

THE SINTO PROCESS: UTILIZING A SiN_x ANTI-REFLECTION LAYER FOR EMITTER MASKING DURING THERMAL OXIDATION

Andreas Wolf, Alexandra Walczak, Sebastian Mack, Edgar A. Wotke, Anke Lemke, Christoph Bertram, Udo Belledin, Daniel Biro, and Ralf Preu
Fraunhofer Institute for Solar Energy Systems (ISE),
Heidenhofstr. 2, 79110 Freiburg, Germany

ABSTRACT

We present a novel method for the industrial fabrication of a silicon solar cell that features an oxide-passivated rear surface. The SINTO process (Silicon Nitride Thermal Oxidation) utilizes a SiN_x layer for masking the front side of the solar cell during the thermal oxidation process. This masking layer prevents the oxidation of the textured and phosphorus-doped emitter surface and limits the growth of the thermal oxide to the uncoated rear surface. After oxidation the SiN_x layer remains at the front side of the cell and serves as an anti-reflection coating (ARC). In this work we investigate the impact of the thermal oxidation process on the SiN_x film and the underlying emitter and analyze the passivation quality of the thermal oxide. The oxidation process results in a sufficiently passivated rear surface with a surface recombination velocity of ~ 40 cm/s, measured after Al-metallization and post-metallization anneal. Measurements of the emitter sheet resistance and Secondary Ion Mass Spectrometry (SIMS) profiling reveal that the SiN_x -coated emitter reorganizes slightly during the oxidation process whereas an uncoated reference is strongly affected. The emitter dark saturation current density is affected as well. Oxide-passivated solar cells are fabricated from Czochralski (Cz) silicon using the SINTO approach. A 136 cm^2 large cell fabricated using industrial processing equipment reaches an efficiency of 17.8% (stable), which demonstrates the feasibility of the SINTO process.

INTRODUCTION

Conventional industrial silicon solar cells suffer from a high rear surface recombination velocity (SRV) and a poor internal reflection of the full area Al back surface field (BSF). When going to thinner wafers, the loss in efficiency due to these drawbacks even increases. A passivated emitter and rear cell (PERC) combines a low rear SRV with a high internal reflection. This concept enables higher efficiencies compared to the Al-BSF technology [1]. In addition, the wafer bow is reduced, which facilitates the use of thin wafers.

Thermal oxides permit excellent and stable surface passivation and were used to fabricate highly efficient silicon solar cells [2]. Moreover the surface passivation by thermal oxidation was shown to be compatible with a rapid high temperature contact firing process allowing the combination of an oxide-passivated rear surface with screen

printed front contacts [1]. However, it is not straightforward to integrate a thermal oxidation process into current industrial production lines [3]. One approach is to start with a thick thermal oxide, which is removed from the front side followed by texturing, emitter formation, ARC deposition and metallization [1]. This sequence requires an initial oxide thickness of 200 to 300 nm, since subsequent processes reduce the oxide thickness. Even in a water vapor ambient the growth of such a thick oxide at relevant temperatures takes several hours, which limits the throughput and increases the manufacturing costs. It is thus favorable to implement the oxidation step later in the sequence. However, high phosphorus doping and the (111)-planes of the textured front in the case of monocrystalline wafers both enhance the oxide growth rate [4] which results in a several times thicker oxide on the textured and diffused front surface compared to the plane, undoped rear surface. The growth of such a thick oxide strongly affects the emitter and the oxide has to be removed from the front side since it increases the reflection losses of an encapsulated cell. Our SINTO approach overcomes these difficulties by using a SiN_x ARC as a protective layer for the textured and diffused front surface during oxidation.

Moreover, the SINTO process utilizes the SiN_x layer for masking the front surface during the wet chemical removal of the emitter from the rear surface. A high passivation quality requires a low surface roughness. Thus, during emitter etch back also the texture should be removed yielding a plane rear surface [5]. The masking layer gives more freedom for the design of the etching process and also enables the use of batch processes instead of single side etching. Using single side etching, the planarization of the rear surface while strictly limiting the etching to the rear surface is challenging.

