Low Surface Recombination Velocity using amorphous Silicon on industrial-type cleaned Surfaces

S. Gloger*, N. Brinkmann, B. Terheiden

University of Konstanz, Department of Physics, P.O. Box X916, 78457 Konstanz, Germany

Abstract

The surface passivation ability of a hydrogenated amorphous silicon (a-Si:H) layer is investigated on industrial-type cleaned p-type (2 Ω cm) FZ and Cz silicon wafers. The cleaning sequence consists of laser/saw damage removal and immersions in aqueous HCl and HF solutions. After this cleaning an effective surface recombination velocity $S_{\text{eff}}$ of 1.0 cm/s is achieved with a deposited and annealed a-Si:H-layer. No RCA or similar elaborate cleaning steps are needed to achieve this low surface recombination velocity. After a firing step in a belt furnace at a wafer temperature of up to 670°C the passivation ability of the a-Si:H layer is fully restored during hydrogen annealing. It is shown that the amount of silicon hydrogen bonds in the a-Si:H layer is correlated to the degradation and recovery of the passivation quality of the a-Si:H layer.

Keywords: Passivation; hydrogenated amorphous silicon; industrial cleaning

1. Introduction

A sufficient surface passivation is needed for highly efficient crystalline silicon (c-Si) single-junction solar cells [1]. For this task the passivation of p-type c-Si surfaces with hydrogenated amorphous silicon (a-Si:H) is a promising alternative to hydrogenated amorphous silicon nitride (a-SiNₓ:H), since the passivation using silicon nitride is reduced due to parasitic shunting on contacted p-type c-Si surfaces [2]. As for screen printed metallization concepts the surface passivation has to be satisfactory after a firing step, it must be thermally stable or restorable after firing. The passivation achieved with an a-Si:H layer is

* Corresponding author. Tel.: +49-7531-88-2074; fax: +49-7531-88-3895.
E-mail address: sebastian.gloger@uni-konstanz.de.

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not thermally stable [3,4], but can be partly restored during an annealing after a firing step, which is shown in the following.

2. Experimental

Two groups of symmetrical lifetime samples are manufactured. For the first group p-type FZ silicon substrates (50×50 mm²) with a resistivity of 2.0 Ω cm and a thickness of 490 and 510 μm are used. For the second group p-type Cz silicon substrates (50×50 mm²) with a resistivity of 2 Ω cm and a thickness of 185 μm (if not otherwise stated) are used.

In the first step the saw damaged surfaces of the Cz-Si samples are removed in diluted NaOH at a temperature of 80°C and the laser damaged edges of the FZ-Si samples are removed in a chemical polishing solution consisting of nitric acid, acetic acid and fluoric acid at room temperature. Afterwards all samples undergo an industrial-type cleaning sequence, consisting of an immersion in diluted HCl and in diluted HF at room temperature. Before and after these immersions the samples are rinsed with deionized water.

A direct plasma enhanced chemical vapor deposition (PECVD) of an intrinsic a-Si:H layer at a set temperature of 225°C using an Oxford PlasmaLab tool follows the cleaning. The thickness of the a-Si:H layer is 105±15 nm for the FZ-Si samples. This value is measured with a scanning electron microscope. For the Cz-Si samples an a-Si:H layer thickness of 35 nm is deduced from the deposition rate. Two batches of the Cz-Si samples receive an additional capping layer. A PECVD a-SiNₓ:H layer with a thickness of 75 nm or a PECVD a-SiCₓ:H layer with a thickness of 60 nm are deposited at a set temperature of 350°C as capping layer.

After the deposition all samples are thermally annealed at a set temperature of 425°C for 16 min to activate the surface passivation by the a-Si:H layer. One batch of samples is fired in an industrial-type belt furnace using a firing profile for front side metallization with peak temperatures varying from 500°C to 800°C. The peak temperatures are determined on the wafer surface. Another batch of samples is thermally annealed at a set temperature of 530°C while the duration is varied. These temperature steps lead to a degradation of the passivation quality of the a-Si:H layer.

