Effective passivation of highly aluminum-doped *p*-type silicon surfaces using amorphous silicon

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Highly aluminum-doped *p*-type emitters prepared by screen printing on crystalline silicon wafers are effectively passivated by plasma-enhanced chemical-vapor deposited amorphous silicon layers. Using the photoconductance decay technique, the authors measure emitter saturation current densities of 800 ± 200 fA/cm^2 for nonpassivated emitters and of 490 ± 120 fA/cm^2 for Al-p^+ emitters passivated with a 20 nm thick amorphous silicon layer deposited at 225 °C. An additional annealing step at 300 °C for 10 min reduces the emitter saturation current density down to only 246 ± 60 fA/cm^2. The measured saturation current densities are the lowest values achieved so far for Al-doped p^+ emitter. © 2007 American Institute of Physics. [DOI: 10.1063/1.2784193]

The main reason of still using *p*-type instead of *n*-type crystalline silicon wafers in today's solar cell production is the technological simplicity of the phosphorus diffusion process of the n^+ emitter. The high-temperature boron diffusion of p^+ emitters has in the past mainly been used in the fabrication of high-efficiency laboratory solar cells, because it is technologically more demanding and tends to induce crystallographic defects in the bulk material, degrading its recombination lifetime.[1,2] However, within recent years technological alternatives to the boron diffusion have appeared, which might allow a simplified p^+ emitter fabrication on *n*-type silicon wafers.[3,4] In this letter, we evaluate and extend the potential of one of these approaches, which is based on a simple screen-printing process of an aluminum paste to form a rear p^+ emitter in *n*-type silicon solar cells. For such Al-p^+ structures, emitter saturation current densities (J_{0e}) in the range from 630 to 2200 fA/cm^2 have been reported in the literature.[5–9] We demonstrate outstanding surface passivation of the screen-printed Al-p^+ region by means of low-temperature-deposited amorphous silicon (*a*-Si) thin films, leading to implied solar cell open-circuit voltages of 667 mV.

We use single-crystalline shiny-etched (100)-oriented 300 μm thick *p*-type float-zone (FZ) silicon wafers of 200 Ω cm resistivity. For the J_{0e} measurements we fabricate asymmetric test structures, where the p^+ emitter is prepared on one side of the wafer and the other surface of the sample is passivated with plasma-deposited silicon nitride (SiN$_x$). After RCA cleaning we deposit a 100 nm thick SiN$_x$ layer by means of remote-plasma enhanced chemical vapor deposition (PECVD).[10] Subsequently, Ferro 5540 (paste A) and DuPond PV322 (paste B) nonfritted aluminum pastes are screen printed onto the opposite surface with an amount of ~8 mg/cm^2. After drying the screen-printed samples at 150 °C for 5 min to vaporize the organic solvents in the Al pastes, the Al-p^+ region is formed in an infrared conveyor belt furnace at 900 °C for 13 s. Additionally, the high-temperature firing step improves the passivation quality of the SiN$_x$ film, achieving surface recombination velocities $S_{\mathrm{SiN}} \lesssim 10$ cm/s after the firing step.[11] In order to passivate the p^+ surface, the residue of the aluminum paste and the aluminum-silicon eutectic are removed from the Al-p^+ region in a boiling 37% solution of hydrochloric acid. Finally, the screen-printed Al-p^+ emitter is passivated by a 20 nm thick *a*-Si film deposition at a deposition temperature of 225 °C in a Plasmalab 80 PECVD reactor from Oxford Plasma Technology. Emitter saturation current densities J_{0e} are obtained from transient photoconductance decay (PCD) measurements using a WCT-100 lifetime tester from Sinton Consulting.[12] From the measured injection-dependent lifetime data we extract the emitter saturation current density J_{0e} by plotting the reciprocal effective lifetime $1/\tau_{\mathrm{eff}}$ versus the excess carrier concentration Δn using the equation[13]