For a conventional Al-BSF cell the SiN_x layer not only serves as an ARC but also as a hydrogen source for emitter and bulk passivation during the firing process [6,7]. The task is to maintain the optical and passivation properties of the SiN_x film while additionally utilizing it for masking the front surface during wet chemical emitter etch back and during the oxidation process.

EXPERIMENTAL

Two separate experiments are performed in this work. The first experiment characterizes the changes in the SiN_x layer and the emitter induced by the etching and

the oxidation process. The second experiment focuses on the achievable surface passivation quality.

Emitter and SiN_x properties

Figure 1 illustrates the process flow for the fabrication of symmetric emitter samples, whose both sides represent the front (illuminated) surface of a solar cell structure. The gray colored bars represent process steps that belong to the cell fabrication process whereas the light blue colored bars mark additional steps for sample characterization. Shiny etched boron-doped float zone (FZ) silicon wafers with a resistivity of 1 Ωcm and a thickness of 250 μm serve as the starting material. The process sequence starts with a dip in diluted HF followed by diffusion in a tube furnace using POCl₃ as phosphorous precursor gas. Two different diffusion processes are applied yielding a sheet resistance of 61 $\Omega/\text{sq.}$ for Emitter E1 and 75 $\Omega/\text{sq.}$ for Emitter E2. After removing the phosphorus-silicate glass (PSG) in HF, a layer of SiN_x is deposited onto both surfaces by means of sputtering [8]. Sputtered SiN_x layers feature a high thermal and chemical stability and are therefore suitable for the SiNTO process. In the next step the samples from each emitter are divided into two groups. For the first group an etching step in KOH simulates the emitter etch back followed by wet chemical cleaning. A short thermal oxidation in a tube furnace with a H₂O-rich atmosphere (wet oxidation) follows. The second group serves as a non-oxidized reference. Subsequently, the samples of both groups receive a contact firing step. Our samples do not feature contacts, however, the firing step also affects the emitter recombination due to defect passivation by hydrogen release [7] and is thus necessary to obtain results that are relevant on cell level.

After this sequence, that renders the cell fabrication process, an HF bath removes the SiN_x layer from all samples and a new SiN_x layer is sputtered onto both surfaces followed by a firing step to activate the hydrogen passivation. This renewed passivation allows us to distinguish between different impacts of the SiNTO process on the emitter recombination: Hydrogen defect passivation on one hand and changes in the doping profile on the other hand.

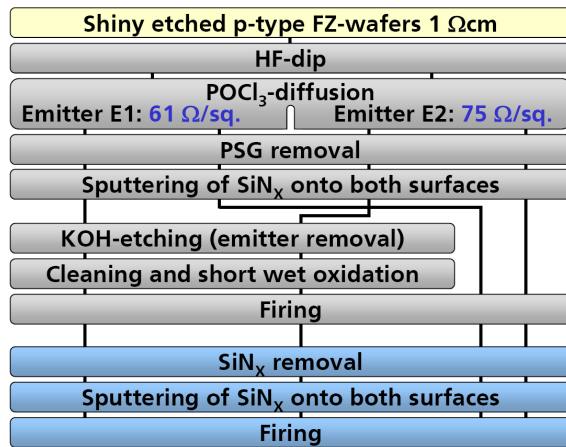


Fig. 1. Process flow for the fabrication of symmetric emitter samples (Experiment 1). Gray colored bars represent the cell fabrication process whereas light blue colored bars mark additional steps for a renewed passivation of the samples.

Throughout the experiment the samples are analyzed using several characterization methods. Inductive coupling enables the contactless determination of the emitter sheet resistance [9], Secondary Ion Mass Spectrometry (SIMS) profiling on samples withdrawn from the process reveals changes of the emitter doping profile, and quasi steady-state photoconductance (QSSPC) [10] measurements permit the determination of the emitter dark saturation current density. Moreover, spectral ellipsometry is used to characterize the SiN_x layer.