Subsequently all samples are annealed in a microwave induced remote hydrogen plasma (MIRHP) reactor [5] to restore the passivation quality of the a-Si:H layer. This annealing is carried out at a set temperature of 370°C for 40 min in an atmosphere consisting of molecular and atomic hydrogen or molecular nitrogen at a reduced pressure.

To examine the passivation quality of the a-Si:H layer after each process step, the effective minority carrier lifetime \( \tau_{\text{eff}} \) of the sample is determined by photoconductance measurements at an excess minority carrier density of \( 1 \times 10^{15} \text{ cm}^{-3} \). For lifetimes higher than 100 μs a photoconductance decay measurement (PCD) is used, while for lifetimes lower than 100 μs a quasi-steady-state photoconductance measurement (QSSPC) is carried out using a Sinton WCT-120 lifetime tester. The effective surface recombination velocity (SRV) \( S_{\text{eff}} \) is extracted from these measurements using \( S_{\text{eff}} = 0.5 \text{ W} (\tau_{\text{eff}}^{-1} - \tau_{\text{bulk}}^{-1}) \) [6]. For the FZ-Si samples an Auger recombination limited bulk lifetime of \( \tau_{\text{bulk}} = 8.0 \text{ ms} \) is assumed, applying the Auger parameterization of [7]. With this value an upper limit for \( S_{\text{eff}} \) is obtained. For the Cz-Si samples a bulk lifetime of \( \tau_{\text{bulk}} = 700 \mu\text{s} \) is assumed.

To relate the bonded hydrogen content of the a-Si:H layer to its passivation ability, Fourier transform infrared spectroscopy measurements (FTIR) are carried out to determine the infrared absorption of the FZ-Si samples after each process step. As a measure for the amount of bonded hydrogen in the a-Si:H layer the baseline corrected IR absorption of the samples is integrated in the interval 550-750 cm\(^{-1}\) (rocking and wagging modes of silicon hydrogen bonds) and in the interval 1900-2200 cm\(^{-1}\) (stretching modes of silicon hydrogen bonds).
3. Results

Directly after the PECVD a-Si:H deposition and a following activation of the passivation by annealing the FZ-Si samples show surface recombination velocities down to $S_{\text{eff}} = 1.0 \text{ cm/s}$ ($\tau_{\text{eff}} = 6.1 \text{ ms}$). For the Cz-Si samples minority carrier lifetimes up to $\tau_{\text{eff}} = 417 \mu\text{s}$ are achieved ($W = 85 \mu\text{m}$) corresponding to $S_{\text{eff}} = 4.1 \text{ cm/s}$.

The lifetimes obtained from photoconductance measurements before the firing step, after the firing step and after a following hydrogen annealing are shown in Fig. 1 (a) for the FZ-Si samples with an a-Si:H layer, in Fig. 1 (b) for the Cz-Si samples with an a-Si:H layer, in Fig. 2 (a) for the Cz-Si samples with an a-Si:H/a-SiNx:H layer stack and in Fig. 2 (b) for the Cz-Si samples with an a-Si:H/a-SiCx:H layer stack.

![Graph showing lifetimes and surface recombination velocities](image)

**Fig. 1.** (a) Minority carrier lifetime $\tau_{\text{eff}}$ of FZ-Si samples with an a-Si:H layer shown as a function of the peak firing temperature (determined at the wafer surface) before firing, after firing and after subsequent hydrogen annealing. Each point represents the lifetime of one sample receiving the respective firing step measured at an excess minority carrier density of $1 \times 10^{15} \text{ cm}^{-3}$. (b) Same quantity shown for Cz-Si samples with an a-Si:H layer.

