Advanced front-surface passivation schemes for industrial n-type silicon solar cells

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ABSTRACT

The n-Pasha n-type silicon solar cell currently achieves an average conversion efficiency of 20.2% using a relatively simple process flow. This bifacial cell concept developed by ECN is based on homogeneously doped p^+ front and n^+ back surfaces. To enhance the cell efficiency, it is important to reduce the carrier recombination within the boron-diffused p^+ region and at its surface. This paper addresses a novel way to tune the boron-doping profile and presents advanced surface passivation schemes. In particular, it is demonstrated that a very thin (2nm) Al_2O_3 interlayer improves the passivation of the boron-doped surface; the Al_2O_3 films were deposited in industrial atomic layer deposition (ALD) reactors (batch or spatial). Moreover, it is shown that the boron-doping profile can be improved by etching back the boron diffusion. On the basis of the results presented, it is expect that n-Pasha solar cells with 21% efficiency will soon be within reach.

Introduction

In 2010 ECN, Tempress and Yingli introduced the n-Pasha cell to the market as a novel bifacial cell concept based on n-type Czochralski-grown (Cz) silicon with homogeneous diffusions, dielectric passivation and printed metallization (Fig. 1) [1]. Recently, Nexolon America selected this cell concept for their production line, enabling the production of bifacial modules [2].

> "The bifacial cell concept allows higher power output per installed Wp."

One of the key benefits of a bifacial cell is the capturing of albedo light from the 'open' rear side. Recent field studies [3] have revealed a higher power generation with these bifacial cells than with monofacial cells during the morning and evening hours, which is when indirect light contributes most to the carrier generation. Even when

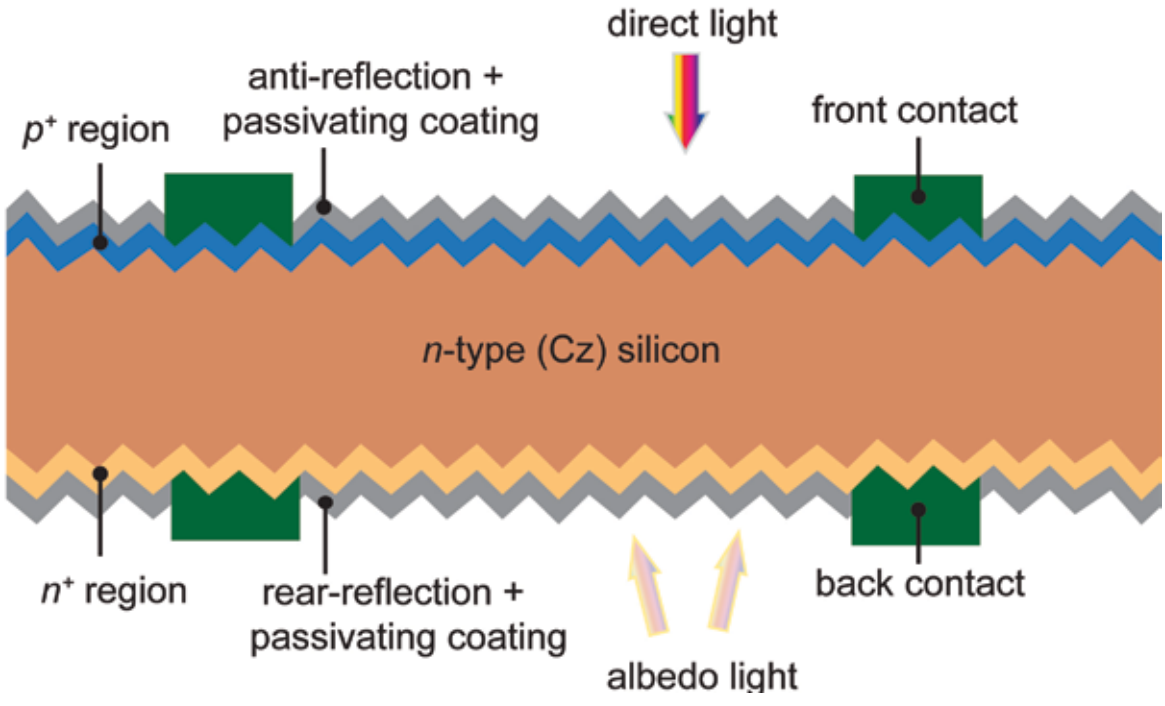

Figure 1. A schematic cross section of the bifacial n-Pasha cell concept, which enables the capture of albedo light.

positioned vertically, for example along roads, bifacial modules are able to generate electricity all day long while the sun moves from east to west. The bifacial cell concept therefore allows higher power output per installed Wp.