Rear surface passivation

The rear surface passivation scheme investigated in this work consists of a thin thermal oxide which is covered by a SiO_x capping layer deposited by plasma enhanced chemical vapor deposition (PECVD). This capping layer prevents spiking of the subsequently evaporated Al layer and ensures a high internal reflection. It would also be possible to grow a sufficiently thick thermal oxide and omit the capping layer deposition. However, a prolonged thermal oxidation increases the thermal budget and induces significant changes in the emitter doping profile that would at least require an adaptation of the diffusion process. The capping layer also enables the use of a screen printed instead of an evaporated Al rear contact, when designing the stack system so that the capping prevents the Al paste from alloying with the Si during the firing process [11].

Figure 2 shows the process flow of the second experiment which investigates the passivation quality that is achievable with a short wet oxidation applied by the SiNTO process. For this purpose symmetric lifetime samples are fabricated whose both sides represent the rear surface of a solar cell structure. The experiment reproduces the complete fabrication process, including the front end processing. Again boron-doped FZ-wafers of 1 Ωcm resistivity are used. A KOH/isopropanol-solution textures both sides with random pyramids and thereby removes the saw damage from the as-cut surfaces. Subsequently, a POCl₃-diffusion forms the emitter followed by a KOH etching step that again removes the diffused emitter from both surfaces. After a wet chemical cleaning sequence a ~20 nm thick oxide is grown in a wet tube furnace oxidation. In the next step, both surfaces receive a SiO_x capping layer deposited PECVD. After evaporation of 2 μm of Al by electron beam (e-gun) evaporation onto both surfaces, the samples are annealed in forming gas at 425°C for 25 minutes. This post metallization anneal (PMA) or “alneal” [12] delivers atomic hydrogen that satu-

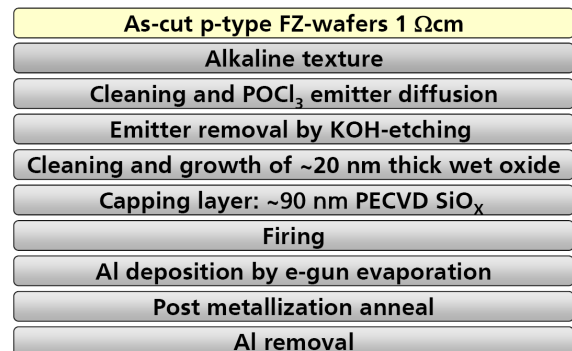


Fig. 2. Process flow for the fabrication of symmetric lifetime samples (Experiment 2).

Table 1: Emitter sheet resistance R_{sheet} after different processing steps measured by inductive coupling

Sample processing stage	Emitter E1 [$\Omega/\text{sq.}$]	Emitter E2 [$\Omega/\text{sq.}$]
After PSG removal	61 ± 3	75 ± 3
After oxidation with SiN _x masking	56 ± 3	66 ± 3
After oxidation without SiN _x masking	-	147 ± 8

rates residual defects at the Si-SiO₂ interface which improves the surface passivation [13]. A wet chemical bath then removes the Al layers which enables the determination of the SRV by means of the QSSPC technique.

RESULTS AND DISCUSSION

Emitter sheet resistance and doping profile

Table 1 lists the sheet resistance R_{sheet} measured after the individual processing steps. Each value represents an average over several samples. Starting from 61 $\Omega/\text{sq.}$ for Emitter E1, the sheet resistance of the SiN_x-coated emitter decreases to 56 $\Omega/\text{sq.}$ during the oxidation. In case of Emitter E2, R_{sheet} reduces from 75 $\Omega/\text{sq.}$ to 66 $\Omega/\text{sq.}$, whereas it increases to 147 $\Omega/\text{sq.}$ for a reference with an unprotected emitter. Figure 3 shows the corresponding SIMS profiles measured on a central part of the wafer. Apparently, the masked emitter reorganizes due to the high process temperature. The peak doping reduces from $\sim 5 \times 10^{20} \text{ cm}^{-3}$ to $\sim 4 \times 10^{20} \text{ cm}^{-3}$ for Emitter E1 and from $\sim 4.5 \times 10^{20} \text{ cm}^{-3}$ to $\sim 3 \times 10^{20} \text{ cm}^{-3}$ for Emitter E2 yielding more active phosphorus doping. A slight drive-in is visible, which is more pronounced in the case of Emitter E2. This emitter is diffused at a lower temperature compared to Emitter E1, which explains the stronger impact of the oxidation process.

