



SiO₂ surface passivation layers – a key technology for silicon solar cells

Stefan W. Glunz^{a,b,*}, Frank Feldmann^{a,b}

^a Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, D-79110 Freiburg, Germany

^b Laboratory for Photovoltaic Energy Conversion, Department of Sustainable Systems Engineering, Albert-Ludwigs-University Freiburg, Germany



ABSTRACT

High-efficiency silicon solar cells strongly rely on an effective reduction of charge carrier recombination at their surfaces, i.e. surface passivation. Today's industrial silicon solar cells often utilize dielectric surface passivation layers such as SiN_x and Al₂O₃. However, a passivation layer well-known from the microelectronic industry, SiO₂, had and has a strong impact on silicon photovoltaics. It allowed to develop the first 20% efficient silicon solar cells in the past and currently experiences a renaissance as the interfacial oxide for silicon-based passivating contacts, thus enabling the next generation of silicon solar cells. This article reviews the properties of SiO₂ passivation layers and their strong impact on the historical and current development of silicon solar cells.

1. Surface passivation of silicon solar cells

1.1. Recombination losses

Photovoltaic energy conversion based on crystalline silicon solar cells is one of the major technological pillars for the enormous success of renewable energies in the last decade. The rapid reduction of leveled costs of electricity is achieved by reduced production costs and increased conversion efficiencies. The ways to increase conversion efficiency are manifold. This task can be compared with fixing a leaky bucket [1,2] which is used to collect as much water as possible. Since the bucket has many holes the question arises which is the first one to be fixed to obtain a better “water collection efficiency”, i.e. cell efficiency.

The holes symbolize different losses as resistive and optical losses and recombination of photo-generated charge carriers. The latter one is often regarded as the most detrimental and complex loss channel in a solar cell. We can distinguish between extrinsic recombination as (Fig. 1)

- surface defect recombination and
- Shockley-Read-Hall recombination via bulk defects

and intrinsic recombination as

- Auger and
- radiative recombination.

Indeed, the leaky bucket features a variety of different holes with different diameters. Therefore, before starting to fix the bucket, a detailed analysis of the situation should be performed. This is a challenging task since there is a strong interaction between the different recombination losses. Fig. 2 shows the intrinsic and extrinsic recombination loss currents of a silicon solar cell at maximum power point (mpp) as a function of the surface recombination at the rear side (S_{back}) [3]. If the surface recombination velocity at the rear side is high ($S_{\text{back}} = 1000 \text{ cm/s}$), we observe a very high loss current of more than 3.5 mA/cm^2 (red area) while the other recombination channels (grey areas) seem to play a negligible role. Therefore, fixing this biggest hole in the bucket should be tackled by reducing the surface recombination velocity at the rear side. In the last decades such reduction of the surface recombination was in fact among the most important improvements of silicon solar cells. And in fact, less water is running out of the bucket, i.e. the total recombination current at mpp is significantly reduced.

While the total recombination loss is reduced with decreasing S_{back} , the loss currents of the other recombination channels are increasing not only relatively but also *absolutely* although material properties such as the bulk lifetime have not changed. The higher absolute loss results from the higher amount of available free charge carriers. In other words: Due to fixing one of the holes (“rear surface recombination”), the water level in the bucket has been raised and the leakage through the other holes is getting larger. This demonstrates the complexity of the optimization of a solar cell which is getting even more complex in real world since additional interactions in the process sequence have to be taken into account.

* Corresponding author.

E-mail address: stefan.glunz@ise.fraunhofer.de (S.W. Glunz).



Fig. 1. The leaky bucket (Drawing: Courtesy of Willi Gertsen, 2018).

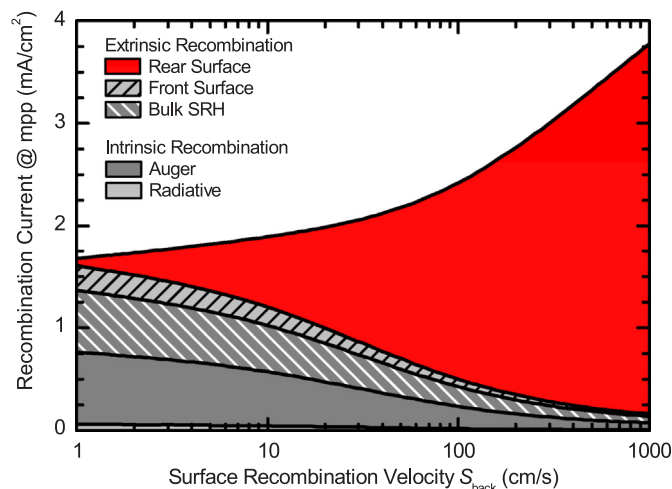


Fig. 2. Recombination losses of silicon solar cells as a function of recombination velocity at the rear side (Data taken from [3]).

1.2. Dielectric layers for surface passivation

The reduction of surface recombination at the front and rear of the solar cell was definitely one of the most important technological advances for industrial n^+p p^+ cells in the last decades [4,5]. Reducing the recombination at the front surface and thus in the emitter with SiN_x layers [6] deposited using plasma-enhanced chemical vapor deposition (PECVD) has improved the blue response and the open-circuit voltage (V_{oc}) of solar cells. The high concentration of hydrogen in such SiN_x layers is partly released in the final firing metallization step and results in an additional hydrogen passivation of bulk defects in multicrystalline silicon. Thus, we have fixed two holes with one additional cell feature. Also, the reduction of the recombination at the rear side had a strong impact since the thickness of industrial solar cells was reduced from more than 300 μm to less than 200 μm in the last decades. This diminishes the impact of bulk recombination while the recombination at the rear surface is getting more and more dominant. As a first measure to reduce S_{back} , the quality of the aluminum paste and the related firing step used for the creation of the p p^+ high-low junction (back surface field, BSF) was strongly improved. This resulted in silicon solar cells

with efficiencies around 20% [7].