The current n-Pasha baseline process yields an average efficiency of 20.2%, with a top efficiency of 20.4% on high-quality Cz material [4]. These cells, and other cells based on n-type Si wafers, compete with p-type PERC cells (rear passivated cells with local contacts) for a spot in the higher-efficiency segment. One of the main advantages of n-type cells as compared to PERC is the absence of light-induced degradation. On the other hand, there are a number of technological and scientific challenges for industrial n-type cells which have to be addressed in order to achieve high efficiencies while remaining cost-competitive:

- (Independent) control of diffused n^+ and p^+ doping profiles.
- Excellent level of passivation of both front and rear surfaces.
- Reduced contact recombination on the p^+ side.
- Minimal consumption of silver paste to contact both sides.
- Insensitivity of cell efficiencies to variations in resistivity of the n-type base.

The last two issues in the list have been successfully addressed in previous articles in this journal [5,6]. After a general discussion on recombination, this paper will address the first two topics, currently the limiting factors of n-Pasha solar cells [7]: the optimization of the boron-doping profile and the passivation.

Physics of carrier recombination in solar cells

The recombination of light-generated electron-hole pairs reduces the conversion efficiencies of solar cells. Although to a certain extent this recombination is inevitable because of intrinsic processes such as Auger and radiative recombination, the recombination can also be enhanced by lattice defects. These defects can form energy states within the silicon band gap, via which charge carriers can effectively recombine: this mechanism is known as *Shockley Read Hall (SRH) recombination*. Such defect states are omnipresent in solar cells as a result of (lattice) defects both in the silicon bulk and at the silicon surface.

Towards n-type silicon base material

Electronically active defects within the bulk of the silicon, such as defects at the grain boundaries and boron–oxygen complexes, can effectively be mitigated by using, respectively, monocrystalline silicon rather than multicrystalline silicon, and n-type silicon rather than (boron-doped) p-type silicon. Switching to n-type silicon is also beneficial, as this material is much less sensitive to transitional metal contaminants, such as Fe [8]. It is precisely these benefits in terms of bulk quality that were the incentive for many institutes and companies to develop solar cells based on n-type monocrystalline silicon base material, such as the n-Pasha cell concept.

Surface recombination

Although a high-quality bulk material in principle allows for high conversion efficiencies, to achieve this potential at the cell level care must be taken to reduce carrier recombination near the surfaces of the cells (Fig. 2). More specifically, one can distinguish between recombination at the metallic contacts and recombination in the well-passivated regions in between.

Since metallic contacts exhibit a very high density of states across the silicon band gap, the metal–silicon interface acts as a 'catalyst' for electron–hole pair recombination. If the silicon underneath the contacts (conventionally termed *emitter* and *back-surface field*) is heavily doped, the conductivity of *one* carrier type is reduced, while it is drastically enhanced for the other. In this way, the metal contacts are effectively made selective for one carrier type (i.e. selective electron or hole contacts are formed [9]), and recombination is suppressed. A parameter governing both the carrier selectivity and the recombination is the recombination current parameter, or (thermal equilibrium) recombination current density [9] (formerly referred to as *emitter* saturation current density, which should ideally be as low as possible. Unfortunately, heavy doping leads to a trade-off, as it enhances Auger recombination, which varies as a function of the square of the majority-carrier density. It is for these reasons that initiatives using (semi-conducting) passivated selective contacts without the necessity of heavy doping have emerged: very high efficiencies have been demonstrated [10]. A well-known example is the use of intrinsic and doped amorphous Si layers in silicon heterojunction solar cells.

Although for metallic contacts heavy doping is consequently required to ensure a low contact resistance and an adequate carrier selectivity, for the regions in between the metallic contacts the function of the doped regions is solely to conduct the carriers laterally. In homogeneously diffused solar cells, such as n-Pasha, the recombination in between the contacts consists of both Auger recombination due to the heavy doping, and surface recombination due to the presence of surface defects (where the interface defect density