![Graph showing lifetimes and surface recombination velocities](image)

**Fig. 2.** (a) Minority carrier lifetime $\tau_{\text{eff}}$ of Cz-Si samples with an a-Si:H/a-SiNx:H layer stack shown as a function of the peak firing temperature (determined at the wafer surface) before firing, after firing and after subsequent hydrogen annealing. Each point represents the lifetime of one sample receiving the respective firing step measured at an excess minority carrier density of $1 \times 10^{15} \text{ cm}^{-3}$. (b) Same quantity shown for Cz-Si samples with an a-Si:H/a-SiCx:H layer stack.

The surface recombination velocity of the samples fired at low temperatures is not affected by the firing step. The following annealing does not improve the lifetime of these samples. The surface
passivation of the samples fired at increasing temperatures is progressively reduced by the firing step. The passivation by an a-Si:H/a-SiNx:H layer stack withstands a higher temperature than the passivation by an a-Si:H layer alone. An a-Si:H/a-SiCx:H layer stack leads not to improved thermal stability of the passivation.

The surface passivation of a degraded a-Si:H layer is partly restored (for the FZ-Si samples fired at a peak temperature of 582-660°C) or fully restored (for the Cz-Si samples fired at a peak temperature of 613-670°C) during the subsequent hydrogen annealing, while it is only marginally restored for an a-Si:H/a-SiNx:H layer stack and an a-Si:H/a-SiCx:H layer stack (see Fig. 1 (a), (b) and 2 (a), (b)). Annealing in nitrogen atmosphere does not reduce the surface recombination velocity of a degraded a-Si:H layer in contrast to annealing in hydrogen atmosphere (not depicted here).

An a-Si:H layer fired at high temperatures loses its passivation ability during the firing step, which is only marginally restored during the following hydrogen annealing. The differences between the temperatures, at which the a-Si:H layers on the FZ- and Cz-Si samples show the same decreased SRV, might occur due to the higher thermal mass of the FZ-Si samples, leading to a longer exposure to elevated temperatures during firing compared to the thinner Cz-Si samples.

The lifetimes obtained from photoconductance measurements before thermal annealing at a temperature of 530°C, after this thermal annealing and after the following hydrogen annealing are shown in Fig. 3 (a) for FZ-Si samples with an a-Si:H layer and in Fig. 3 (b) for Cz-Si samples with an a-Si:H layer and Cz-Si samples with an a-Si:H/a-SiNx:H layer stack. The surface passivation of the samples thermally annealed at a set temperature of 530°C for increasing durations is progressively reduced by this annealing. As for the fired samples the surface passivation is partly (for the FZ-Si samples) or fully (for the Cz-Si samples) restored during hydrogen annealing for the a-Si:H layer, while it is only marginally restored for the a-Si:H/a-SiNx:H layer stack (see Fig. 3 (a), (b)).

The IR absorption obtained from FTIR measurements of FZ-Si samples is shown in Fig. 4 in relation to the IR absorption of the respective samples before firing. In Fig. 4 (a) this ratio is shown after a firing step with varied peak temperature and after subsequent hydrogen annealing. In Fig. 4 (b) the ratio is shown after thermal annealing at a set temperature of 530°C.

With increasing firing temperature the amount of hydrogen silicon bonds in the a-Si:H layer is progressively reduced during the firing step. Hydrogen annealing increases the IR absorption of the a-

![Figure 3](image1.png)

![Figure 4](image2.png)
Si:H layer by an average value of 0.16 times the value of the particular layer before firing for the interval 550-750 cm\(^{-1}\). For the interval 1900-2200 cm\(^{-1}\) hydrogen annealing increases the IR absorption by an average value of 0.21 times the value of the particular layer before firing. Annealing in nitrogen atmosphere increases the IR absorption for both intervals by an average value of less than 0.01 times the value of the particular layer before firing (not depicted here).