In the case of an unmasked emitter, the high oxide growth rate prevents an activation of inactive phosphorus. Instead, the fast transformation of the highly doped Si surface layer into SiO₂ consumes phosphorus atoms [4], which results in a drastically increased sheet resistance (see Table 1 and Fig. 3).

Emitter dark saturation current density

The QSSPC measurements yield an effective carrier lifetime τ_{eff} evaluated at an excess carrier concentration of $\Delta n = 5 \times 10^{14} \text{ cm}^{-3}$, representing low level injection conditions. In this case the emitter dark saturation current density [14]

$$J_{0e} = \frac{qWn_i^2}{2(N_A + \Delta n)} \left[\left(\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{bulk}}} \right)^{-1} - \frac{W^2}{D\pi^2} \right]^{-1} \quad (1)$$

follows from the sample thickness W , the Auger recombination-limited bulk lifetime $\tau_{\text{bulk}} = 3.0 \text{ ms}$ [15], the diffusion constant $D = 27 \text{ cm}^2/\text{s}$, the doping density

$N_A = 1.5 \times 10^{16} \text{ cm}^{-3}$, and the intrinsic carrier concentration $n_i = 9.5 \times 10^9 \text{ cm}^{-3}$ with $q = 1.6 \times 10^{-19} \text{ C}$. This saturation current limits the open circuit voltage V_{OC} of a solar cell to values below

$$V_{\text{OC,max}} = V_{\text{th}} \ln \left(\frac{J_{\text{SC}}}{J_{0e}} + 1 \right) \quad (2)$$

using the thermal voltage $V_{\text{th}} = 25.7 \text{ mV}$ and a short circuit current density value of $J_{\text{SC}} = 33 \text{ mA}/\text{cm}^2$ for a non-textured cell.

Figure 4 displays the dark saturation current density and the corresponding voltage limit $V_{\text{OC,max}}$ at different stages of the process sequence shown in Fig 1. The saturation current J_{0e} of both masked Emitters E1 and E2 reduces by 34% during oxidation and is not affected by a subsequent firing step, whereas firing reduces J_{0e} of the non-oxidized reference by 42% (Emitter E1) and 50% (Emitter E2). Apparently, the high temperature during both oxidation and firing induces a hydrogen release from the SiN_x layer resulting in the passivation of residual