For an even more effective suppression of surface recombination, rear structures with partial contacts (PRC) and dielectric surface passivation are transferred into industrial production [8]. This structure well-known as passivated emitter and rear cell (PERC) has additionally the advantage to improve the internal reflection of long-wavelength light. The strong positive charge of the SiN_x layer which is used to passivate the n -type emitter of n^+p industrial cells would result in an inversion layer on the weakly doped p -type rear surface. Therefore, a new passivation layer with a strong negative charge, Al_2O_3 , was introduced to photovoltaics a few years ago [9,10]. Such layers are either deposited by atomic layer deposition or plasma-enhanced vapor deposition [11]. Most of today's PERC-type solar cells use Al_2O_3 with an additional SiN_x capping layer allowing for conversion efficiencies of around 22% and 21% on mono- and multicrystalline silicon, respectively [12,13].

However, when reviewing today's most frequently used dielectric layers for the rear surface passivation of PERC cells in industrial production, i.e. SiN_x and Al_2O_3 [8], one should not forget the most influential and natural surface passivation for silicon solar cells: thermally grown silicon dioxide, SiO_2 . In this article we will review the impact of SiO_2 surface passivation layers which have allowed for the successful development of silicon solar cells with efficiencies of more than 20%. Actually, SiO_2 experiences a renaissance as the interfacial oxide for silicon-based passivating contacts for the next generation of silicon solar cells as discussed in the second part of this publication.

2. SiO_2 for photovoltaic applications – a review

It is fair to say that the passivation of the surfaces of silicon solar cells was THE enabler for achieving efficiencies greater than 20%. The first and most natural choice for surface passivation is a thermally grown SiO_2 . Thermal oxides were the key technology for microelectronics [14–16] and were adapted already very early in the history of silicon solar cells.

2.1. Metal insulator semiconductor solar cells

One of the first applications of oxides in silicon photovoltaics was as a thin intermediate layer in metal-insulator-silicon (MIS) structures [17–21]. The oxide allows to reduce the recombination at the metal interface and to utilize the work function difference between the metal contact and silicon in the semiconductor more effectively thereby inducing an effective junction. The junction between the front metal contacts could be either established by an inversion layer (IL) enhanced by charges incorporated in a SiN_x layer [21] or by an additional phosphorus diffusion resulting in the so called MIS- n^+p (MINP) cell structure [22]. Such MINP cells showed a high open-circuit voltage of 678 mV [23] and a very good blue response. The MIS-IL cell (see Fig. 3) was later produced by the German company Nukem [24].

Thin oxides were also used in polysilicon/ SiO_x structures [25,26] for photovoltaic applications which have experienced a renaissance in the last years as described in detail in a later section of this paper.

2.2. Front surface passivation

In most of today's silicon solar cells more conventional contacts are utilized where the passivation layer is only applied in-between the front contact and a direct metal-semiconductor contact is established. In 1978, Fossum and Burgess [27] oxidized the front surface of a simple $p^+ n n^+$ BSF cell with a thin SiO_2 layer and achieved open-circuit voltages in the range of 620 mV compared to cells without oxide exhibiting only up to 590 mV. Later on this concept was optimized and led to the first passivated emitter solar cells (PESC) [28]. The PESC structure featured a contact opening in the front oxide smaller than the contact finger itself, reducing the metal-semiconductor recombination.

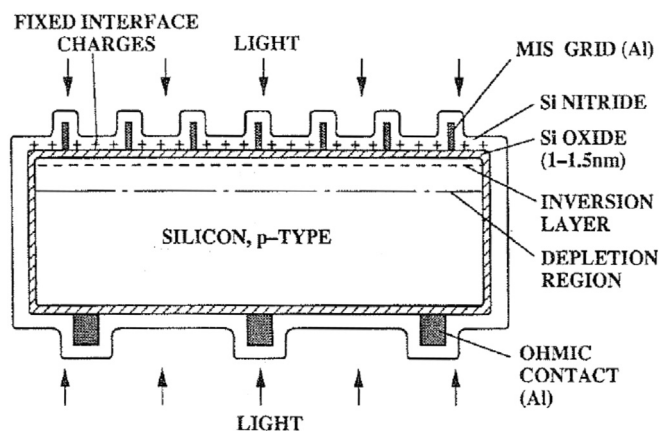


Fig. 3. Cross section of a bifacial MIS inversion solar cell. Reprinted from Ref. [24], with the permission of WIP Renewable Energies.

With such cells open-circuit voltages of more than 650 mV and efficiencies of 19% were achieved [28,29]. The early PESC cells still had a flat front surface and thus it was a logical step to combine surface passivation with surface texturing to achieve higher efficiencies. In fact, the microgrooved PESC cell (see Fig. 4) was the first silicon solar cell to achieve efficiencies greater than 20% [30].