Fig. 4. (a) IR absorption of the FZ-Si samples after firing and after subsequent hydrogen annealing shown relative to the IR absorption of the respective samples before firing. This ratio is displayed as a function of the peak firing temperature (determined at the wafer surface). Each filled symbol represents the value of the IR absorption integrated baseline corrected in the interval 550-750 cm\(^{-1}\) for one sample while the empty symbols represent the values for the interval 1900-2200 cm\(^{-1}\). (b) Same quantity shown for FZ-Si samples after thermal annealing at a set temperature of 530°C and after subsequent hydrogen annealing.

With increasing duration of thermal annealing at a set temperature of 530°C, the amount of hydrogen silicon bonds in the a-Si:H layer is also progressively reduced during annealing. Hydrogen annealing increases the IR absorption of the a-Si:H layer by an average value of 0.42 times the value of the particular layer before firing for the interval 550-750 cm\(^{-1}\). For the interval 1900-2200 cm\(^{-1}\) hydrogen annealing increases the IR absorption by an average value of 0.54 times the value of the particular layer before firing.

The amount of hydrogen silicon bonds in the a-Si:H layer is already reduced during activation of the passivation by annealing. The IR absorption after activation of the passivation by annealing is reduced to a fraction of 0.68 compared to the value directly after the deposition for the interval 550-750 cm\(^{-1}\) (not shown here). For the interval 1900-2200 cm\(^{-1}\) the IR absorption after activation of the passivation by annealing is reduced to a fraction of 0.56 compared to the value directly after the deposition (not depicted here).

4. Conclusion

A surface passivation with a surface recombination velocity of \(S_{\text{eff}} = 1.0\) cm/s is achieved with an annealed a-Si:H-layer on a p-type 2\(\Omega\)cm FZ-Si substrate after an industrial-type cleaning. On a Cz-Si substrate of the same doping type and resistivity a surface recombination velocity of \(S_{\text{eff}} = 4.1\) cm/s is achieved with an annealed a-Si:H-layer. No RCA or similar elaborate cleaning steps are needed to achieve these low surface recombination velocities.

After a firing step in a belt furnace at peak wafer temperatures up to 670°C the passivation quality of an a-Si:H layer is fully restored for the Cz-Si substrate by means of hydrogen annealing. Also after thermal annealing at a set temperature of 530°C for up to 64 min the passivation quality of an a-Si:H layer is fully restored during hydrogen annealing.
During firing steps at elevated temperatures and annealing at 530°C for prolonged duration the amount of silicon hydrogen bonds in an a-Si:H layer is decreased. This finding is in accordance to measurements presented in [8]. During hydrogen annealing the amount of silicon hydrogen bonds is increased again by an atmosphere of molecular and atomic hydrogen, as shown in [8]. This increase of silicon hydrogen bonds leads to a recovery of the passivation quality for an a-Si:H layer degraded by thermal annealing at a set temperature of 530°C or firing at temperatures of 580-670°C. For an a-Si:H layer degraded at higher firing temperatures the passivation quality is only marginally restored by hydrogen annealing. Using lower firing temperatures the passivation is not degraded by firing and therefore not improved by hydrogen annealing.

We assume that firing at temperatures above 760°C deteriorates the abruptness of the a-Si:H/c-Si interface [9], so that hydrogen is detained from being bonded at the a-Si:H/c-Si interface and thus rehydrogenation of the interface is hindered.

An a-SiNₓ:H capping layer increases the thermal stability of the passivation of an a-Si:H layer, although not to the extent shown in [4]. Also an a-SiNₓ:H capping layer acts as diffusion barrier for hydrogen and inhibits a recovery of a thermally degraded a-Si:H layer by hydrogen annealing. An a-SiCₓ:H capping layer does not increase the thermal stability of the passivation of an a-Si:H layer, but acts as diffusion barrier for hydrogen like an a-SiNₓ:H capping layer and inhibits a recovery of an a-Si:H layer by hydrogen annealing after thermal degradation.

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