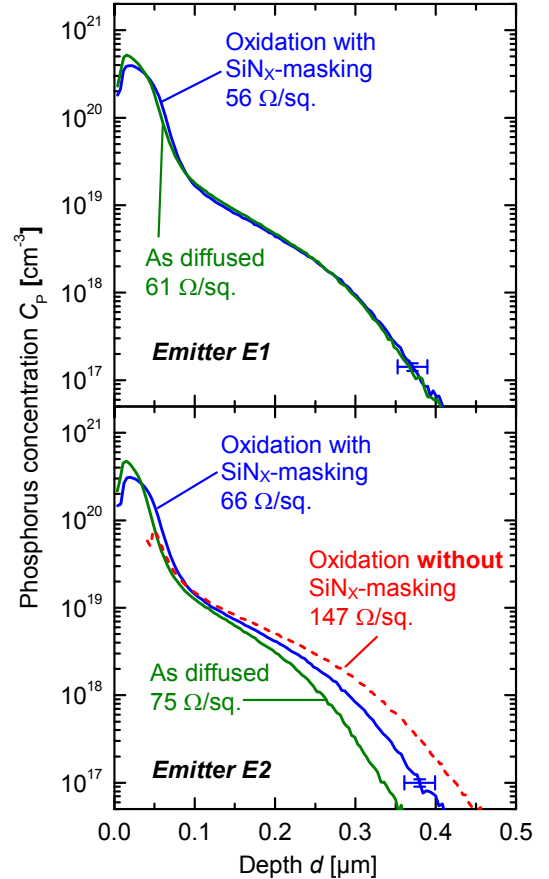


Fig. 3. Doping profile of Emitter E1 (top) and E2 (bottom) after diffusion (green solid lines) and after oxidation with (blue solid lines) and without (red dashed line, only E2) a SiN_x masking layer. The latter profile is shifted to the right corresponding to the Si thickness consumed during oxidation. The decrease of the Phosphorous concentration towards the surface is assumed to be an artifact of the SIMS measurement.

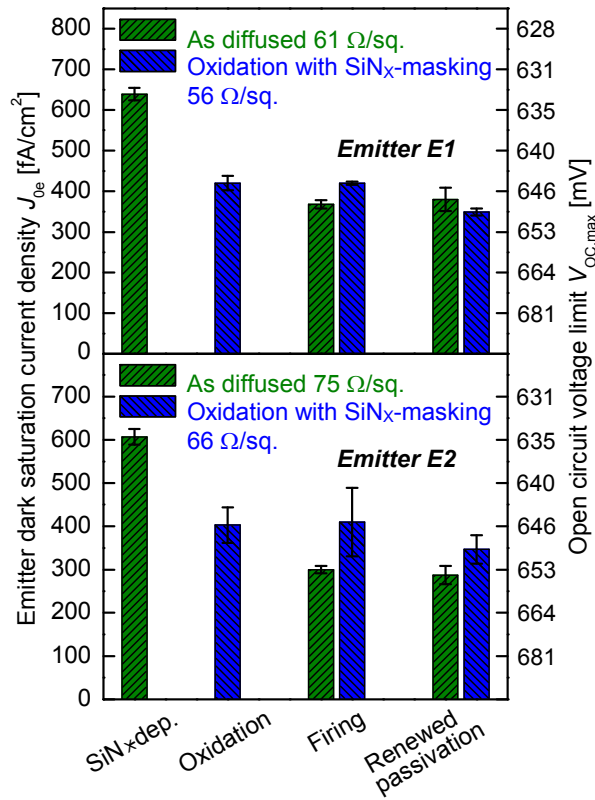


Fig. 4. Dark saturation current density of Emitter E1 (top) and E2 (bottom) at different stages of the process sequence shown in Fig. 1. The $V_{OC,max}$ -scale on the right hand side follows from Eq. (2). The error bars solely represent a statistical component (standard deviation) and no systematic uncertainty.

defects [6]. However, the above described reorganization of the phosphorous doping during the oxidation process might affect J_{0e} as well. To allow a diversification between the impact of the hydrogen passivation on one hand and the reorganization on the other hand, the samples receive a renewed passivation. This procedure consists of the last three light blue colored process steps of the sequence from Fig 1. Apparent from Fig. 4, renewing the passivation does not affect the non-oxidized references, whereas it reduces J_{0e} for the oxidized samples by ~15%. This finding shows that for the analyzed samples hydrogen defect passivation is more effective during the rapid firing step compared to the tube furnace oxidation process. After an initial hydrogen release, outdiffusion of hydrogen from the SiN_x layer and the Si/SiN_x-interface might occur during the long oxidation process, leading to a partly depassivation. This hydrogen depletion would also explain why the firing step does not show any impact on J_{0e} for the oxidized samples.

To prevent blistering, the sputtered SiN_x layers applied in this work feature a lower hydrogen content compared to the sputtered layers used for conventional cells [16]. Since no blistering is observed, future experiments will consider layers with an increased hydrogen content, which could result in a more pronounced defect passivation during oxidation.