2.3. Front and rear surface passivation

The traditional way to improve the electrical quality of the rear surface i.e. to reduce carrier recombination was the implementation of a high-low junction commonly known as a back surface field.¹ The BSF decreases the number of minority carriers at the rear surface of the cell and thus reduces recombination rather by changing carrier statistics than reducing the surface defect density. By alloying aluminum into the rear surface of p-type silicon solar cells a robust and well-performing structure is obtained [32]. The performance can be even improved if boron is mixed into the Al paste to increase the doping concentration of the p^+ -layer [33,34]. This structure has been the workhorse for the photovoltaic industry until today.

However, the potential of cells with surface passivation at front and rear is substantially higher as already shown by several groups in the 1980s. At University of New South Wales the PESC design was extended by reducing the local contacts at the rear to a minimum and passivating the rest of the rear surface with SiO_2 . This cell structure featuring partial rear contacts, also well known as the PERC cell, resulted in efficiencies of more than 22% [35]. The reduced carrier recombination at the rear surface improved both the open-circuit voltage and the short-circuit current of the solar cell.² The current was further boosted by the increased internal reflection of light at the rear surface improving the light-trapping of weakly absorbed infrared light. In fact the system silicon- SiO_2 -metal is an almost perfect mirror which benefits additionally from total reflection especially if the rear oxide is thick enough [36].

At the same time, researchers of Stanford University presented a 1-sun version [37] of an interdigitated back-contact (IBC) solar cells which was originally developed for high-concentration applications [38]. Using this sophisticated cell structure, efficiencies of 22.3% and very high open-circuit voltages above 700 mV could be achieved. As for the PERC structure, both sides of the cell are passivated very efficiently. The carrier separation takes place at the rear side at relatively small

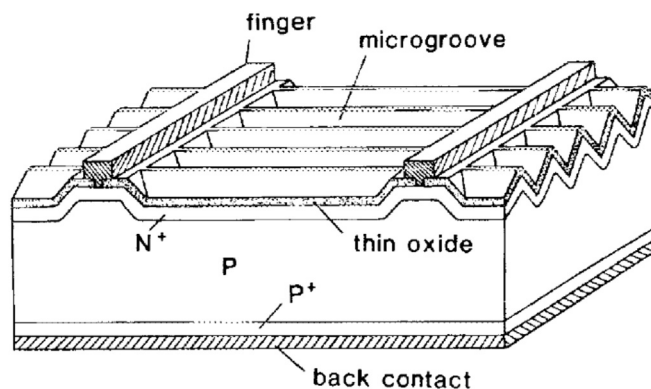


Fig. 4. Microgrooved PESC cell. Reprinted from Ref. [30], with the permission of AIP Publishing.

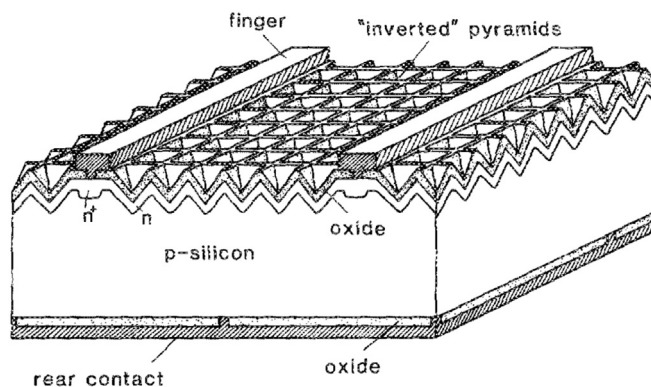


Fig. 5. Structure of a PERC cell. Reprinted from Ref. [35], with the permission of AIP Publishing.

point-like diffused regions. Thus, most of the photo-generated carriers have to diffuse from the front to the rear and the front surface passivation is of even greater importance compared to other cell architectures. A simplified version of such IBC cells [39] was the blueprint of SunPower's Gen 1 and Gen 2 IBC solar cells [40–42].

For both developments, PERC and IBC, a significantly improved oxidation using a chlorine-containing oxidation atmosphere process was used [35,43]. The addition of chlorine-containing materials like TCA or HCl to the O_2 flow during oxidation was introduced in microelectronics [14,44] since it reduces the concentration of mobile Na^+ ions which create instabilities in MOS devices. Such chlorine-containing atmosphere also removes other residual metallic impurities from the wafer surface and, therefore, considerably higher carrier lifetimes and cell efficiencies can be achieved.

In the following years both cell types reached higher and higher efficiencies finally achieving an efficiency of 25% [45,46] using the passivated emitter and rear, locally diffused cell (PERL). The main feature which was added to the original PERC cell were heavily doped p^+ -regions under the rear contact points which was either achieved by boron diffusion as in the PERL structure [47,48] or aluminum alloying as in the local back surface field (Al-LBSF) structure. [49] This reduces the recombination at the remaining small metallized regions and increases the open-circuit voltage and is utilized in modern industrial cells as well. A similar feature i.e. local n^+ -regions under the front contact openings also known as selective emitter was added to improve the front performance. Another improvement of the later PERL/LBSF cells was the optimization of the front side optics. Early PERC cells [35] just used a thick (~ 100 nm) thermal oxide at the front as passivation and antireflection layer. However, due to the low refractive index of SiO_2 this is a non-ideal solution. Therefore, thinner oxides (< 30 nm) capped by a higher refractive material like TiO_2 were used [50,51].

¹ This term is still the most commonly used term although relating the function of the high-low junction to an electric field is misleading [31].

² Note that the original PERC did utilize only pure ohmic rear contact points. The introduction of an additional aluminum or boron BSF was introduced later in the Local Back Surface Field (LBSF) or passivated emitter and rear, locally diffused cell (PERL) cell, respectively (see below).