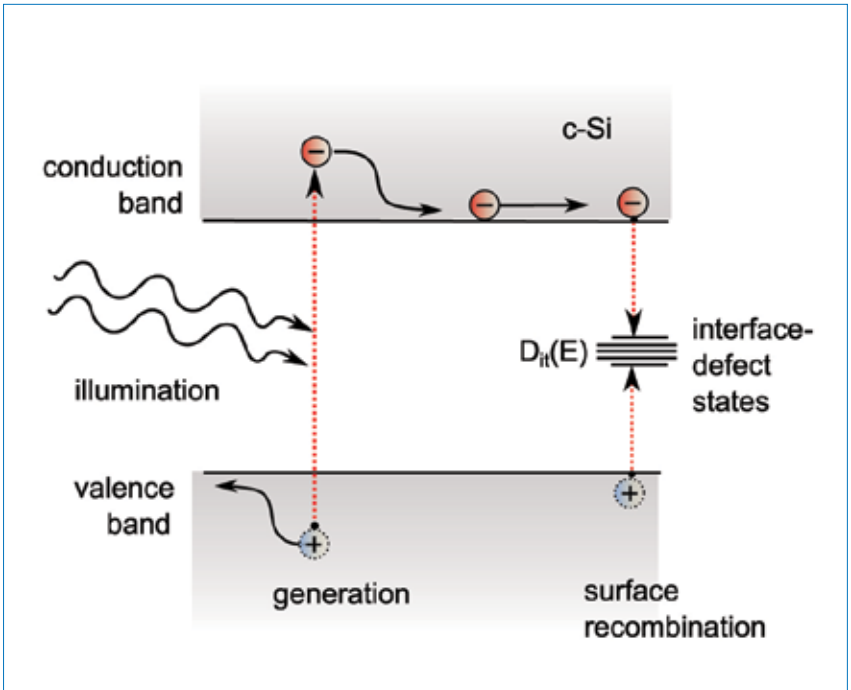

Figure 2. A schematic band diagram of silicon, showing the generation of excess carriers by the absorption of light and the surface recombination of excess charge carriers via interface defect states.

is denoted by D_{it}). In the following sections, improvements to the p^+ doped region and to the surface passivation, both aiming to reduce the front-surface recombination, will be addressed.

Doping-profile optimization

For the n-Pasha cells, the boron and phosphorus diffusions are performed in a Tempress industrial tube furnace using BBr_3 and $POCl_3$ as precursors, respectively. The phosphorus n^+ region at the rear provides additional lateral conductivity for electrons, which makes the n-Pasha concept less sensitive to changes in the n-type bulk resistivity and allows the use of a bulk material with a high resistivity of 10Ω•cm [6]. The latter consideration is of importance for n-type solar cells, as the variation in base resistivity of n-type ingots is higher than for p-type ingots because phosphorus has a higher segregation coefficient than boron. The efficiency improvements of n-Pasha cells through using a shallower doped n^+ region, while maintaining the lateral transport properties, have recently been reported by the authors [5,6]. Here, however, the focus will be on improving the boron-doping profile.

Fig. 3(a) shows the electrochemical capacitance–voltage (ECV) profile of a standard boron diffusion of the n-Pasha cell with a sheet resistance R_s of 60Ω/sq. This standard profile (profile 1) exhibits a boron-depleted region within the first 10 to 30nm; the depleted region originates from the higher solubility of boron in SiO_2 than in Si. SiO_2 is intentionally formed after boron diffusion to reliably remove the boron-rich layer (BRL), a Si-B compound which is otherwise difficult to remove and is detrimental to surface passivation [11]. The boron-depleted region of profile 1 can, however, be etched back, resulting in doping profiles 2 and 3. Note that the application of dielectrics for surface passivation in the work reported in this paper does not reintroduce such a depletion region because of the synthesis at low temperatures.

To study the effect of the three different doping profiles of Fig. 3(a) on the recombination current density, the profiles served as input for 2-D Atlas simulations [12]. In Fig. 3(b) the simulated J_0 value of each profile is shown as a function of the surface recombination velocity (SRV). Removal of the boron-depleted region in profiles 2 and 3 yields a reduction in J_0, both for well-passivated surfaces with low SRVs and for surfaces without passivation, such as the contacted regions, having high SRVs. A recent study by Black et

