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Long-term stability of Al_2O_3 passivated black silicon

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Abstract

In this work we report on the long-term stability of black silicon surfaces passivated with atomic layer deposited (ALD) 20 nm thick Al_2O_3 films on p- and n-type FZ c-Si substrates. The results are directly compared with random pyramid textured counterparts. The effective surface recombination velocity S_{eff} has been measured within a time frame of one year after activation of surface passivation. The results demonstrate that after an initial slight degradation during the first month S_{eff} values stabilize around 45 and 25 cm/s on p- and n-type black silicon samples, respectively. These values are enough to guarantee stable high efficiency in interdigitated back-contacted (IBC) c-Si(n) solar cells (> 24.5%) using black silicon nanostructures on the front side. Similar, although weaker, losses are also observed in surface passivation on textured samples covered by Al_2O_3 with equal thickness, indicating that the origin of the instability might be independent of surface morphology.

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Keywords: Black silicon; Nano-texturing; Surface passivation; Lifetime; Atomic layer deposition; Al_2O_3; Solar cells

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1. Introduction

Black silicon, from now on b-Si, reduces drastically surface reflectance in the useful absorption solar spectrum of c-Si solar cells [1, 2]. An interdigitated back-contacted (IBC) structure with their contact-free front surface simplifies the introduction of b-Si etching in the fabrication chain. In order to guarantee high efficiencies IBC c-Si solar cells not only low reflectance but also very good front surface passivation are mandatory.

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Surface passivation is a critical issue due to the large black silicon surface area. Nowadays some works have demonstrated that excellent passivation of b-Si nanostructures can be reached using atomic layer deposited (ALD) Al_2O_3 films [3, 4]. Those films combine electrical and chemical passivation, achieving effective surface recombination velocities S_{eff} well below 20 cm/s on p- and n-type c-Si and mc-Si materials.

Recently lab-scale b-Si IBC cells passivated with ALD Al_2O_3 with efficiencies beyond 22% on both p– and n-type c-Si substrates have been demonstrated [2, 5]. However, the passivation stability of b-Si covered by ALD Al_2O_3 films has not been analyzed yet. This aspect is crucial if b-Si etching wants to be introduced as a realistic alternative in the solar cell fabrication process.

In this work we report on the one year passivation stability of ALD Al_2O_3 passivated b-Si using both p- and n-type substrates.

2. Experimental

2.1. Texturing and surface passivation

High quality p- and n-type 2.7±0.2 Ωcm <100> FZ c-Si, 4” wafers (285 ± 10 um thickness) were used in the study. Black silicon was performed by etching both surfaces through a cryogenic inductively coupled plasma reactive-ion etching process (ICP-RIE) at -120 ºC using SF_6 and O_2 as etching gases. As can be seen in Fig. 1ab, nano-texturing etching results in densely and randomly pillars distributed on the silicon surface with heights and widths less than 1 μm and 200 nm respectively.

Reference samples were textured on both sides by anisotropic etching in tetramethylammonium hydroxide (TMAH), isopropanol (IPA) and DI water (320 ml:350 ml:3300 ml) at 80ºC (75 min) resulting in random pyramid surfaces.

After the etching, the wafers were RCA cleaned before the atomic layer deposition of 20 nm thick Al_2O_3 layer at 200ºC for both b-Si and reference samples. In the ALD process, TMA was used as the aluminum source and water as the oxidant. After ALD Al_2O_3 passivation, all wafers were cut in quarters to explore the optimum annealing temperature previously to the monitoring of the surface passivation stability with the time. The annealing stage was performed in forming gas ambient during 15 min considering different annealing temperatures in the 375-450ºC range.