However, the lower passivation quality of these thinner oxides was a challenge. Thus, an intentional Alneal step was introduced [52]. From microelectronics it was well known that the reduction of water in the oxide layer, which occurred at the SiO_2/Al interface at temperatures between 300 °C and 450 °C, resulted in the release of atomic hydrogen which improved the Si-SiO₂ interface significantly [53]. Such an Alneal step comes for free in PERC cells due to the rear Al electrode. In contrast, on the front side an additional thin Al layer was deposited, a low-temperature step was performed, the Al layer was etched and the additional antireflection layer was deposited. These front layer systems allowed for very high currents ($> 42 \text{ mA/cm}^2$) and high voltages ($> 700 \text{ mV}$). Also carrier lifetime measurements on oxide-passivated samples showed the beneficial effect of an Alneal step [54].

PERL cells at that time used local boron and phosphorus diffusion (as reflected by the label “locally diffused”). This process was simplified by substituting the local boron diffusion for a local laser Al firing process [55] or by thermal alloying of Al paste after an laser opening of the rear passivation layer [56]. The latter process is the standard of current industrial PERC cells with efficiencies up to 22% [12].

Due to the excellent passivation quality of SiO_2 layers, the surface recombination velocity in oxide-passivated PERC devices is strongly reduced. Additionally, the internal reflection at the Si-SiO₂-Al rear surface is very high allowing for an excellent light trapping. Therefore, it can be expected that even very thin silicon solar cells should show a very high performance. In fact, Wang et al. could fabricate a PERL cell with a thickness of 47 μm exhibiting an efficiency of 21.5% and a very high voltage of close to 700 mV [57]. Later on, it was possible to show that even on a 37 μm thin silicon solar cell it is possible to achieve an efficiency of 20.2% ($V_{\text{oc}} = 675 \text{ mV}$, $J_{\text{sc}} = 36.6 \text{ mA/cm}^2$, $FF = 81.9\%$) [58,59]. Additionally, it was shown that cells on low-quality silicon benefited from the reduction of the thickness due to an improved ratio of diffusion length to thickness [58].

In the last decade very attractive industrial PERC process sequences based on thermal oxidation were developed [60–62] and the production technology for thermal oxidation was improved to increase through-put [63,64]. However, due to the excellent physical properties of Al_2O_3 i.e. its strong negative built-in charge, most of today's PERC-type solar cells use Al_2O_3 with an additional SiN_x capping layer for the rear side passivation [8]. For the passivation of the front side a thin SiO_2 layer under the front SiN_x antireflection layer is still of interest, since it improves surface passivation and also reduces significantly the effect of potential-induced degradation (PID-s) [65].

3. Electrical properties of SiO_2 passivation layers

3.1. Physical properties

For the electrical characterization of dielectric passivation layers, the following physical parameters are of major interest:

- the interface state density, D_{it} (E), (unit: $\text{eV}^{-1} \text{ cm}^{-2}$), which has to be determined as a function of energy since the defect levels are distributed over the whole bandgap,
- the capture cross sections for electrons and holes, σ_n and σ_p (unit: cm^{-2}),
- and the density of fixed charges in the layer, Q_f (unit: cm^{-2}) resulting in a shift of the flat-band voltage, V_{FB} (unit: V).

Due to the great importance of the Si-SiO₂ system for the CMOS technology it has been studied extensively in the last decades [15,66]. While capacitance voltage measurements on MOS structures are used to determine V_{FB} and D_{it} [67], a modified version of deep-level transient spectroscopy (DLTS) was used to determine σ_n and σ_p [67,68]. The main findings [69–71] are that the Si-SiO₂ interface features

- very low D_{it} values in the range of $10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ (especially after

an Alneal step)

- capture cross sections which are highly asymmetric $\sigma_n \approx 100 \times \sigma_p$
- and a low positive fixed charge density $Q_f \approx 10^{11} \text{ cm}^{-2}$ which results in a small negative V_{FB} .

3.2. Determination of surface recombination velocity

The measured values of D_{it} , Q_f , σ_n and σ_p , can be used to calculate the surface recombination velocity, S , for different doping concentrations and excess carrier densities [43,69,72,73]. The calculated S values show a decrease with decreasing doping concentrations. Due to the asymmetry of electron and hole capture cross section, S is generally lower on n-type silicon and shows a weaker dependence on the excess carrier density [43,69]. It could be shown that these predictions of the surface recombination velocity are in good agreement with values determined from quantum efficiency measurement of devices [69] and carrier lifetimes on moderately doped test samples [74]. The analysis of the SiO_2 passivation quality on highly doped silicon surfaces shows an effective surface passivation for n-type surfaces, i.e. phosphorus emitters [75–77]. However, the passivation quality achieved on silicon with a high boron doping was much lower [78]. In fact, high-efficiency n-type PERL-type cells with boron emitter showed severe instabilities [79]. Such boron emitters have to be passivated with a negatively charged dielectric layer, like Al_2O_3 [80].