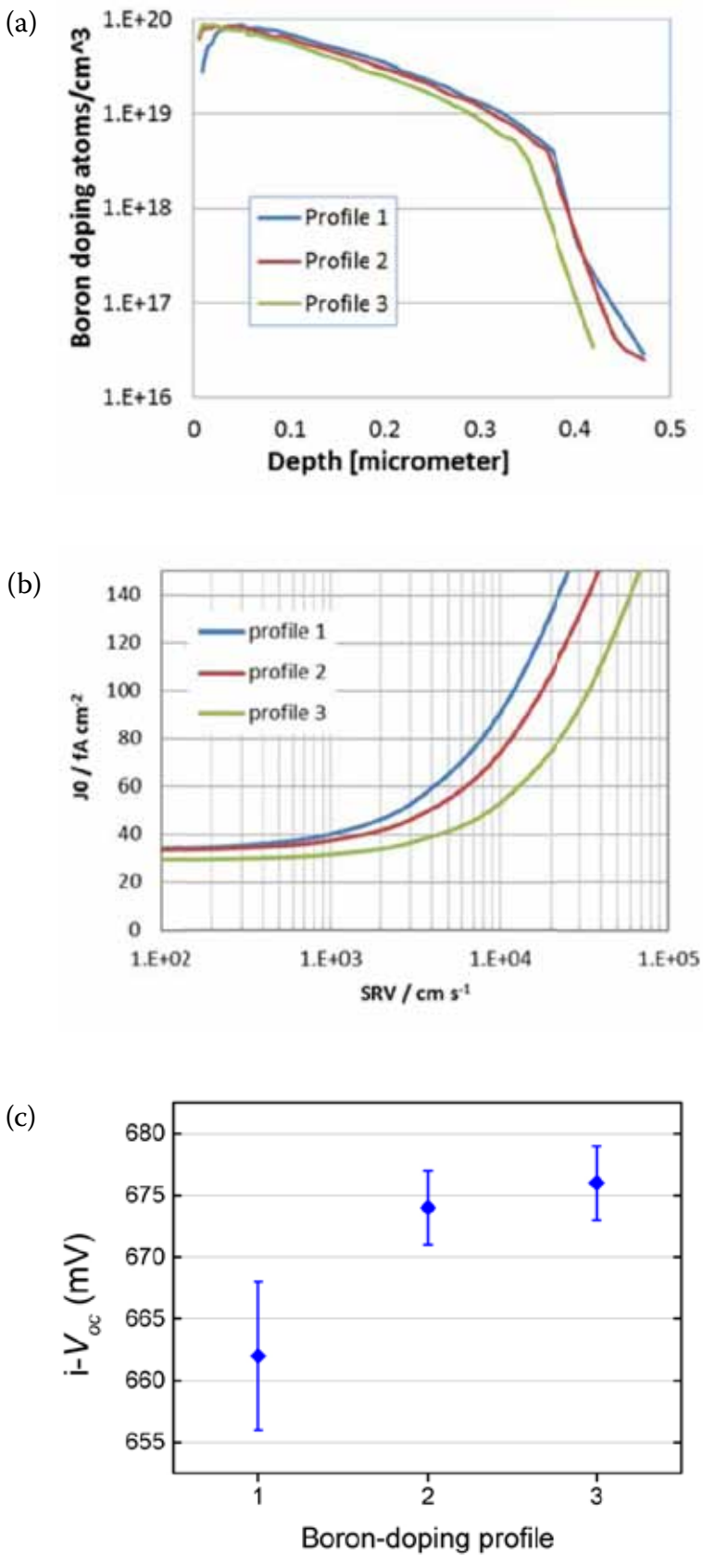

Figure 3. (a) ECV profiles of a standard boron-doped surface (profile 1) and after etching (profiles 2 and 3); (b) J_0 as a function of the SRV of the boron-doped surfaces, from Atlas simulations; (c) implied open-circuit voltage of symmetrically diffused $p^+/n/p^+$ samples passivated by NAOS/SiN_x, measured by QSS-PC.

al. [13] showed that the interface defect density (D_{it}) is independent of the boron-dopant concentration at the Si surface of the $Si/SiO_2/Al_2O_3$ interface. The benefits of etching the boron-depleted region can therefore be fully explained by the decreased minority-carrier (i.e. electron) concentration at the surface, which results in a lower surface recombination and hence in a lower J_0.

To experimentally determine J_0 of the different diffusion profiles, symmetrically diffused and textured $p^+/n/p^+$ samples were fabricated with the diffusion profiles in Fig. 3(a). The samples were passivated by the conventional n-Pasha front-passivation scheme: nitric acid oxidation (NAOS) [14] plus 70nm hydrogenated amorphous silicon nitride (a-SiN_x:H, or in short, SiN_x), deposited by (remote) plasma-enhanced chemical vapour deposition (PECVD). This SiN_x layer also serves as an anti-reflection coating. The results from quasi-steady-state photoconductance (QSS-PC) measurements are shown in Fig. 3(c). Etching back the diffusion profile 1 to profile 2 leads to an improvement of ~12mV in the implied open-circuit voltage i-V_{oc}, corresponding to a significant reduction in J_0 of 50fA/cm^2 per side. The additional i-V_{oc} gain obtained by extending the etch, however, is quite small (profile 3). Moreover, profile 3 results in a higher sheet resistance than for the other two profiles: 85Ω/sq. vs. 60Ω/sq. for profiles 1 and 2. The higher sheet resistance reduces the lateral conduction of holes and may affect the fill factor of the cells. For diffusion profile 2, however, there is no significant increase in sheet resistance.

> "Etching back the p^+ region is both a simple and an effective approach for optimizing diffusion profiles."

The benefit of using doping profile 2 is also confirmed at the cell level. The V_{oc} of the cells increases by 6mV, resulting in an efficiency gain of ~0.2% abs. (Table 1). Therefore, etching back the p^+ region is both a simple and an effective approach for optimizing diffusion profiles. The next step is to improve the passivation of the p^+ surface.