After renewing the passivation, a comparison between the oxidized sample and the non-oxidized reference

(right hand side of Fig. 4) reveals the impact of the emitter reorganization on J_{0e} . The profile change induced by the oxidation slightly reduces J_{0e} for Emitter E1, whereas J_{0e} slightly increases in case of Emitter E2. Note that in the first case, a lower sheet resistance is accompanied by a decrease in J_{0e} . Several physical effects take place during the emitter reorganization. On one hand, the activation of previously electrically inactive phosphorus leads to an increased Auger recombination. On the other hand the amount of inactive excess phosphorous reduces, which might have an impact as well [17]. Moreover, if the active surface doping changes, the SRV at the Si/SiN_x-interface is affected as well [18]. Measurements of the active doping profile for example by spreading resistance analysis [19] and advanced numerical modeling [20] should give a better understanding but are not carried out in this work.

Properties of the SiN_x layer

Characterization by means of an ellipsometer allows to analyze the impact of the individual processing steps on the thickness and the optical constants of the sputtered SiN_x layer. For this purpose a stack consisting of the Si substrate, the SiN_x film and a porous surface layer that describes the surface roughness is modeled. Using an additional layer of native oxide between the substrate and the SiN_x layer shows no significant impact and is therefore omitted. Measurements are performed at wavelengths between 250 nm and 1000 nm at 65°, 70°, and 75° incidence. A Tauc-Lorentz oscillator model [21] is applied to describe the optical constants of the SiN_x film.

The KOH emitter etch and the wet chemical cleaning reduce the layer thickness by a few nm. The high temperature of the oxidation process causes a further thickness reduction of the same order. Such a densification of the SiN_x film was described earlier and attributed to the release of hydrogen during high temperature processing [22]. However, the thickness reduction observed in this work is much smaller. The whole sequence, KOH etching, cleaning, and oxidation, reduces the thickness of the SiN_x layer by less than 10 nm. Figure 5 shows the refractive index determined for an oxidized and fired SiN_x layer as well as for a solely fired reference. Both the refractive index n and the extinction coefficient k (not shown) of the oxidized sample exhibit a slight reduction compared to the reference. This trend is observed on several samples throughout this experiment. For PECVD SiN_x films of comparable composition several authors observed no change or even a slight increase of the refractive index due to a densification during high temperature processing [22,23]. Moreover, for near stoichiometric SiN_x films ($n \approx 1.9$ at 633 nm) at wavelengths above 250 nm a reduction in k due to an increase in the optical band gap E_g during thermal treatment was reported. The same trends, a higher E_g (and thus lower k) of the oxidized samples compared to the reference, are observed for the sputtered SiN_x layers of this work, although the refractive index is considerably higher. Hong et al. [23] suggested that the release of hydrogen from near stoichiometric SiN_x would render the films with structural properties closer to that of stoichiometric Si₃N₄ with a high optical band gap of $E_g > 5$ eV.

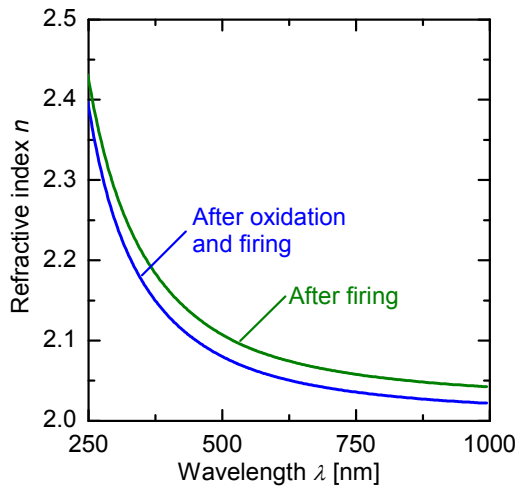


Fig. 5. Refractive index of the SiN_x layer determined by fitting a Tauc-Lorentz-Model to the spectral ellipsometry data. The blue line corresponds to a cleaned, oxidized, and fired SiN_x layer, the green line represents a sample that is solely fired.