Due to the rather low density of fixed oxide charge, SiO_2 fully relies on the reduction of the interface state density. This passivation mechanism is also known as chemical passivation. Other passivation layers as SiN_x or Al_2O_3 exhibit a high number of positive or negative fixed charges, respectively. This leads to a reduction of one the types of charge carrier in the underlying silicon which can reduce the surface recombination velocity, known as field-effect passivation. Such field effect passivation can be induced artificially for SiO_2 passivation layers by applying an external voltage via a gate electrode [81,82] or by deposition of corona charges [73,83,84]. In such experiments, the measured surface recombination velocity as a function of the applied charge results in a peak-shaped curve which shows very low surface recombination velocities for high positive or negative corona charge densities. A maximum recombination velocity is observed when the ratio of the hole and electron density at the interface equals the ratio of the electron and hole capture cross sections: $p_s/n_s = \sigma_n/\sigma_p$ [73]. Since the Corona surface charges are not long-term stable and can be washed away, this additional field effect passivation could not be utilized in real devices up to now. Recently, Bonilla and Wilshaw have presented a technique to create stable charges on SiO_2 based on a chemical preparation of the surface and heat treatments [85,86].

4. SiO_x for passivating contacts

As has been pointed out above, thermally grown SiO_2 layers strongly contributed to the advancement of silicon solar cell efficiency and facilitated the understanding of surface passivation schemes. While for industrial PERC/PERT cells PECVD SiN_x and PECVD (ALD) Al_2O_3 are the dominant dielectric surface passivation layers, ultra-thin SiO_x layers which are implemented into poly-Si based passivating contacts have attracted growing interest recently [87].

4.1. Metal-insulator-semiconductor junctions

An early application of ultra-thin SiO_x layers was in MIS solar cells. The insertion of a thin SiO_x layer between the c-Si substrate and the metallization led to appreciable gains in V_{oc} [88,89] compared to a Schottky contact.

The working principle of a MIS contact relies on the depletion of one type of carrier at the surface by using a metal with a suitable work function. The interfacial oxide presents a resistance to the charge carriers and reduces interface traps which would otherwise lead to an

unfavorable pinning of the Fermi level at the surface. By passivating surface states the metal-insulator barrier height ϕ_{mi} and the semiconductor-insulator barrier height ϕ_{si} determine the surface band bending in the c-Si and one obtains either a minority carrier or majority carrier diode [90]. For instance, the Al/SiO_x/c-Si(p) ($\phi_{mi} = 3.2$ eV) structure yields an inverted c-Si surface and can function properly as a solar cell. The underlying physics regarding charge carrier transport has been subject to discussion. Apparently, the MIS theory, which describes majority carrier flow by tunneling through the oxide barrier, described most experimental observations best. This topic was thoroughly discussed in a review paper [91].

The band bending underneath the contact can be enhanced by sandwiching a 5 nm thin CsCl layer between the oxide layer and aluminum. This led to an increase in V_{oc} by about 20 mV and an efficiency of 19.6% [92]. However, a more effective approach to increase V_{oc} was the insertion of a diffused region underneath the interfacial oxide. The device was referred to as MINP solar cell and a V_{oc} of 678 mV was demonstrated on a planar solar cell [23]. After the discovery of SiN_x as a well-passivating anti-reflection coating, substantial progress in the development of the MIS- n^+p (or MINP) solar cell was attained in the Hezel group [21]. An independently confirmed efficiency of 21.1% had been reached with a textured MIS- n^+p solar cell featuring a SiO₂-based partial rear contact (PRC) scheme and a double layer ARC at the front [93] (Fig. 6).

4.2. Poly-Si based passivating contacts

4.2.1. From microelectronics to photovoltaics

Recently, interest has been renewed in poly-Si/SiO_x contacts. This technology was originally pioneered by the microelectronics industry for its application in high-speed bipolar junction transistors (BJTs) and was thoroughly reviewed by Post et al. [94]. At that time one challenge was the scaling of the base width and the lateral dimensions of these devices without increasing the peripheral component of the emitter capacitance, which would have been detrimental to its AC characteristics. This required very thin emitters which (i) were difficult to realize and (ii) suffered from increased minority carrier recombination as these emitters became transparent for minority carriers. On the other hand, the poly-Si emitter (see simplified schematic in Fig. 7b) solved both of these issues very elegantly. Firstly, the poly-Si emitter acted as a diffusion source thereby enabling the formation of a very shallow junction within the c-Si base. Secondly, minority carrier back-injection from the base into the emitter was significantly reduced. The latter effect was further strengthened by the deliberate growth of a very thin interfacial oxide before poly-Si deposition. Thereby, current gain values higher than 300 could be realized. Although the wet-chemical growth of an interfacial oxide boosted current gain, it, in turn, increased the emitter resistance significantly [94,95]. This posed a problem for BJTs where device dimensions were ever shrinking and therefore, a lot of work had

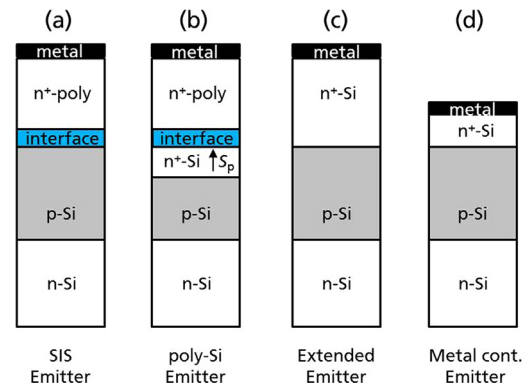


Fig. 7. Schematic diagrams of (a) an SIS emitter, (b) a polysilicon emitter, (c) an extended emitter, and (d) a metal contacted emitter (redrawn from Ref. [94]).