Surface passivation of n-Pasha cells

For a long time, no satisfactory solution existed for the passivation of boron-doped p^+ surfaces. It is known that passivation by thermally grown silicon dioxide, although initially providing reasonable levels of passivation, is subject to significant light-induced degradation [15]. Moreover, the passivation of boron-doped surfaces by SiN_x, which is the commonly used material for the passivation of n^+ surfaces, generally results in low passivation, or even none at all [14]. The poor passivation performance on a p^+ surface can be explained by its large positive fixed charge density ($Q_f > 2 \cdot 10^{12} cm^{-2}$), which increases the minority-carrier (i.e. electron) density near the surface.

In 2008 ECN reported the significant improvements in the passivation of p^+ doped Si by adding a chemical oxide below the SiN_x; the oxide is grown at room temperature by a nitric acid oxidation of silicon (NAOS) [14]. This breakthrough in the passivation of boron-doped surfaces enabled the industrial development of low-cost n-type Si solar cells. Around the same time, however, a superior passivation of p^+ surfaces was discovered: Al_2O_3 prepared by atomic layer deposition (ALD) [16]. The excellent level of passivation could be attributed to a

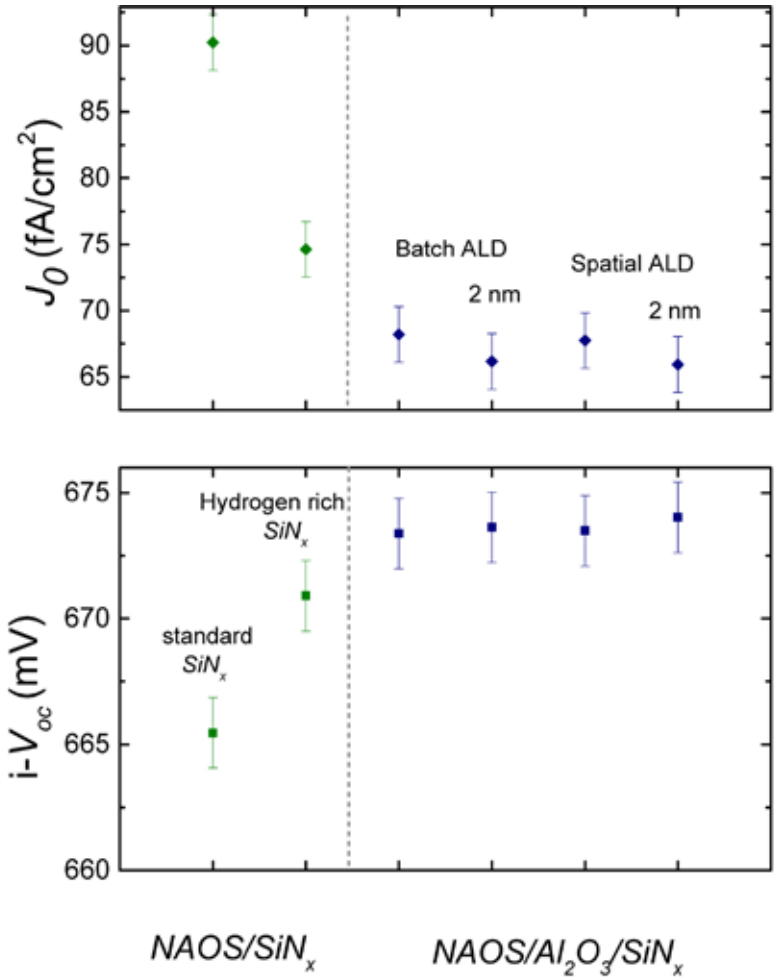

Figure 4. Recombination current density (a) and implied open-circuit voltage (b), as measured by quasi-steady-state photoconductance measurements of symmetrically boron-diffused p+/n/p+ samples with random-pyramid texture (Rs = 60Ω/sq.), passivated by different passivation schemes.

		I_{sc} [A]	J_{sc} [mA/cm^2]	V_{oc} [V]	*FF*	η [%]
Boron profile 1 (standard)	avg	9.31	39.0	0.647	0.784	19.7
Boron profile 2 (etched back)	avg	9.35	39.1	0.653	0.779	19.9

Table 1. *I-V* results for cells with the boron-doping profiles 1 and 2, passivated by NAOS/SiN_x.

very low interface defect density and a high *negative* fixed charge density ($Q_f \approx -5 \cdot 10^{12} cm^{-2}$) [17]. However, reactors with significant throughput were not available at the time. Since the discovery of passivation by Al_2O_3, industry has put a lot of effort into high-volume manufacturing by ALD, resulting in the development of, for example, spatial and batch ALD reactors for Al_2O_3. Although Al_2O_3 can also be deposited by PECVD, the requirement of very thin (~1–3nm) Al_2O_3 films for p^+ passivation of cells makes ALD the ideal candidate. A comparison between ALD Al_2O_3 passivation and the conventional passivation scheme of the p^+ surface of n-Pasha is therefore highly relevant.

