



Firing stability of $\text{SiN}_y/\text{SiN}_x$ stacks for the surface passivation of crystalline silicon solar cells

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ABSTRACT

In the photovoltaic industry contacts to crystalline silicon are typically formed by firing of screen-printed metallization pastes. However, the stability of surface passivation layers during high temperature contact formation is a major challenge. Here, we investigate the thermal stability of the surface passivation by amorphous silicon nitride double layers ($\text{SiN}_y/\text{SiN}_x$). The SiN_y passivation layer is silicon rich with refractive index larger than 3. Whereas the SiN_x capping layer has a refractive index of 2.05. Compared to pure hydrogenated amorphous silicon, the nitrogen in the SiN_y passivation layer improves the firing stability. We achieve an effective surface recombination velocity after a conventional co-firing process of (5.2 ± 2) cm/s on *p*-type ($1.5 \Omega\text{cm}$) FZ-silicon wafers at an injection density of 10^{15}cm^{-3} . An analysis of the improved firing stability is presented based on FTIR and hydrogen effusion measurements. The incorporation of an $\text{SiN}_y/\text{SiN}_x$ stack into the passivated rear of Cz silicon screen-printed solar cells results in an energy conversion efficiency of 18.3% compared to reference solar cells with conventional aluminum back surface field showing 17.9% efficiency. The short circuit current density increases by up to 0.8mA/cm^2 compared to conventional solar cells due to the improved optical reflectance and rear side surface passivation.

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1. Introduction

Highly efficient PERC (passivated emitter and rear cell) solar cells apply a high-quality dielectric surface passivation of the emitter and the base [1]. Thermally grown silicon dioxide layers exhibit an excellent surface passivation. However, the low-throughput furnace-process is disadvantageous for industrial applications. Therefore, low-temperature-deposited dielectrics represent an attractive alternative. The main requirements for industrial applications are:

- Thermal stability of surface passivation against the high temperature co-firing step.
- Improved internal reflectance at the rear side.
- No parasitic shunting at the rear contacts [2].

So far, various passivation layers, deposited by plasma-enhanced chemical vapor deposition (PECVD) were investigated [3–23]. Using PECVD technique offers opportunities for cost

saving due to the high throughput. Hydrogenated amorphous silicon nitride ($\text{a-SiN}_x\text{:H}$) layers provide an excellent surface passivation quality [3]. The passivation quality and firing stability depends strongly on the refractive index of the passivation layer [3,4]. A refractive index of $n \approx 2.5$ results in low effective surface recombination velocities S_{eff} for the as deposited state, whereas a layer with $n \approx 2.05$ performs best after a firing step ($T=800\text{--}900 \text{ }^\circ\text{C}$) [5]. The latter configuration is e.g. used for conventional screen-printed solar cells to passivate the phosphorous-diffused emitter at the front [5]. The passivation of these SiN_x films, deposited in an NH_3 -rich gas mixture, relies on the field effect passivation provided by a high density of fixed positive charges in the insulating SiN_x films [6]. Additionally, the surfaces are passivated by atomic hydrogen (H) released from the precursor gases during the PECVD deposition. However, parasitic shunting between the back contacts and the inversion layer underneath the SiN_x interface was found to deteriorate the cell performance for *p*-type surfaces [2].

In contrast, intrinsic hydrogenated amorphous silicon (a-Si:H) films deposited on crystalline Si exhibit, if any, only small charge densities and therefore do not cause parasitic shunting [2]. These films provide the same low S_{eff} values as thermally grown SiO_2 [7–10]. This is because atomic hydrogen (H) is released during PECVD deposition. It saturates the dangling bonds at the interface,

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and thereby decreases the interface state density [11]. However, during the high-temperature co-firing step the surface passivation quality degrades significantly. Depositing an hydrogenated silicon carbide (a-SiC_x:H) layer on silicon results in the same low surface recombination velocities as passivation by SiO₂ [12,13]. Moreover, the measured effective lifetime of 250 μs on 1 Ωcm FZ-Si after a firing step shows the improved thermal stability of an a-SiC_x:H passivation layer compared to a-Si:H [12]. It corresponds to $S_{\text{eff}} \approx 60$ cm/s. However, as single layer it provides a rather low internal reflectance at the rear when compared to SiO₂ [14]. Depositing a hydrogenated amorphous silicon oxide a-SiO_x:H capping layer on the a-Si:H layer results in an excellent internal reflectance at the rear, which is comparable with thermally grown SiO₂ [15]. However, applying temperatures above 400 °C severely deteriorates the passivation quality [16]. Plagwitz [11] and Ulyashin et al. [17] showed that depositing an a-SiN_x:H capping-layer (in short: SiN_x) with $n_{\text{SiN}} \approx 2.05$ on top of the a-Si:H film, not only protects the a-Si:H layer from the aluminum (Al) rear metallization but also improves the thermal stability of the surface passivation. Recent investigations by Gatz et al. [18] reveal an enhanced thermal stability of these films when increasing the deposition temperature of the SiN_x capping layer from 300 °C to 400 °C. However, the a-Si:H/SiN_x stacks were only shown to be stable for firing at $T < 750$ °C thus requiring special low temperature metallization pastes. Applying standard pastes with firing temperatures of 800–900 °C the surface passivation deteriorates severely. Double or triple stack systems based on a-SiO_x:H and a-SiN_x:H demonstrated a S_{eff} below 60 cm/s after a high temperature firing step [19,20]. Together with an improved internal reflectance, it results in an increase in short circuit current density J_{sc} . A double layer stack of amorphous hydrogenated silicon-rich oxynitride capped with a-SiN_x:H showed a passivation quality, which is close to the modeled maximum. It is based on positive charges in the layer and an excellent thermal stability against a high temperature firing step [21]. The concentration of oxygen and nitrogen atoms is approximately in the 10% region.

