PASSIVATION OF SCREEN-PRINTED ALUMINIUM-ALLOYED EMITTERS FOR BACK JUNCTION N-TYPE SILICON SOLAR CELLS

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ABSTRACT: We present a detailed study on effectively surface-passivated aluminium-doped p^+ emitters to further enhance the efficiency of our *n*-type silicon solar cells featuring a full-area screen-printed Al-alloyed rear emitter. We investigated two different passivation layers both well suited for highly doped p^+ silicon: plasma-enhancedchemical-vapour-deposited amorphous silicon (a-Si) and atomic-layer-deposited aluminium oxide (Al₂O₃). We show that for an effective emitter passivation (i) a careful preparation of the emitter surface and (ii) low emitter thicknesses are essential. Combining these two aspects, we have achieved extraordinary high implied open-circuit voltages of 673 mV for a-Si- and 679 mV for Al₂O₃-passivated Al-alloyed emitters, corresponding to emitter saturation current densities of 128 fA/cm² and 89 fA/cm², respectively.

Keywords: Surface Passivation, Aluminium-alloyed Emitter, n-type Silicon Solar Cells

1 INTRODUCTION

Today's solar cell fabrication is mainly focused on cells produced of boron-doped crystalline silicon material. Yet the greatly growing solar cell market has entailed a feedstock shortage of *p*-type Si over the past years, directing the intention to *n*-type material. *n*-type Si provides superior electrical properties: higher and more stable diffusion lengths compared to *p*-type Si on account of a lower sensitivity to metallic impurities and many other non-metallic defects [1]. The two only companies, SunPower and Sanyo, producing high-efficiency solar cells today, use n-type Si wafers which underlines the large potential of this material for the application to industrial high-efficiency cells. Thus, a suitable solar cell fabrication process should yield high efficiencies. However, the high temperature boron diffusion needed for the formation of the p^+ emitter is technologically challenging and can lead to a severe degradation of the electronic bulk properties [2]. During recent years, aluminium alloying has become a promising alternative for the p^+ emitter formation of *n*-type back junction Si solar cells. For back junction Si solar cells featuring an easy-to-fabricate screen-printed Al_{p^+} emitter along with a high-efficiency front side, we have recently achieved efficiencies exceeding 20 %, demonstrating the high

potential of this n^+np^+ cell structure (Figure 1 (a), floatzone (FZ) Si, aperture area 4 cm²) [3]. Using a technological simplification of this structure featuring an industrially feasible front and rear side metallisation, we have already fabricated 18 % efficient large-area solar cells [4].

Although alloying of screen-printed aluminium is integrated in the processing sequence of conventional *p*-type silicon solar cells for a long time, there is only little knowledge on the demands on the Al-alloved region for an effective surface passivation, which is an important prerequisite for the fabrication of highefficiency n^+np^+ solar cells. Different kinds of passivation layers are appropriate for the application to highly Al-doped surfaces [3, 5, 6]: (i) amorphous silicon (a-Si) prepared by means of plasma-enhanced chemical vapour deposition (PECVD) [7] and (ii) aluminium oxide (Al₂O₃) produced by atomic layer deposition (ALD) [8]. Though both passivation layers have already been successfully applied to our $Al-p^+$ emitters, the precise demands on the Al emitter properties for a best possible surface passivation have not been examined in detail yet.

In this work, we focus on the properties of different screen-printed surface-passivated Al-alloyed emitters to further enhance the efficiencies of our n^+np^+ cells. These properties, e.g. the emitter depth and the doping profile,



Figure 1: (a) Structure of our high-efficiency n^+np^+ *n*-type Si solar cells with screen-printed aluminium-alloyed rear emitter. (b) Structure of the test samples used in this study for the characterisation of different Al- p^+ emitter profiles featuring an a-Si or Al₂O₃ passivation. Although using *p*-type boron-doped silicon as bulk material, we nevertheless refer to the Al- p^+ region as *emitter*.

play an important role for the cell performance as has been shown in simulations [9]. Our investigations hence concern two main issues: (i) the formation of the p^+ emitter affected by the firing conditions of the aluminium alloying process and (ii) the preparation of the Al-doped Si surface for a subsequent deposition of an a-Si or an Al₂O₃ passivation layer.

2 SAMPLE FABRICATION

2.1 Sample Structure

In the course of this study, we fabricated simple test structures to characterise the influence of the emitter thickness and the surface preparation on the effectiveness of the a-Si and Al_2O_3 passivation. A schematic cross section is displayed in Figure 1 (b).