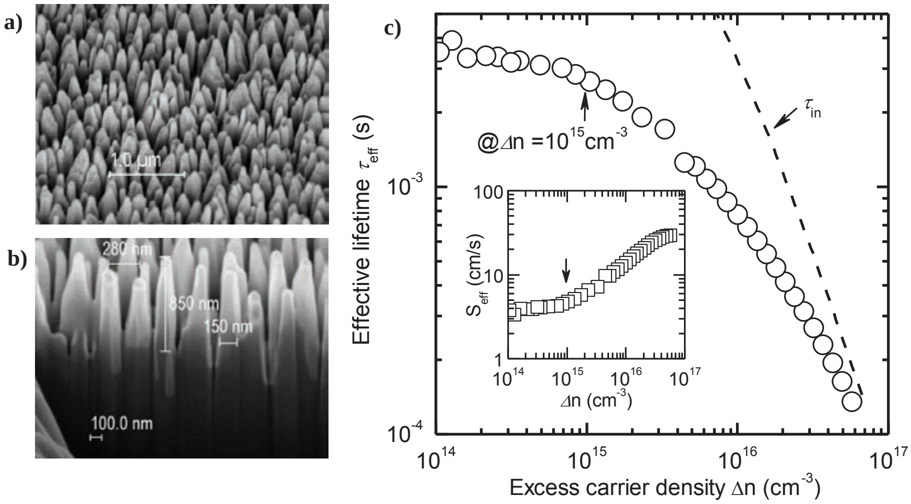

Fig. 1. a) and b) SEM images showing examples of b-Si surface morphology indicating main nano-pillars dimensions. (c) τ_{eff} and S_{eff} (in the inset) vs. excess carrier density Δn for a symmetrical b-Si n-type sample annealed at 400 ºC 10 min.

2.2. Lifetime and surface passivation measurements

Effective surface recombination velocity S_{eff} was extracted from effective lifetime τ_{eff} vs. excess carrier density Δn measurements (see Fig. 1c) using quasy-steady-state photoconductance QSS-PC technique (WCT-120 apparatus, Sinton Instruments) by means of eq. (1), where w is the wafer thickness and τ_{in} the lifetime related to intrinsic recombination mechanisms (Auger and band to band) using the parametrization reported by Richter et al. [6]. S_{eff} was always evaluated for an injection carrier excess of $\Delta n=10^{15}$ cm^{-3} and samples were stored at room conditions in the dark between measurements.

$$\frac{1}{\tau_{eff}} - \frac{1}{\tau_{in}} \cong \frac{2S_{eff}}{w} \qquad (1)$$

3. Results

3.1. Annealing temperature study. Initial surface passivation

It is well known that surface passivation activation of ALD Al_2O_3 films both on polished as well as on randomly textured c-Si surfaces requires a thermal annealing in the 350-450ºC range [7]. For our b-Si samples, the best option is to perform the annealing around 400ºC independently of the substrate polarity as is shown in Fig. 2. Excellent S_{eff} values of 16.0 and 5.5 cm/s on p- and n-type material respectively are achieved (see table I). Notice that b-Si surface passivation is quite similar to that achieved on textured reference samples.

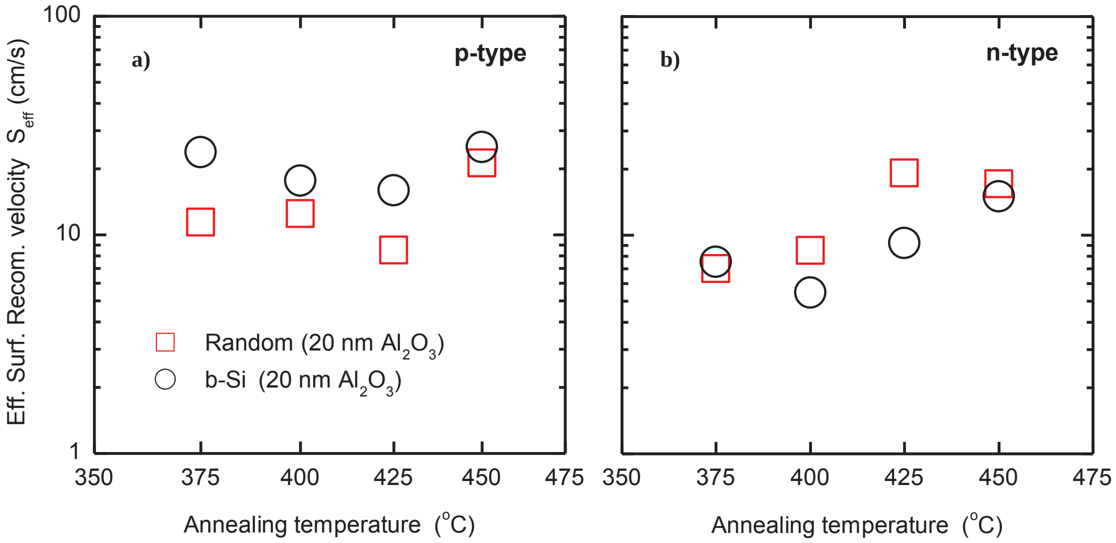

Fig. 2. S_{eff} vs. annealing temperature for random (squares) and b-Si (circles) textured surfaces on a) p- and b) n-type substrates.

