long wavelength range. The optical influence of the Al₂O₃ coatings may even be positive for 30 nm thick layers (not shown). The difference of light absorption from 300 nm to 1175 nm between coated and uncoated samples is smaller than 5% (not shown). All textures show excellent light trapping in a comparison with the Yablonovitch limit [2] (solid black line).

From the effective minority carrier lifetime, τₑff of the b-Si structures and a polished Si reference, all passivated by thermally activated 100 nm Al₂O₃ layers, an upper limit for the effective surface recombination velocity Sₑff was determined assuming infinite bulk lifetime. In Fig. 1b Sₑff of the samples with different surface morphologies are plotted over the excess charge carrier density. In the range between 10¹⁵ cm⁻³ ≤ ΔN ≤ 10¹⁶ cm⁻³ all samples exhibit effective surface recombination velocities
Fig. 1. (a) Experimental absorption spectra of the shallow (blue, solid), intermediate (red, dashed) and deep (green, dotted) b-Si structures coated with 100 nm Al₂O₃. For comparison, simulated spectra of a perfect anti-reflection coating (dash-dotted black) and a Lambertian surface (Yablonovitch limit [2], solid black) are plotted as well. (b) Injection level dependent maximum effective surface recombination velocity of the three model structures in comparison to a polished reference passivated with 100 nm Al₂O₃. The samples were annealed in low pressure Ar ambient at 425 °C for 30 min.

Fig. 2. (a) SEM micrograph of the intermediate b-Si sample passivated by 100 nm Al₂O₃ as presented in Fig. 1. The low refractive index dielectric layer very homogeneously covers the surface perfectly conformal.

below 100 cm/s. For comparison, a standard aluminum back surface field on similar material obtains values of 500 cm/s [13], whereas Al₂O₃ passivation schemes achieve values down to 4 cm/s on unstructured material of comparable doping density [14]. State-of-the-art high efficiency solar cells reaching open circuit voltages over 650 mV work with effective surface recombination velocities of 65 cm/s down to 20 cm/s [13]. Oh et al. [1] report S_{eff} values of over 50 cm/s for their 18.2% efficient metal etched b-Si solar cell including a shallow emitter, even though their structures appear to be optically slightly weaker than our ICP-RIE structured surface presented in Fig. 2. However, there is still room for improvement concerning the opto-electronic performance of our b-Si structures. Incorporating thinner Al₂O₃ layers with improved passivation quality will lead to injection level independent lifetimes on all our b-Si structures without affecting the optical performance.

4. Conclusions

The optical absorption of the three b-Si surfaces is strongly enhanced near the optical band edge and close to the Yablonovitch limit, due to pronounced scattering at the nanostructures. At the same time the
Si nanostructures can be effectively passivated. The differences in the optical performance of the shallow and intermediate samples are small compared to the differences in electronic performance. While the intermediate structure shows an effective surface recombination ($S_{eff} < 13 \text{ cm/s}$) close to that of the flat reference sample, the shallow and deep structure exhibit much higher values. This difference is not only a consequence of the enlarged surface area itself, but more likely an effect of the plasma induced stress in the near-surface bulk. However, the extremely low effective surface recombination velocity in the intermediate b-Si sample demonstrates the feasibility to reach a decent lifetime level which is commensurable for highly efficient solar cells. Hence, our passivation scheme finally opens the road for a new generation of black silicon devices in photovoltaics and opto-electronics.

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References