Several industrial passivation schemes for symmetrically diffused and textured $p^+/n/p^+$ samples were compared with the conventional boron profile of n-Pasha (profile 1 of Fig. 3(a)). First, the standard surface passivation of n-Pasha cells (NAOS/SiN_x) was directly compared with the passivation by Al_2O_3 films on NAOS. The Al_2O_3 films were deposited in a batch ALD reactor from ASM or by spatial ALD in a Levitech reactor, and capped by 70nm PECVD SiN_x. Generally, Al_2O_3 passivation is enhanced by annealing the films around the optimum temperature of 400°C. In this case, however, the passivation was activated by the thermal budget of the PECVD SiN_x deposition process and a subsequent firing step (~800°C). The results are summarized in Fig. 4. The passivation schemes comprising 2nm Al_2O_3 yield a significant reduction in J_0, from 90fA/cm² to 66fA/cm², as compared to conventional passivation; this can be attributed to the very low interface defect density and the high negative fixed charge density associated with the Al_2O_3 films. The Al_2O_3 films prepared by the two ALD deposition systems performed similarly, indicating the robustness of the ALD process.

> "The passivation schemes comprising 2nm Al_2O_3 yield a significant reduction in J_0, as compared to conventional passivation."

Second, it was found that the conventional p^+ surface passivation by NAOS/SiN_x can also be improved. A reduction in J_0 from 90fA/cm² to 75fA/cm² was achieved by tuning the a-SiN_x:H towards a more hydrogen-rich composition. This improvement can be attributed to an increased level of chemical passivation induced by the additional hydrogenation of the Si/SiO_2 interface [18]. More details concerning the specific experiments on p^+ surface passivation can be found in the literature [19], in which the passivation of the n^+ surface is also addressed.

Interestingly, the high level of passivation of the p^+ surface by Al_2O_3 can be further enhanced by improving the surface pretreatment, which conventionally consists of a diluted hydrofluoric (HF-) dip. Fig. 5 shows the effect on the i-V_{oc} of using a novel chemical pretreatment on a $p^+/n/n^+$ lifetime sample with boron-doping profile 1, passivated by NAOS/SiN_x. The gain in i-V_{oc} is even higher when the new pretreatment is combined with Al_2O_3 passivation of the p^+ surface (i.e. NAOS/Al_2O_3/SiN_x), yielding i-V_{oc} values of 676mV. Table 2 shows the *I-V* results for cells having the new chemical pretreatment but using the standard passivation scheme. Improvements solely to the chemical pretreatment led to a gain in conversion efficiency of 0.3% abs., which is the result of a higher V_{oc}. It is expected that this efficiency will be increased even further by implementing Al_2O_3 surface passivation.

Conclusions and outlook

The efficiency of n-Pasha solar cells is limited by the charge carrier recombination within the boron-doped p^+ region and at its surface. In this paper several industrially feasible approaches have been identified for reducing the recombination at the front side. First, the boron-depletion region can be reduced by etching the boron-doped surface; in combination with NAOS/SiN_x passivation, this results in a lower recombination current density and higher cell efficiencies. Second, the passivation of a standard p^+ diffusion profile can be improved by using 2nm Al_2O_3 deposited by batch or spatial ALD. Finally, a novel chemical pretreatment, in combination with standard passivation by NAOS/

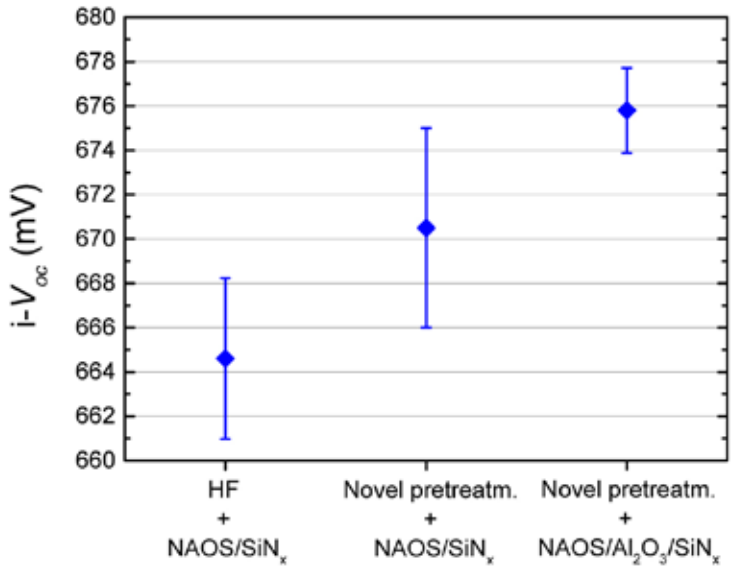

Figure 5. Implied open-circuit voltage for textured $p^+/n/n^+$ samples having different surface pretreatments and different p^+ surface passivation, with NAOS/SiN_x passivation of the n^+ surface.