3.2. Long-term surface passivation stability study

Once initial surface passivation is activated, S_{eff} was periodically monitored in both b-Si and randomly textured samples during one year (~8700 hours). As can be seen in Fig. 3, some slight surface passivation degradation, especially noticeable during the first month (< 1000 h), occurs on b-Si samples compared with their corresponding reference. However S_{eff} seems to stabilize to values of 45 ± 10 and 25 ± 2 cm/s on p- and n-type substrates respectively independently of the annealing temperature as is shown in table 1. Therefore surface passivation quality changes from outstanding to very good at the end of the study.

The origin of this surface passivation degradation is still unclear but it might be due to a slight loss of field-effect passivation, i.e. a decrease in charge with time in the Al_2O_3 film, which also explains the small increase of S_{eff} on random textured samples with the same Al_2O_3 thickness. Notice that electrical passivation mechanism plays a crucial role in b-Si surfaces which are much more sensitive to charge than planar samples [4]. However more research is necessary to address final conclusions.

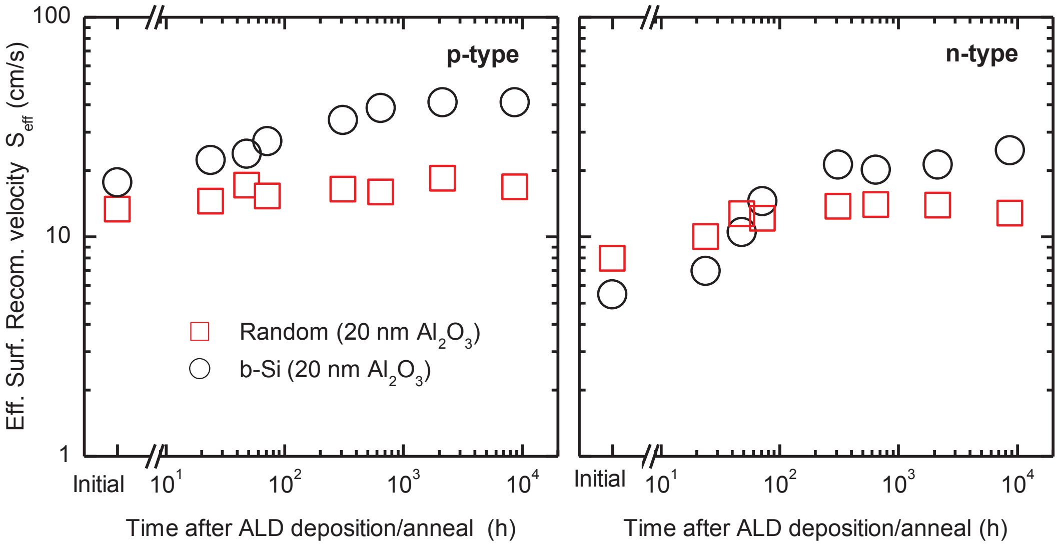

Fig. 3. S_{eff} vs. time after ALD deposition and anneal for random (squares) and b-Si textured surfaces (circles) on a) p-type and b) n-type substrates. Samples were previously annealed at 400ºC.

Table 1. Initial and final (enclosed in parenthesis in bold) Seff values (@Δn=1015 cm-3) for b-Si and random pyramid textured samples on p- and n-type substrates.