been dedicated to controllably reduce the emitter resistance by applying higher thermal annealing temperatures which enhanced the break-up (or balling up) of the interfacial oxide layer but in turn diminished the current gains [96]. When applying very high annealing temperatures, the poly-Si epitaxially regrows and the structure turns into that of an extended emitter (Fig. 7c) which behaves similarly to a conventional BJT (Fig. 7d). Another distinctive structure is the SIS emitter (Fig. 7a) which refers to a poly-Si contact which is not subjected to a high-temperature anneal and, therefore, the dopants are confined to the poly-Si layer. Very high current gains of more than 10,000 were reported for this structure [97] but the current gain was a strong function of the applied voltage and, more importantly, the electrical characteristics of these devices degraded during operation [98]. Finally, the poly-Si emitter without deliberately grown interfacial oxide (still a very thin oxide is inevitably present [96]) has been commercialized as its lower emitter resistance enabled faster switching devices.

In contrast to BJTs, poly-Si-based contacts with interfacial oxide are the natural choice for solar cell applications as low J_0 values rather than very low contact resistivity values are required. Already in the 1980s researchers applied this technology to silicon solar cells with the aim to boost V_{oc} [26,97,99]. For instance, J_0 values of 10–20 fA/cm² had been obtained with poly-Si/SiO_x contacts and SIPOS (semi-insulating poly-Si) contacts [99] and a V_{oc} of 720 mV was measured on a 50 μ m thin solar cell test structure where both sides were covered with n -type SIPOS and a Ga-In contact was realized at the edge [26]. For p -type poly-Si/SiO_x and SIPOS contacts significantly higher J_0 values were reported by Kwark et al. [100] which agrees with the lower gain enhancement factors of pnp transistors. Motivated by the need for very low specific contact resistivities in order to realize IBC solar cells which operate efficiently under concentrated sunlight [101], Gan and Swanson introduced poly-Si contacts with thicker, thermally grown

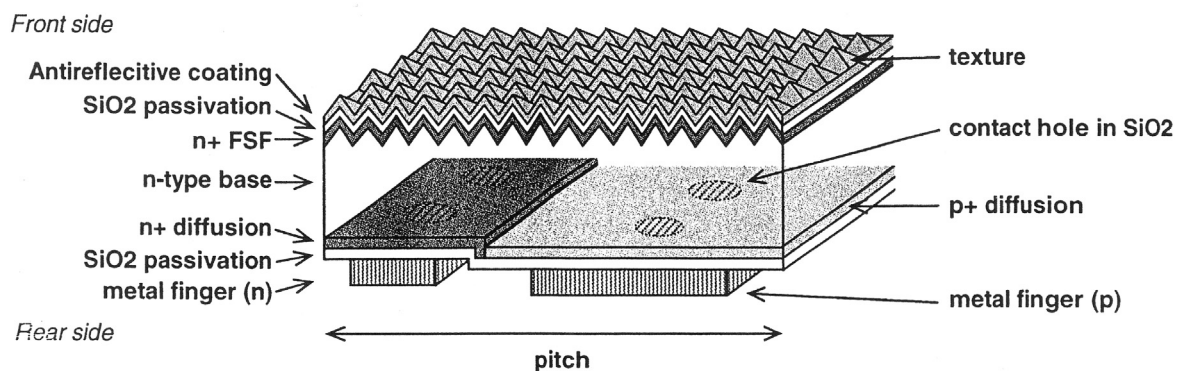


Fig. 6. IBC solar cell by SunPower. Reprinted from Ref. [40], with the permission of WIP Renewable Energies.

interfacial oxide layers which were subjected to a high-temperature anneal at 1050 °C thereby deliberately forming pinholes in the oxide layer [25]. As a result, reasonably low J_0 values of 24 fA/cm² (35 fA/cm²) had been obtained at a very low specific contact resistivity of 18 $\mu\Omega$ cm² for *n*-type (*p*-type) poly-Si emitters. In the years after 1990, publications on this technology were quite rare and the next notable publication was that by Borden et al. in 2008. Their study dealt with poly-Si/SiO_x contacts realized by standard microelectronic processing equipment (RTO, LPCVD, RTP) [102]. In 2013, Feldmann et al. published the first solar cell featuring a boron-diffused emitter and a passivating rear contact (TOPCon) which achieved an efficiency of more than 23% [103,104]. Due to the one-dimensional majority carrier flow in the base of a solar cell featuring a full-area passivating contact, the excellent surface passivation, and low contact resistivity, a V_{oc} above 700 mV and FF above 82% could be achieved. The passivating contact was realized by growing a thin interfacial oxide in HNO₃, depositing a Si-rich SiC_x layer by PECVD, thermal annealing at 800–900 °C, and a hydrogen passivation step. For TOPCon structures it was shown that replacing the HNO₃ oxide for an oxide either grown in ozonated water or ozone ambient enhanced the thermal stability (especially on textured surfaces). Furthermore, XPS measurements of the different oxides hinted at a correlation between higher stoichiometry of the oxide and better thermal stability [105].