		I_{sc} [A]	J_{sc} [mA/cm²]	V_{oc} [V]	*FF*	η [%]
Standard HF dip	avg	9.31	39.0	0.649	0.785	19.8
Improved oxide pretreatment	avg	9.30	38.9	0.655	0.788	20.1

Table 2. *I-V* results for improved oxide pretreatment on the p^+ surface vs. the standard HF dip in combination with symmetrical NAOS/SiN_x passivation.

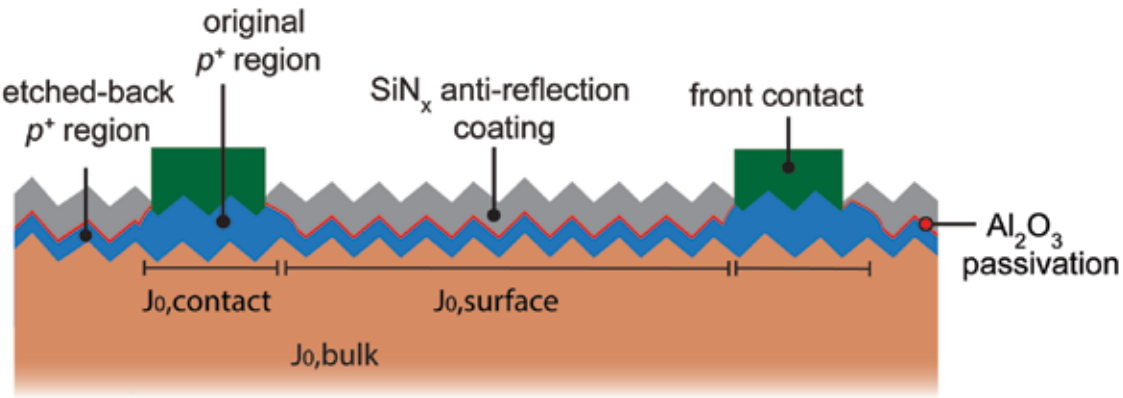

Figure 6. Schematic cross section of a potential new design of the front side of an n-Pasha cell, comprising Al_2O_3 surface passivation and selective p^+ regions which are highly doped under the metallic contacts.

SiN_x, also demonstrates improvements in n-Pasha efficiency of 0.3%. Photoconductivity measurements indicate that further improvements in efficiency may be gained by combining the novel pretreatment with Al_2O_3 passivation.

> "Further improvements in efficiency may be gained by combining the novel pretreatment with Al_2O_3 passivation."

The results presented in this paper will be implemented in n-Pasha cells in the next few months. These modifications pave the way for realizing conversion efficiencies of 21% on high-quality Cz wafers.

As a next step to reducing J_0 of the front surface, an implementation of selective doping under the contacts is being considered for n-Pasha cells (Fig. 6). This area selectivity allows a separate optimization of $J_{0,contact}$ and the contact resistance on the one hand, and of $J_{0,surface}$ and the lateral conduction of holes on the other. This helps to reduce the metal contact recombination associated with the p^+ diffusion, which is an important loss factor for n-type Si cells.

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References

[1] Burgers, A.R. et al. 2010, "19% efficient n-type Si solar cells made in pilot production", *Proc. 25th EU PVSEC*, Valencia, Spain, pp. 1106–1109.

[2] PR Newswire 2013, "n-PASHA alliance awarded 100 MW n-type technology and equipment order for Nexolon Turnkey Project in USA" [http://www.prnewswire.com].

[3] Van Aken, B. & Carr, A.J. 2014, "Relation between indoor flash testing and outdoor performance of bifacial modules", *Proc. 29th EU PVSEC*, Amsterdam, The Netherlands [forthcoming].

[4] Romijn, I. 2014, presentation at SNEC 8th Int. PV Power Gen. Conf., Shanghai, China.

[5] Romijn, I. et al. 2012, "Industrial n-type solar cells : Towards 20% efficiency", *Photovoltaics International*, 15th edn, pp. 81–90.

[6] Romijn, I. et al. 2013, "Cost effective n-Pasha solar cells with efficiency above 20%", *Photovoltaics International*, 20th edn, pp. 33–40.