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau_{\mathrm{bulk}}} + \frac{S_{\mathrm{SiN}}}{W} + \frac{J_{0e}\Delta n}{q n_i^2 W}, \qquad (1)$$

where W is the wafer thickness and $n_i = 1 \times 10^{10}$ cm^{-3} is the intrinsic carrier concentration of silicon at 300 K. It is assumed that the excess carrier concentration Δn is uniform throughout the base, which is not strictly valid for large surface recombination velocities. Due to the given asymmetry between the front and the rear side of the sample the emitter saturation current density tends to be underestimated up to 10% for the worst-case scenario.[13] Due to the high substrate resistivity of 200 Ω cm, all lifetime measurements in this study are performed under high-injection conditions. To verify the PCD results, we also performed quasi-steady-state measurements[12] on the same samples, which resulted in the same J_{0e} values as the PCD measurments within a range of ±5%.

Figure 1(a) shows a cross-sectional scanning electron microscopy (SEM) picture of a screen-printed Al-p^+ sample obtained from an ultrahigh resolution Hitachi S-4800 field emission SEM. The Al-doped p^+ region appears brighter than the high-resistivity bulk of the silicon wafer due to the potential contrast.[14] From this picture we determine the Al-p^+ depth to be 8 ± 1 μm. Figure 1(b) shows a SEM micrograph of the deposited *a*-Si layer on top of the Al-p^+ region. The *a*-Si layer thickness is determined from this micrograph to be 20 ± 2 nm.

Figure 2 shows the measured doping profile of the Al-p^+ region obtained by the electrochemical capacitance voltage
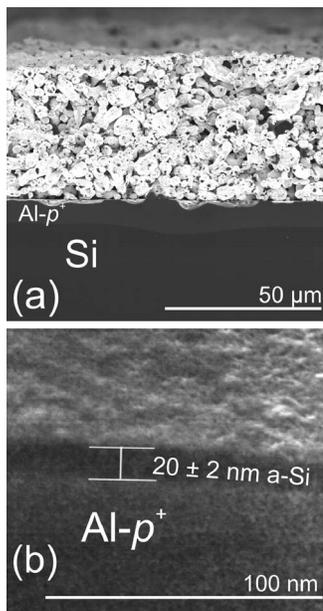
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FIG. 1. (a). SEM micrograph of a cross section of a screen-printed Al-p^+ emitter. The Al-p^+ region is clearly visible as brighter contrast below the residual Al paste. The emitter thickness is 8 ± 1 μm. (b) SEM micrograph of a cross section of the Al-p^+ region after etching off the Al and the Al–Si eutectic as well as 3 μm of the Si. The surface is passivated with a 20 ± 2 nm thick a-Si layer.

(ECV) profiling technique with the aid of a WEP CVP21 ECV profiler. The doping profile of the screen-printed Al-p^+ region shows a pronounced peak close to the surface that probably originates from residual aluminum-rich ($\sim$1 at. % Al content as determined by energy dispersive x-ray analysis) structures on the surface which are not effectively removed during the HCl etching.[15] This concentration peak can be removed in KOH solution at 70 °C. In our experiments, 3 μm of the 8 ± 1 μm thick Al-p^+ region are etched off, which is demonstrated in Fig. 2 by ECV measurements taken before and after KOH etching. The emitter thickness after KOH etching was determined from SEM micrographs at different sample positions to be 5 ± 1 μm, indicating that the Al-p^+ emitter is completely closed after etching. The sheet resistance is determined from four-point-probe measurements to be 50 $\Omega/\square$ for the 8 μm deep emitter and to be 70 $\Omega/\square$ for the 5 μm deep Al-p^+ emitter.