In 2014, Römer et al. demonstrated for the first time that very low J_0 values (less than 10 fA/cm²) can be attained with *p*-type poly-Si contacts [106] following the approach of Gan and Swanson. Today, several groups have reported J_0 values lower than 10 fA/cm² for *n*-type poly-Si/SiO_x passivating contacts while maintaining contact resistivities sufficiently low for solar cell contacts [104–113]. While higher J_0 values have been typically measured for *p*-type poly-Si/SiO_x contacts, the number of papers reporting J_0 values lower than 5 fA/cm² increases steadily (1 fA/cm² [114], 4 fA/cm² [115], 5 fA/cm² [116]). One of the key processes enabling such low J_0 values is an effective hydrogenation of the poly-Si/SiO_x contact which reduces the interface trapped charge density at the Si/SiO_x interface. Hydrogen can be effectively supplied by a hydrogen plasma (e.g. remote plasma hydrogen passivation [117]) or can be released from H-containing films like Al₂O₃ [118] or SiN_x [110,114,119]. For instance, Mack et al. reported that the J_0 of a *p*-type poly-Si contact was reduced from about 13 fA/cm² down to 1 fA/cm² by firing [114]. While these low J_0 values were all achieved on shiny-etched or planarized *c*-Si surfaces, it was reported that the J_0 of *p*-type contacts drastically increased on textured surfaces. By comparing planar (100)- and (111)-oriented *c*-Si surfaces, Larionova et al. could successfully ascribe the lower passivation quality on textured surfaces to a drastically increased recombination rate on (111) oriented surfaces [120]. The reason for this increase was attributed to the considerably higher D_{it} on (111)-oriented Si known from previous studies. Interestingly, passivating textured surfaces is not a problem for *n*-type poly-Si/SiO_x contacts. For instance, Stodolny et al. reported J_0 values as low as 4 fA/cm² (compared to 2 fA/cm² on planar surfaces) using LPCVD equipment [110]. Using industrial PECVD equipment, TOPCon structures have achieved very low J_0 values of about 2–4 fA/cm² and 1–2 fA/cm² on textured and planar surfaces, respectively [121].

Poly-Si/SiO_x passivating contacts not only enable an excellent surface passivation but also an improvement of bulk properties. It has been reported that *n*-type poly-Si/SiO_x contacts doped by ion implantation yielded an improved bulk lifetime [122]. Liu et al. investigated this more in detail and found a strong gettering effect for poly-Si/SiO_x contacts doped by POCl₃ and BBr₃ diffusion [123].

4.2.2. Charge carrier transport

For the description of charge carrier transport across the poly-Si/*c*-Si junction of BJTs three models were proposed: “oxide tunneling model” [125], “segregation model”, and “grain boundary mobility model”, and were compared to each other in Ref. [94]. It is important to note that the applicability of each model strongly depends on the used

processes and the type of poly-Si emitter. An instructive example for BJTs can be found in Ref. [126]. It can be said that the “oxide tunneling” model explained best the reduction of the base current and the increase of the emitter resistance of BJTs with deliberately grown interfacial oxide (see Fig. 7a and b) [125]. The assumption that tunneling is the dominant transport mechanism was further substantiated by the weak temperature dependence of these devices [94,127]. The weakness of the model is that the electrical characteristics of both *n*pn and *p*np transistors cannot be explained with one unifying parameter set (with respect to electron/hole barrier height). Moreover, the model predicts that a slight current gain enhancement would come at the expense of a very high emitter resistance which does not reflect the experimental findings [128–130].

For photovoltaic applications two limiting cases of poly-Si based passivating contacts can be distinguished: (i) passivating contacts with very thin tunnel oxides [100,104] and (ii) passivating contacts with thicker oxides where tunneling is less efficient and pinholes are required for sufficiently low ρ_c values [25,106]. Both structures have in common that dopants are diffusing from the poly-Si into the *c*-Si during the high-temperature anneal. For type I devices the main function of this shallow diffused region is to increase the tunnel current [131] while for type II devices it reduces the recombination rate at the pinholes [132].

The impact of pinholes in the oxide on the electrical characteristics of MIS solar cells had already been discussed by Green [133]. He stated that a maximum pinhole areal density of 10^{−5} would not interfere with the electrical properties of the MIS solar cell. The effect of the high-temperature anneal on the integrity of the interfacial oxide had been studied by Wolstenholme et al. in great depth and the oxide break-up could be well correlated with a reduction of the emitter resistance and an increase of the base saturation current [96]. A similar trend was observed by Feldmann et al. for TOPCon structures featuring a ~1.2 nm thin oxide grown in HNO₃ (see Fig. 8). However, a reduced emitter resistance was observed for $T_{\text{anneal}} = 900$ °C at which the interfacial oxide seemed to be continuous according to TEM. In this state there seems to be a coexistence of tunneling and pinhole transport. By means of 2D device modelling Hamel et al. [134] could explain this result by the formation of a limited number of pinholes in the oxide which are hardly observable in TEM. Therefore, an alternative technique not only capable of visualizing pinholes but also capable of quantifying the pinhole density has been developed [135,136]. Recently, a 3D model based on a model for PERC-type solar cells [137] which accounts only for transport via pinholes was published [132,138]. The strength of this model is that it explains the symmetric behavior of *n*-type and *p*-type poly-Si contacts with thick oxides (type II) observed by Gan and

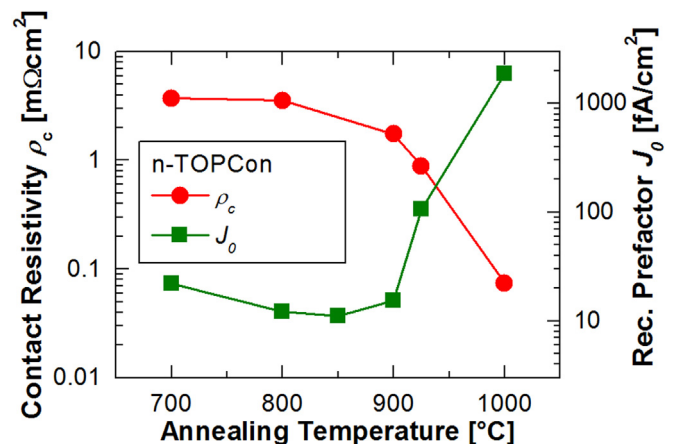


Fig. 8. J_0 and contact resistivity as a function of annealing temperature. For annealing temperatures above 900 °C the interfacial oxide loses its integrity and the recombination increases significantly [124].