[7] Janssen, G.J.M. et al. 2013, "Power loss analysis of n-Pasha cells validated by 2D simulations", *Proc. 28th EU PVSEC*, Paris, France.

[8] Macdonald, D. & Geerligs, L.J. 2004, "Recombination activity of interstitial iron and other transition metal point defects in p- and n-type crystalline silicon", *Appl. Phys. Lett.*, Vol. 85, No. 18, p. 4061.

[9] Cuevas, A. et al. 2013, "Misconceptions and misnomers in solar cells", *IEEE J. Photovolt.*, Vol. 3, No. 2, pp. 916–923.

[10] Feldmann, F. et al. 2014, "Passivated rear contacts for high-efficiency n-type Si solar cells providing high interface passivation quality and excellent transport characteristics", *Solar Energy Mater. & Solar Cells*, Vol. 120, pp. 270–274.

[11] Vlooswijk, A.H.G., Venema, P. & Komatsu, Y. 2010, "Boron processing in solar cell industry: Boron diffusion in silicon wafers", in *Boron: Compounds, Production and Application*, Perkins, G.L., Ed. Hauppauge, New York: Nova Science Publishers, pp. 543–549.

[12] Silvaco 2014, Atlas Device Simulation Framework [http://www.silvaco.co.uk/products/tcad/device_simulation/atlas/atlas.html].

[13] Black, L.E. et al. 2014, "Effect of boron concentration on recombination at the p-Si–Al_2O_3 interface", *J. Appl. Phys.*, Vol. 115, No. 9, p. 093707.

[14] Mihailetchi, V.D., Komatsu, Y. & Geerligs, L.J. 2008, "Nitric acid pretreatment for the passivation of boron emitters for n-type base silicon solar cells", *Appl. Phys. Lett.*, Vol. 92, No. 6, p. 063510.

[15] Thomson, A.F. & McIntosh, K.R. 2009, "Degradation of oxide-passivated boron-diffused silicon", *Appl. Phys. Lett.*, Vol. 95, No. 5, p. 052101.

[16] Hoex, B. et al. 2007, "Excellent passivation of highly doped p-type Si surfaces by the negative-charge-dielectric Al_2O_3", *Appl. Phys. Lett.*, Vol. 91, No. 11, p. 112107.

[17] Dingemans, G. & Kessels, W.M.M. 2012, "Status and prospects of Al_2O_3-based surface passivation schemes for silicon solar cells", *J. Vac. Sci. Technol. A: Vac., Surf., Films*, Vol. 30, No. 4, p. 040802.

[18] Dingemans, G. et al. 2011,

"Effective passivation of Si surfaces by plasma deposited SiO_x/a-SiN_x:H stacks", *Appl. Phys. Lett.*, Vol. 98, No. 22, p. 222102.

[19] Saynova, D.S. et al. 2013, "Dielectric passivation schemes for high efficiency n-type c-Si solar cells", *Proc. 28th EU PVSEC*, Paris, France, pp. 1188–1193.

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Gijs Dingemans works at ASM on process development for solar and semiconductor applications. He received his Ph.D. in 2011 from Eindhoven University of Technology. Gijs has authored and co-authored more than 35 publications in the field of thin-film deposition, surface passivation and solar cells.

Ernst Granneman is one of the founders of Levitech BV, which specializes in developing ALD Al_2O_3 processes and systems for the passivation of c-Si solar cells. Prior to joining Levitech in 2009, Ernst worked for ASM International in various capacities. He carried out his Ph.D. research at the FOM Institute for Atomic & Molecular Physics in Amsterdam.

Ingrid Romijn joined ECN Solar Energy in 2004, where she started working as a researcher and later on (2006) as a project leader in the crystalline silicon group. Research topics included passivating layers, optimization of SiN_x deposition systems and (advanced) p-type solar cell concepts. During 2011 the focus of her work shifted towards the development and industrialization of n-type cell concepts. In 2012 Ingrid became the topic coordinator for industrial n-type cells and modules at ECN Solar Energy.

Gaby Janssen joined ECN in 1986 as a researcher and project manager. She has been working on topics relating to the simulation, characterization and optimization of materials for energy conversion technologies. In 2011 she joined the solar energy department at ECN, where she is now working on the modelling and simulation of PV cells.

Erwin Kessels is a professor at Eindhoven University of Technology, leading the plasma and materials processing group in the Department of Applied Physics. The group's research focuses on the deposition of (ultra)thin films by methods such as (plasma-enhanced) chemical vapour deposition and atomic layer deposition, with the main application areas being nanoelectronics and photovoltaics. Erwin has been working on surface passivation since the early 2000s and he was one of the pioneers in the field of Al_2O_3 films for Si surface passivation.

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