Figure 3 shows the measured inverse effective lifetime $1/\tau_{eff}$ as a function of the injection density Δn for the same
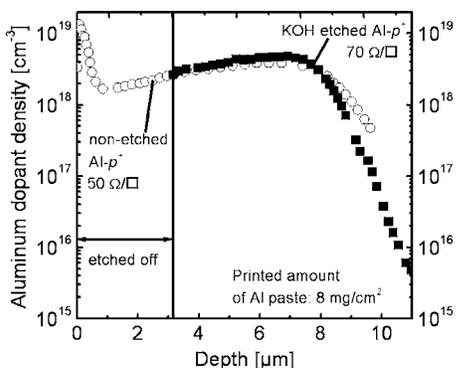

FIG. 2. Doping profiles of the same screen-printed Al-p^+ emitter before and after etching in KOH, measured by ECV profiling. During the etching $\sim$3 μm of the silicon is removed.

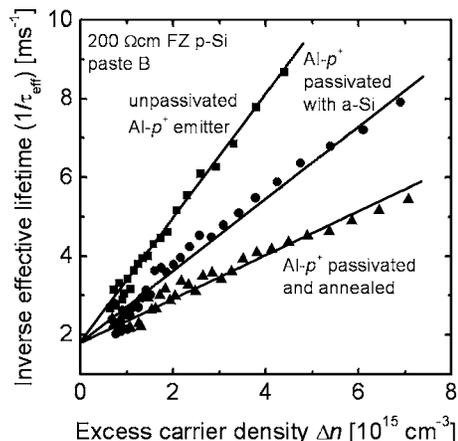FIG. 3. Measured inverse effective lifetime $1/\tau_{eff}$ as a function of the excess carrier density Δn of a 200 Ω cm FZ p-Si wafer. The Al-p^+ region covers only one side of the wafer; the other surface is well passivated by SiN$_x$.

sample in three different states exemplarily for paste B. The steepest slope is obtained directly after the Al paste and the Al–Si eutectic have been etched off and 3 μm of the p^+ region have been removed. Using a linear fit of Eq. (1) to the measured data results in an emitter saturation current density of $J_{0e} = 800 \pm 200$ fA/cm^2. Note that before KOH etching we measure a J_{0e} of 680 ± 170 fA/cm^2. This lower J_{0e} value results from the doping peak at the surface, effectively reducing the surface recombination rate. After 20 nm a-Si deposition on the KOH-etched emitter a significant reduction in the slope can be observed, resulting in a J_{0e} value of 490 ± 120 fA/cm^2. Finally, the lowest slope is measured for the sample after an additional 300 °C annealing for 10 min, resulting in a J_{0e} value of only 246 ± 60 fA/cm^2. The experimental results in Fig. 3 prove that screen-printed Al-p^+ emitters can be very effectively passivated with low-temperature deposited amorphous silicon films.

In addition to the measured J_{0e} values, the implied open-circuit voltage is calculated using the expression

$$V_{oc,impl} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_{0e}} + 1\right), \qquad (2)$$

where $kT/q = 25.86$ mV at 300 K and a realistic short-circuit current density J_{sc} of 38.6 mA/cm^2 is assumed. The latter J_{sc} value has recently been achieved on n-type Si solar cells with a screen-printed Al-p^+ emitter.[4] Using the J_{0e} of 680 ± 170 fA/cm^2, we calculate a $V_{oc,impl}$ of 640 ± 6 mV for the nonpassivated Al-p^+ surface. This is quite high compared to experimentally realized n-type Si solar cells with Al-p^+ emitter showing maximum V_{oc} values of 627 mV.[4] This may be due to the Al paste and the Al–Si eutectic that remained on the p^+ emitter surface in these cells, increasing the surface recombination velocity on the Al-p^+ surface, whereas our emitter surface is free from metallic residuals and thus may result in lower J_{0e} values.

Figure 4 shows the effect of low-temperature annealing on the emitter saturation current of a-Si passivated screen-printed Al-p^+ emitters. The annealing was interrupted minute by minute for the lifetime measurements. Both pastes in this study behave similarly. Before annealing we measure J_{0e} values of 576 ± 144 fA/cm^2 for paste A and of 490 ± 120 fA/cm^2 for paste B. After only 1 min of annealing at 300 °C a pronounced decrease in J_{0e} to 371 ± 92 fA/cm^2 for paste A and 328 ± 82 fA/cm^2 for paste B is observed.