Analysis of rear surface passivation quality

The QSSPC technique enables the determination of the effective carrier lifetime τ_{eff} throughout the process sequence shown in Fig. 2. The surface recombination velocity [24]

$$S = \frac{W}{2} \left[\left(\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{bulk}}} \right)^{-1} - \frac{W^2}{D\pi^2} \right]^{-1} \quad (3)$$

then follows from τ_{eff} and the above listed parameters (see Eq. (1)). Figure 6 displays the effective lifetime and the corresponding recombination velocity. Starting from $\sim 80 \mu\text{s}$ after the growth of the thin oxide the effective carrier lifetime decreases during the deposition of the SiO_x capping layer. The firing process quenches the lifetime to a few μs . This strong decrease is partly due to breaking of hydrogen bonds, which results in an increased interface trap density. However, the passivation recovers during the Alneal process yielding a SRV of $\sim 40 \text{ cm/s}$, which represents a sufficient passivation. For a fired and alnealed thick thermal oxide a similar SRV of 38 cm/s was reported [1] allowing efficiencies above 19% while using screen printed front contacts.

Cell results

Finally, solar cells are fabricated from conventionally pulled boron-doped 3 Ωcm Czochralski (Cz)-Si using the SiNTO approach. Figure 7 presents the process flow which is quite similar to the sequence from Fig. 2. Additionally, the single sided SiN_x-deposition is introduced after the POCl₃-diffusion, screen printing of the front contacts occurs prior to contact firing step and a laser alloys the local rear contacts (laser fired contacts, LFC) [25] before the final annealing step. Industrial processing equipment is used for all fabrication steps except for the Al-deposition by e-gun evaporation. The frontend processing is carried out in an industrial production line at Deutsche

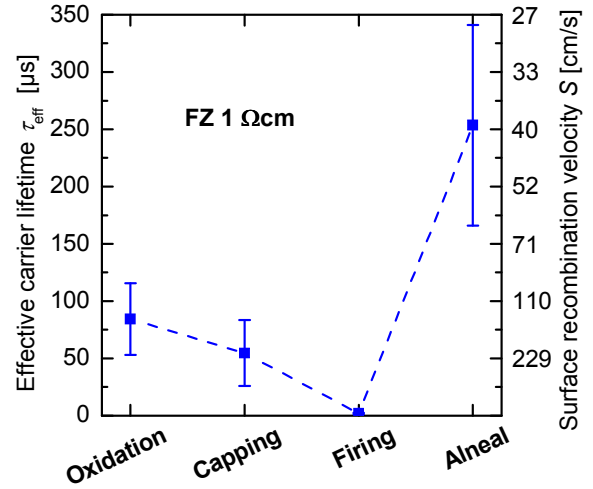


Fig. 6. Effective carrier lifetime (left hand scale) measured on symmetric lifetime samples during the process sequence shown in Fig. 2 starting from the oxidation. The corresponding surface recombination velocity (right hand scale) follows from Eq. (3). The error bars only represent a statistical component (standard deviation) and no systematic uncertainty.

Cell GmbH, Freiberg, Germany, whereas passivation and backend processing is performed at Fraunhofer ISE Photovoltaic Technology Evaluation Center (PV-TEC) [26].