Annealing Temperature (ºC)	S_{eff} (cm/s) p-type	S_{eff} (cm/s) n-type
b-Si + 20 nm ALD AL_2O_3		
375	23.9 (**33.9**)	7.5 (**24.3**)
400	17.7 (**40.9**)	5.5 (**24.7**)
425	16.0 (**34.7**)	9.2 (**27.2**)
450	25.2 (**55.7**)	15.0 (**26.7**)
Random pyramids + 20 nm ALD AL_2O_3		
375	11.4 (**16.8**)	7.0 (**15.7**)
400	13.3 (**16.8**)	8.0 (**12.8**)
425	8.5 (**22.7**)	19.2 (**39.7**)
450	21.3 (**25.7**)	17.2 (**31.6**)

4. Expected photovoltaic efficiencies on stable n-type IBC cells

Taking into account stabilized S_{eff} values we can predict final photovoltaic efficiencies of n-type IBC cells with b-Si at the front surface and device thickness about 260 μm using PC1D software [8]. For that purpose, we consider a back-junction structure (see inset in Fig. 4a) with the following constraints: a) the same front reflectance of a test device with b-Si surface and 20 nm ALD measured in a previous work [5] (see Fig 4a) and considering a 96% back reflection. b) Emitter recombination current density, J_{oe}, is set to 10 fA/cm^2 and c) base recombination current density, J_{ob}, is dominated by both front surface and bulk recombination with ideally passivated base contacts. d) Negligible series resistance due to base and rear metallization grid ohmic losses. Constraints b) and c) can be achieved easily in a state-of-art IBC cells based on rear point contact structure [9] or alternatively on the HIT concept [10], whereas consideration d) can be overcome using both a small pitch between base and emitter interdigitated regions, e.g. ~ 100 µm, and a two level metallization scheme.

Efficiencies contours under standard test conditions (AM1.5G 1 kW/m^2 solar spectrum and T=25ºC) vs. bulk lifetime τ_{Bulk} and effective front surface recombination velocity S_F are shown in Fig 4b. It is clear that n-type IBC cells fabricated with high quality substrates, i.e. $\tau_{Bulk} > \sim 1$ ms, can reach initial efficiencies and short-circuit current densities as high as 26.5% and 42.9 mA/cm^2 respectively, relaxing to values up to 24.5% and 41.7 mA/cm^2 once front surface passivation is stabilized with S_{eff} values around 25 cm/s.

We can conclude that S_{eff} values, especially on n-type substrates, guarantee enough surface passivation to obtain high photovoltaic efficiencies even using a high demanding structure as is the IBC solar cell.

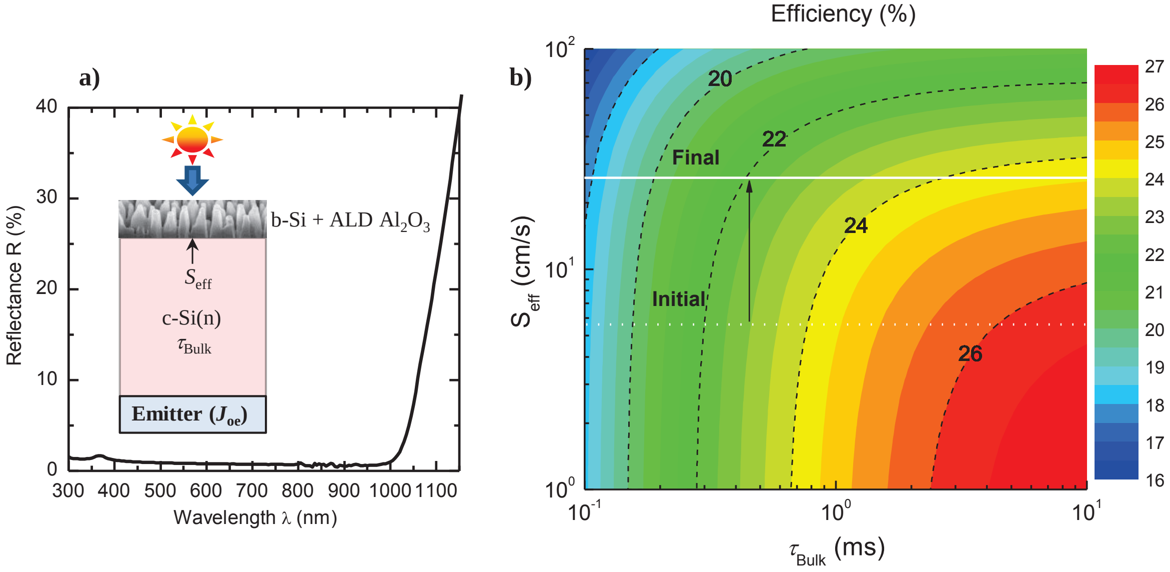

Fig. 4. (a) Measured reflectance of a sample with b-Si. The simulated back junction structure is shown in the inset. (b) Simulated photovoltaic efficiencies under standard text conditions STC (AM1.5G 1kW/m^2 solar spectrum, T=25ºC) vs. S_F and τ_{Bulk} for a n-type 260 µm thick device with 3 Ωcm bulk resistivity.