2.2 Processing Sequence

The processing sequence of our test samples is shown in Figure 2. We used shiny-etched FZ silicon wafers with a resistivity of $100 \Omega cm$ as bulk material. Since the emitter properties do not depend on the kind of bulk doping, we chose p-type boron-doped silicon for evaluation reasons, nevertheless referring to the $Al-p^+$ region as emitter. After RCA cleaning, a PECVD SiN_x layer (refractive index 2.1) is deposited on the front side. Then, a commercially available aluminium paste (Ferro 5540) is screen-printed on the entire rear surface and dried to remove the solvents. The emitter is alloyed during a firing step in a conveyor belt furnace at a peak temperature of 900 °C and, at the same time, the SiN_x layer is annealed for an increase of the front surface passivation. We prepared four different $Al-p^+$ emitter profiles by varying the peak temperature time t_{peak} from 5 s to 8 s. Paste residuals and the Al-Si eutectic layer are subsequently etched off in hydrochloric acid [10]. KOH solution is used to prepare the surface for the subsequent passivation, see section 3.2. Four different etching times t_{etch} from 0 s to 180 s are applied here. Then, the emitter is passivated by a PECVD a-Si or an ALD Al₂O₃ layer with thicknesses ≥ 30 nm. In conclusion, the Al₂O₃coated samples are annealed in a forming gas ambient at a temperature of 425 °C.

2.3 Sample Characterisation

Quasi-steady-state photoconductance (QSSPC) measurements [11] were performed to determine the total saturation current density J_0 of our test samples under high injection conditions [12, 13] and at an evaluation temperature of 300 K. To investigate the Al- p^+ emitter under similar conditions as in its solar cell application, we use an asymmetric test sample structure (Figure 1 (b)). Therefore, J_0 consists of a sum of the differing contributions from the SiNx front and the emitter/a-Si or emitter/Al2O3 rear side. By means of reference samples, which are SiN_x-coated on both sides, the Al- p^+ emitter saturation current density $J_0^{\text{Al-}p+}$ can be determined from J_0 measurements. Alternatively, the implied open-circuit voltage $V_{oc,impl}$ can be calculated by assuming a short-circuit current density J_{sc} of 38 mA/cm² which is a lower boundary value for this kind of cell structure [3]:

$$V_{oc,impl} = \frac{kT}{q} \ln \left(\frac{J_{sc}}{J_0^{Al-p^+} + J_0^{SiN_x}} + 1 \right)$$



Figure 2: Processing sequence of our test samples for the characterisation of surface-passivated $Al-p^+$ emitters.

In addition, scanning electron microscope (SEM) pictures were taken to examine the thickness and the surface structure of the Al-alloyed emitters. Electrochemical capacitance voltage (ECV) measurements were carried out to detect the aluminium doping profiles.

3 RESULTS AND DISCUSSION

3.1 Non-passivated $Al-p^+$ Emitters

The peak temperature time for alloying directly corresponds to the depth of the Al emitter [10]. To evaluate this dependency, cross-sectional SEM images of the Al-alloyed emitter after removal of the paste matrix and the Al-Si eutectic were investigated, see Figure 3. The interface between the Al- p^+ emitter and the *p*-type bulk is clearly visible due to the potential contrast and can therefore be used for thickness measurements.

Figure 4 (a) shows the emitter depth as a function of the peak temperature time t_{peak} . The longer t_{peak} , the more silicon dissolves in the molten aluminium paste during the alloying process and the more silicon recrystallises epitaxially while cooling down afterwards [10].



Figure 3: Cross-sectional SEM image of a screen-printed Al-alloyed p^+ emitter. After removal of the paste matrix and the Al-Si eutectic, Al-containing crystalline structures remain on the surface.



Figure 4: (a) Emitter thickness and (b) implied opencircuit voltage of non-passivated Al emitters as a function of the peak temperature time. One symbol represents a measurement on one sample. Error bars in (a) arise from thickness measurements on 15 to 20 different positions on the samples. Lines are guides to the eye.

Therefore, the thickness of the $Al-p^+$ region increases with the peak temperature time.

The influence of the emitter thickness on the implied open-circuit voltage is shown in Figure 4 (b). With increasing thickness, the shielding effect of the highly Al-doped region improves, preventing electrons from reaching the recombination active surface and leading to increased $V_{oc,impl}$ values. For non-passivated Al-alloyed emitters, high emitter thicknesses are therefore advantageous. We have achieved $V_{oc,impl}$ values of 648 mV without passivation for a peak temperature time of 8 s, which corresponds to an emitter thickness of 12 µm.



Figure 5: ECV doping profile measurements of an Al-alloyed emitter ($t_{\text{peak}} = 6 \text{ s}$) (a) without etching, (b) after 20 s, (c) after 80 s and (d) after 180 s KOH etching.