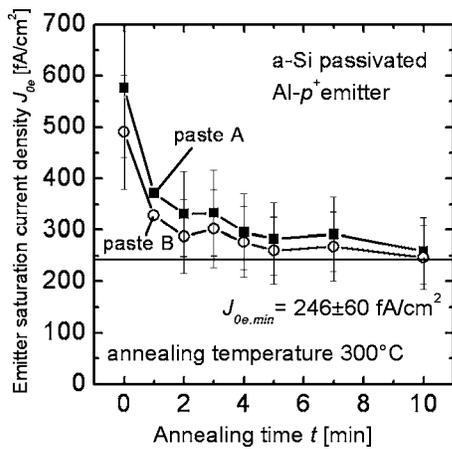FIG. 4. Impact of annealing time at 300 °C on the emitter saturation current density J_{0e} of an a-Si passivated Al-p^+ emitter. An annealing period of 10 min at 300 °C gives a minimum saturation current density of $J_{0e.\min}$ =246±60 fA/cm^2.

Annealing up to 10 min gives a minimal measured J_{0e} of only 258±64 fA/cm^2 for paste A and 246±60 fA/cm^2 for paste B. These are the lowest J_{0e} values achieved so far for screen-printed Al-p^+ emitters. Note that a similar annealing effect as shown in Fig. 4 has recently been reported for a-Si-passivated boron-doped p^+ emitters.[16,17] The minority-carrier surface recombination velocity S_{n0} is extracted using PC1D simulations. In these simulations, it is assumed that the bulk of the Al-p^+ region is Auger limited. We determine the S_{n0} to be $\geqslant 5 \times 10^4$ cm/s for the unpassivated surface. For the a-Si passivated and annealed Al-p^+ emitter with the measured J_{0e} of 246±60 fA/cm^2 a surface recombination velocity S_{n0} between 7000 and 13 000 cm/s is calculated. A minimum S_{n0} value of 800 cm/s has recently been published for a-Si-passivated boron-doped p^+ emitters at comparable sheet resistance.[18] However, regarding the much lower complexity of forming a screen-printed Al-p^+ emitter, the S_{n0} values achieved in this study are still remarkably low. Our lowest measured J_{0e} values correspond to implied open-circuit voltages of $V_{\text{oc.impl}}$=667±6 mV for paste A and $V_{\text{oc.impl}}$=665±6 mV for paste B, clearly demonstrating the high-efficiency potential of a-Si passivated screen-printed Al-p^+ emitters. Electrical contacts to the a-Si passivated emitter could, e.g., be made by evaporating an Al grid and annealing it at low temperature.[19]

We attribute the observed excellent passivation properties of a-Si films on Al-p^+ surfaces to the high degree of interface passivation with atomic hydrogen. From *in situ* spectroscopic ellipsometry and infrared spectroscopy it is known that a 30 Å thick a-Si layer with very high hydrogen content ($\sim$17 at. %) forms at the c-Si surface during deposition.[20] A part of this hydrogen effectively saturates dangling bonds at the a-Si/c-Si interface, reducing interface recombination. During annealing some of the hydrogen is released from the a-Si layer and diffuses toward the interface, where it passivates additional dangling bonds.

In conclusion, we have demonstrated that it is possible to passivate screen-printed Al-p^+ regions by means of amorphous silicon. Emitter saturation current densities of 490 fA/cm^2 were achieved by depositing 20 nm thick a-Si layers on etched Al-p^+ emitters. After annealing at 300 °C, the emitter saturation current densities decreased to 246 fA/cm^2. The outstanding passivation properties of a-Si on screen-printed Al-p^+ emitters have been attributed to the saturation of dangling bonds at the a-Si/c-Si interface by hydrogen originating from the a-Si layer.

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