In this paper, we investigate hydrogenated amorphous silicon nitride passivation stacks (SiN_y/SiN_x) with silicon rich SiN_y and a SiN_x capping layer. This approach combines the excellent surface passivation of a-Si:H with the excellent firing stability of silicon nitride SiN_x layers. The main idea is to increase the thermal stability of the surface passivation by supplying minor amounts of NH₃ during the PECVD a-Si:H deposition in order to reduce hydrogen effusion during a conventional screen-printing firing process. Moreover, it is known that the positive charge density, responsible for the parasitic shunting, is strongly reduced compared to SiN_x if the N content in the amorphous film is low [22,23].

2. Experimental

2.1. Preparation of SiN_y/SiN_x double layers

In this study, FTIR measurements, hydrogen effusion, and lifetime investigations are performed using *p*-type boron-doped 1.5 Ωcm, shiny etched float-zone silicon wafers with a thickness of 290 μm. For the PERC solar cells we use 200 μm-thick 2 to 3 Ωcm, *p*-type boron-doped, Cz-silicon wafers. The nitrogen-rich amorphous SiN_y passivation layers are deposited by a direct plasma PECVD single chamber reactor (Plasmalab μP, Oxford). Deposition temperature, plasma power, pressure and total gas flow remain constant during the deposition. The composition of the SiN_y passivation layer is modified by varying the NH₃-content in the SiH₄/NH₃ (/H₂) gas mixture resulting in refractive indices from 3.20 to 4.16. The SiN_x capping layer is deposited by an inline

microwave PECVD system (SiNA, Roth & Rau). Throughout all experiments the plasma power, pressure, total gas flow, deposition temperature and deposition time are kept constant resulting in a capping layer thickness of 100 nm and a refractive index n_{SiN} of 2.05. For comparison, we also deposit SiN_x single layers with refractive indices ranging from 1.9 to 3.1 by a remote plasma PECVD single chamber reactor (Plasmalab 80plus, Oxford) varying the SiH₄-flux in the SiH₄/NH₃/H₂ gas mixture. For FTIR, H effusion and lifetime investigations the 1.5 Ωcm, shiny-etched FZ wafers are cleaned in a wet chemical RCA process immediately followed by the SiN_y deposition. Afterwards, a 100 nm-thick SiN_x capping layer with $n_{\text{SiN}} = 2.05$ is deposited on top.

To determine the effective surface recombination velocity S_{eff} after a firing step, symmetrical SiN_y/SiN_x passivated FZ silicon wafers with a thickness of 290 μm pass through a belt furnace (DO-FF-8.600-300, Centrotherm) with a set peak temperature of 900 °C and a belt velocity of 5.9 m/min. The dwell time at the peak temperature is approximately 3 s.

2.2. Characterization methods

The real part of the refractive index n of the dielectric layers are characterized by a monochromatic ellipsometer (Plasmos) based on a He/Ne laser ($\lambda = 632.8$ nm) with an incident angle of 70°. Single layers with a high NH₃-content in the gas mixture are deposited on shiny etched FZ-Si wafers, which feature a refractive index $n = 3.87$. Decreasing the NH₃-content in the gas mixture and therefore increasing the silicon content in the dielectric layer results in an increased refractive index. That exceeds therefore the limit in accuracy of the monochromatic ellipsometry when the PECVD layer is deposited on c-Si. Therefore, single layers with a high silicon content are deposited on 1.1 mm-thick BOROFLOAT[®] glass with a small refractive $n = 1.46$. InfraRed (IR) absorption measurements were performed on a Bruker Equinox 55 Fourier transform IR Spectrometer (FTIR) using a mid IR source and a DTGS detector. The FTIR spectra were collected from 5000 to 200 cm⁻¹ with a resolution of 4 cm⁻¹. For each spectrum 2000 scans were accumulated to improve the signal-to-noise-ratio.

Hydrogen effusion experiments reveal information on the hydrogen content of single layers and their thermal stability in SiN_y/SiN_x double layers. Our samples are annealed during effusion with a heating rate of 20 K/min in vacuum. By means of a mass spectrograph we detect out-diffused hydrogen atoms and molecules in real time. In case of hydrogenated amorphous silicon we expect an hydrogen effusion peak at a characteristic temperature (T_{eff}), which is a measure of the thermal stability of the hydrogen in the a-Si:H layer. Further details about the measurement technique were described elsewhere [24].

We measure the effective lifetime τ_{eff} of symmetrically passivated *p*-type FZ Si wafers by means of the quasi-steady state photoconductance (QSSPC) method [25,26]. By attributing the total measured recombination rate to the interface, we estimate the upper limit for the effective surface recombination velocity

$$S_{\text{eff}} = \frac{W}{2\tau_{\text{eff}}} \quad (1)$$

with the effective lifetime τ_{eff} measured by QSSPC and the wafer thickness W .

2.3. Solar cells

We apply the SiN_y/SiN_x surface passivation to the rear of PERC solar cells using 200 μm-thick Czochralski-grown (100)-oriented, boron-doped 2 to 3 Ωcm pseudo-square silicon wafers. Fig. 1 shows the solar cell design. In the solar cell process a dielectric coating on the rear allows for a single side texturing and phosphorus diffusion

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