3.2 Surface Preparation

The abrupt solidification of the Al-Si melt at the eutectic temperature leads to the formation of crystalline structures on the emitter surface, which contain aluminium inclusions [14], see Figure 3. To remove these structures and to successively etch off the Al-doped surface region, we used KOH solution with an etch rate of 1.3 µm/min. Figure 5 displays ECV doping profiles of the Al-alloyed emitters that were exposed to KOH etching for different times. Additionally, to examine the effect of etching on the surface properties, SEM pictures of the differently etched emitter surfaces were taken, see Figure 6. Before etching, Al-containing pyramidal structures in different sizes and in groups or strings cover the emitter surface (Figure 6 (a)). With increasing etching time, these structures are underetched (20 s, Figure 6 (b)) and totally removed for persistent etching (exceeding 80 s, Figure 6 (c)), resulting in a smooth surface.

3.3 Passivated Al- p^+ Emitters

Figure 7 shows the implied open-circuit voltage for differently etched, a-Si- and Al₂O₃-passivated Al emitter surfaces. It is clearly visible that the surface preparation strongly influences the passivation properties. Al- p^+ emitters which still possess the pyramidal Al-containing structures show an equivalent $V_{\text{oc,impl}}$ developing as the non-passivated emitters with only a slight shift upwards of approximately 5 to 10 mV, compare to Figure 4.



Figure 6: SEM pictures of the Al-alloyed emitter surface in dependence of the etching time in KOH solution: (a) without etching, (b) after 20 s etching and (c) exceeding 80 s etching. A well-prepared surface is essential for an effective passivation.



Figure 7: Implied open-circuit voltage after 0, 20, 80 and 180 s KOH etching and passivation with a-Si or Al_2O_3 layers. Encircled values indicate best $V_{oc,impl}$ for emitter thicknesses of 3 µm after etching. Lines are guides to the eye.

Emitter surfaces still featuring the Al-containing structures cannot be passivated very effectively. However, if those structures are removed, the a-Si and Al₂O₃ coatings greatly improve the implied open-circuit voltage. Henceforth, there is a clear trend to enhanced surface passivation for decreasing emitter thicknesses. On the one hand thinner $Al-p^+$ emitters exhibit a lower electron shielding effect, on the other hand the recombination within the emitter bulk is reduced. Since the emitter surface is very effectively passivated by the a-Si or Al₂O₃ films, the reduced shielding effect is hardly noticeable. The diminished emitter recombination though leads to improved implied open-circuit voltages towards low emitter thicknesses. Therefore, $V_{oc,impl}$ is only increased up to 12 mV (a-Si) and 18 mV (Al2O3) for 8 µm thick emitters (12 µm before etching), but up to 33 mV (a-Si) and 41 mV (Al₂O₃) for an emitter thickness of 3 µm (7 µm before etching).

Combining thin Al- p^+ emitters and etching times long enough to remove the Al-containing structures, we have achieved $V_{oc,impl}$ values of 673 mV for a-Si- and 679 mV for Al₂O₃-passivated 3 µm thick Al-alloyed emitters. This corresponds to extraordinary low emitter saturation current densities of 128 fA/cm² for a-Si- and 89 fA/cm² for Al₂O₃-passivated Al- p^+ emitters.

4 SUMMARY

We have investigated the requirements on the properties of screen-printed aluminium-alloyed emitters for an effective surface passivation by PECVD a-Si or ALD Al₂O₃ layers. Simple lifetime test structures featuring a front side SiN_x and a rear Al- p^+ emitter were fabricated for this purpose.

For non-passivated $Al-p^+$ emitters the implied opencircuit voltage rises with increasing emitter thickness. We have obtained $V_{oc,impl}$ values up to 648 mV for a thickness of 12 µm.

Before the deposition of an additional passivation layer on the emitter to further increase $V_{oc,impl}$, a careful surface preparation is essential. This was accomplished by etching the samples in KOH solution. After removing Al-containing crystalline structures, arising on the emitter surface during the alloying process, the passivation quality improves with decreasing emitter thickness. Therefore, particularly thin Al- p^+ emitters feature excellent electronic properties. We have achieved implied open-circuit voltages of 673 mV for a-Si- and 679 mV for Al₂O₃-passivated 3 µm thick Al-alloyed emitters, corresponding to emitter saturation current densities of 128 fA/cm² and 89 fA/cm², respectively. To our knowledge, these are the lowest emitter saturation current densities for screen-printed Al-alloyed emitters reported so far.

By implementing these optimised passivated $Al-p^+$ emitters into our n^+np^+ back junction solar cells, we expect efficiencies significantly above 20 %. Beyond *n*-type solar cells, the results of this study are of interest for an efficiency increase of *p*-type silicon solar cells with a commonly used Al back surface field.

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