Figure 8 schematically illustrates the device structure. The rear surface passivation consists of a thin thermal oxide covered by a SiO_x capping layer deposited by PECVD. Conventional screen printing is used for the front metallization. The emitter sheet resistance is $\sim 60 \Omega/\text{sq.}$, measured after the oxidation process. Due to the geometry of the sample holder, the Al rear contact does not cover the whole rear surface of the cell. To evaluate the potential of a full area rear contact, some cells are scribed by a laser and subsequently cleaved removing $\sim 3 \text{ mm}$ of the wafer edge. The resulting cell area is 136 cm^2 . Table 2 lists the parameters of the illuminated current-voltage (IV) curve measured for a cell with cleaved edges. The IV-meas-

As-cut p-type Cz-wafers 3 Ωcm
Alkaline texture
Cleaning and POCl ₃ emitter diffusion
SiN _x deposition (front surface)
Rear emitter etch back
Cleaning and growth of $\sim 20 \text{ nm}$ thick wet oxide
Capping layer rear surface: $\sim 90 \text{ nm}$ PECVD SiO _x
Screen printing of front contacts
Firing
Al deposition by e-gun evaporation (rear surface)
Local rear contact formation (LFC)
Annealing

Fig. 7. Process sequence for the fabrication of solar cells using the SiNTO approach. Light blue colored bars represent process steps carried out in a production line at Deutsche Cell GmbH, Freiberg, Germany. Gray colored bars indicate processing at the PV-TEC pilot line. Fig. 8 schematically illustrates the resulting device structure

Table 2: IV parameters of a 136 cm² large SiNTO device with cleaved edges. The measurements are performed using an industrial cell tester equipped with a flash lamp. The notation “annealed” refers to a measurement after hotplate annealing at 200°C for 20 minutes, “stabilized” denotes a measurement after 35 h illumination at 0.3 suns. Both measurements are not confirmed.

	V_{OC} [mV]	J_{SC} [mA/cm ²]	FF [%]	η [%]
annealed	634	37.3	76.7	18.1
stabilized	629	37.2	76.2	17.8

urements are performed using an industrial cell tester equipped with a flash lamp. Prior to the measurements, the cell is first annealed at 200°C for 20 minutes to deactivate the boron-oxygen complexes [27] and subsequently illuminated for 35 hours at 0.3 suns to fully stabilize the device. An efficiency of 18.1% (annealed) and 17.8% (stabilized) is achieved, demonstrating the high potential of the SiNTO approach. The stabilized open circuit voltage of $V_{OC} = 629$ mV and short circuit current density above 37 mA/cm² confirm a high quality of the rear surface passivation.

SUMMARY AND OUTLOOK

A new approach for the industrial fabrication of an oxide-passivated Si solar cell with screen printed front contacts is presented. The SiNTO process utilizes the SiN_x ARC as a masking layer during the emitter etch back and the oxidation. An analysis of the emitter doping profile and sheet resistance reveals that the masked emitter slightly reorganizes during the oxidation process resulting in a decreased sheet resistance and peak doping. Hydrogen release from the SiN_x layer during the oxidation reduces the emitter recombination, however, for the SiN_x layers analyzed in this work the passivation during firing is more effective. Only minor impacts of the oxidation on the optical properties of the SiN_x layer are observed. Using a thin thermal oxide and a PECVD SiO_x capping for the rear surface passivation results in a SRV of 40 cm/s after firing, Al-metallization, and PMA. A 136 cm² large solar cell fabricated from Cz-Si using industrial processing equipment achieves an efficiency of 17.8% (stabilized).

Future experiments will focus on the adaption of the hydrogen content of the sputtered SiN_x films and on the impact of the emitter reorganization on the contact resistance of screen-printed Ag-contacts. Moreover, a modification of the diffusion process might allow the growth of a thicker thermal oxide omitting the use of a capping layer.

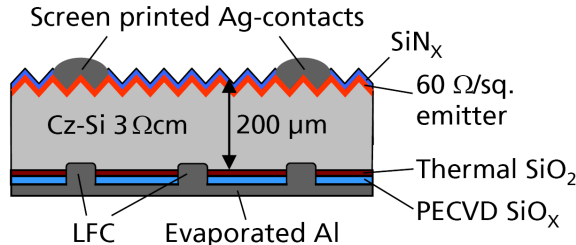


Fig. 8. Schematic of the device fabricated using the SiNTO approach. The rear surface passivation consists of a thin thermal oxide covered by a SiO_x capping layer deposited by PECVD.

Acknowledgments

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