5. Conclusions

In this work we report on the long-term stability of black silicon surfaces passivated with atomic layer deposited, (ALD), Al_2O_3 on p- and n-type FZ c-Si substrates. The effective surface recombination velocity S_{eff} has been measured within a window time of one year after activation of surface passivation. Results demonstrate that after an initial slight degradation during the first month S_{eff} values stabilize around 45 and 25 cm/s on p- and n-type black silicon samples respectively. These values are enough to guarantee stable high efficiency in interdigitated back-contacted c-Si(n) solar cells (> 24.5%) using black silicon nanostructures on the front side. The origin of this surface passivation degradation is still unclear but it might be due to a slight loss of field-effect passivation provided by the ALD Al_2O_3 films.

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References

[1] Otto M, Algasinger M, Branz H, Gesermann B, Gimpel T, Füchsel K, Käsebier T, Kontermann S, Koynov S, Li X, Naumann V, Oh J, Sprafke A. N, Ziegler J, Zilk M, Wehrspohn.Black silicon photovoltaics. Advanced optical materials; 2015; 3: 147-164.

[2] Savin H, Repo P, Von Gastrow G, Ortega P, Calle E, Garín M, Alcubilla R. “Black silicon solar cells with interdigitated back-contacts achieve 22.1% efficiency”. Nature Nanotechnology; 2015; 10: 624-628.

[3] Allen T, Bullock J, Cuevas A, Baker-Finch S, Karouta F. Reactive ion etched black silicon texturing: a comparative study. Proc. of 40th IEEE Photovoltaic Specialist Conference, Denver, USA, 2014, pp. 562-566.

[4] Von Gastrow G, Alcubilla R, Ortega P, Yli-koski M, Conesa-Boj S, Fontcuberta i Morral A, Savin H. Analysis of the atomic layer deposited Al2O3 field-effect passivation in black silicon. Solar Energy Materials & Solar cells; 2015; 142: 29-33.

[5] Ortega P, Calle E, Von Gastrow G, Repo P, Carrió D, Savin H, Alcubilla R. High-efficiency black silicon interdigitated back contacted solar cells on p-type and n-type c-Si substrates. Progress in Photovoltaics: Research and Applications; 2015; 23(11): 1448-1457.

[6] Richter A, Glunz S.W, Werner F, Schmidt J, Cuevas A. Improved quantitative description of Auger recombination in crystalline silicon. Physical Review B **86**, 165202 (2012).

[7] Dingemans G, Kessels WMM. Status and prospects of Al_2O_3-based surface passivation schemes for silicon solar cells. Journal of vacuum Science and Technology A; 2012; 30(4): 040802-1.

[8] Clugston DA, Basore P. PC1D Version 5: 32-bit Solar Cell Modelling on Personal Computers, 26th IEEE Photovoltaic Specialists Conference, Anaheim, USA, 1997, pp.207- 210.

[9] Cousins PJ, Smith DD, Luan HC, Manning J, Dennis TD, Waldhauer A, Wilson KE, Harley G, Mulligan GP. Gen III: improved performance at lower cost. 35th IEEE PVSC, Honolulu, HI, USA, 2010.

[10] Masuko K, Shigematsu M, Hashiguchi T, Fujishima D, Kai M, Yoshimura N, Yamaguchi T, Ichihashi Y, Mishima T, Matsubara N, Yamanishi T, Takahama T, Taguchi M, Maruyama E, Okamoto S. Achievement of more than 25% conversion efficiency with crystalline silicon heterojunction solar cell. IEEE Journal of Photovoltaics; 2014; 4(6): 1433-1435.