Swanson [25] and Roemer et al. [106,115].

The model actually predicts two operating regimes (assuming a pinhole radius of 2 nm, see Fig. 5 in [138])

- a) for very high pinhole densities above $\sim 1 \times 10^9 \text{ cm}^{-2}$ (corresponding to an areal density of about 10^{-4}) $\log(J_0)$ increases linearly with decreasing $\log(\rho_c)$
- b) for pinhole densities $< 1 \times 10^7 \text{ cm}^{-2}$ (corresponding to an areal density of about 10^{-6}) J_0 is no longer a function of the pinhole density but is dominated by the effective recombination velocity at the c-Si/SiO_x surface

Interestingly, the transition from regime a) to regime b) occurs of a pinhole areal density at around 10^{-5} as predicted by Green [133].

However, from the literature it is known that the pinhole model does not explain the J - V characteristics of non-annealed poly-Si/SiO_x/c-Si structures, which also yielded significant current gain enhancement factors [139]. For these devices the “oxide tunneling” model is more appropriate. Steinkemper et al. have performed a simulation study for type I passivating contact structures featuring very thin oxides considering only transport via quantum mechanical tunneling [131]. Recently, temperature-dependent J - V measurements of TOPCon structures featuring an about 1.2 nm thin oxide layer revealed that tunneling seems to be the dominant transport path for contacts with intact oxide [140]. This is further supported by the fact that the contact resistivity shown in Fig. 8 takes similar values for $T_{\text{anneal}} = 700^\circ\text{C}$ and $T_{\text{anneal}} = 800^\circ\text{C}$. Since the formation of pinholes in the oxide is a thermally activated process described by a given activation energy, one would expect significantly different pinhole densities at 700°C and 800°C , respectively, and, therefore, different contact resistivities which is not the case here. Still it is conceivable that a tiny pinhole areal density exists which might help to reduce ρ_c . By applying $T_{\text{anneal}} > 900^\circ\text{C}$ a significant density of pinholes readily forms and adversely affects the surface passivation quality provided by the passivating contact (see Fig. 8).

In conclusion, both models have their justification depending on which passivating contact structure has to be described (i.e. type I and type II). From the discussion above, it is obvious that although the principal structure of the passivating contacts is similar, the process steps differ quite significantly, particularly the thickness of the oxide and the final thermal treatment, which makes it difficult to generalize theories about the underlying physical transport mechanisms. Especially for passivating contacts with interfacial oxides thinner than 2 nm a coexistence of both current transport paths can be anticipated. The transition from type I to type II devices depends on the oxide stoichiometry and thickness as well as the applied annealing temperature.

4.2.3. Application to solar cells

The implementation of poly-Si based passivating contacts into lab-scale solar cells has enabled record efficiencies. The best solar cell featuring top/rear contacts is an n-type solar cell featuring a boron-diffused emitter and a passivating rear contact. An efficiency of 25.8% [141,142] has been demonstrated. Moreover, a world-record efficiency of 22.3% has been achieved by transferring this solar cell structure to n-type high-performance mc-Si [143]. On p-type c-Si, the first solar cell with phosphorus-doped and boron-doped TOPCon top/rear contacts achieving a V_{oc} of 694 mV and a FF of 81.1% was demonstrated in Ref. [144]. Nogay et al. have demonstrated that FF up to 84% can be achieved with this structure [145]. By using an IBC structure featuring both polarities at the rear an efficiency of 26.1% has been very recently reached [146].

Stodolny et al. published the first solar cell featuring a poly-Si rear contact which was processed using industrial equipment [110]. While lab cells typically feature evaporated Ag or Al contacts, contact formation was done by screen-printing Ag and fast-firing. The advantage

of this process is that the SiN_x supplies hydrogen to the contact very effectively. However, it has been shown that conventional Ag pastes consumed a large fraction of the poly-Si [116]. Even for almost 300 nm thick p-type poly-Si contacts a strong increase in $J_{0,\text{met}}$ has been observed [114]. Another drawback of such thick poly-Si layers is associated with free carrier absorption which reduces the IR response of the solar cell significantly.

Considering the successful implementation of poly-Si/SiO_x passivating contacts and the very active research and development, it is likely that the next generation of industrial silicon solar cells will be based on such contact systems. This makes SiO₂ once again an important enabling technology for c-Si photovoltaics.

5. Conclusion

Due to its superior electrical properties which allow a dramatic reduction in surface recombination velocity dramatically, SiO₂ passivation layers had a strong impact on the history of silicon solar cells and allowed development of the first advanced silicon solar cell architectures such as IBC or PERC with efficiencies above 20%. Thus, it paved the way for the current rapid development in silicon photovoltaics and passivation layers as Al₂O₃ or SiN_x. Being a real evergreen, it enables technologies for the next generation of cells such as passivating contacts and is thus a true key technology for silicon photovoltaics.

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