

# *Surface Passivation of Crystalline Silicon Solar Cells: A Review*

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*In the 1980s, advances in the passivation of both cell surfaces led to the first crystalline silicon solar cells with conversion efficiencies above 20%. With today's industry trend towards thinner wafers and higher cell efficiency, the passivation of the front and rear surfaces is now also becoming vitally important for commercial silicon cells. This paper presents a review of the surface passivation methods used since the 1970s, both on laboratory-type as well as industrial cells. Given the trend towards lower-cost (but also lower-quality) Si materials such as block-cast multicrystalline Si, ribbon Si or thin-film polycrystalline Si, the most promising surface passivation methods identified to date are the fabrication of a p–n junction and the subsequent passivation of the resulting silicon surface with plasma silicon nitride as this material, besides reducing surface recombination and reflection losses, additionally provides a very efficient passivation of bulk defects. Copyright © 2000 John Wiley & Sons, Ltd.*

## **INTRODUCTION**

Crystalline silicon (c-Si) is an *indirect* semiconductor and hence recombination losses in this material occur largely via defect levels within the bandgap. These defects are located within the volume and at the surfaces of the sample (bulk and surface defects). There are extrinsic (i.e. processing related) and intrinsic (i.e. silicon-related and hence unavoidable) defects. While pure silicon is free of intrinsic defects, the density of extrinsic bulk defects can be reduced to negligible levels using suitable Si growth methods such as float-zone (FZ) growth. Owing to the involvement of non-silicon atoms, the situation is more complicated at the Si surface.<sup>1</sup> The surface represents the largest possible disturbance of the symmetry of the crystal lattice and hence, due to non-saturated ('dangling') bonds, a large density of defects ('surface states') within the bandgap exists at the surface of the crystal. These dangling bond defects can also be divided into intrinsic and extrinsic defects. There are typically additional processing related extrinsic surface defects, for instance due to dislocations or chemical residues and metallic depositions on the surface. In order to keep surface recombination losses at c-Si surfaces at tolerable levels, they must be electronically well passivated. In the case of solar cells, the chosen surface passivation scheme must be long-term stable (> 20 years) and, if applied to the illuminated cell surface, stable against the ultraviolet (UV) photons of sunlight.

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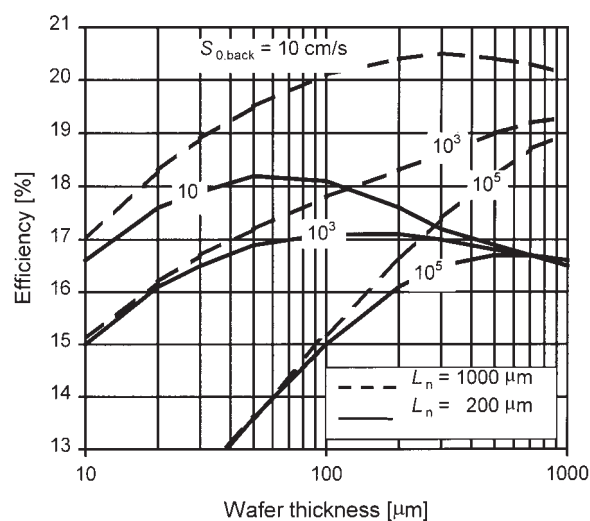


Figure 1. PC1D (version 5.2)<sup>4</sup> calculations of the 1-sun efficiency of an  $n^+p$  c-Si solar cell as a function of the wafer thickness. Parameters are the base diffusion length  $L_n$  (200 and 1000  $\mu\text{m}$ ) and the rear surface recombination velocity parameter  $S_{0,\text{back}}$  (10,  $10^3$ , and  $10^5$   $\text{cm s}^{-1}$ ). The cell features an emitter with a  $V_{\text{oc}}$  potential of 675 mV (junction depth 0.5  $\mu\text{m}$ , erfc profile, surface concentration  $1 \times 10^{20} \text{ cm}^{-3}$ , midgap surface states with  $S_{n0} = S_{p0} = S_{0,\text{front}} = 10^4 \text{ cm s}^{-1}$ ), relatively good light trapping properties (75% internal reflection at both surfaces), and a wavelength independent front surface reflection loss of 10%

There are two fundamentally different types of surfaces in a c-Si solar cell: metallised and non-metallised surfaces. Metal–silicon interfaces feature very high surface recombination velocities and hence need to be carefully designed to avoid excessively large recombination losses. Similarly, in order to ensure a good blue response of the cell, the illuminated non-metallised surface regions need to be well passivated and not too heavily doped in order to avoid the formation of a ‘dead layer’. In the case of laboratory c-Si cells, the importance of the passivation of both cell surfaces is well recognised. In the 1980s, advances in the passivation of both cell surfaces led to the first c-Si solar cells with 1-sun efficiencies above 20%.<sup>2,3</sup> The surface passivation features of these cells will be discussed below.

A major contributor (30–50%) to the cost of today’s commercial c-Si photovoltaic (PV) modules are the Si wafers. Given the recent advances in the area of wafer sawing (wire saw technique), the possibility has arisen to fabricate very thin wafers ( $< 200 \mu\text{m}$ ) with kerf losses below 200  $\mu\text{m}$ . This means that a given Si ingot provides up to 50% more Si wafers than has previously been possible! In order to exploit the economic benefits associated with these developments, several PV companies are presently introducing thinner Si wafers into their solar cell production lines. Obviously, with reducing cell thickness the relative importance of rear surface recombination increases. The standard Si wafers used today by the PV industry (CZ or block-cast multicrystalline material) are boron doped (resistivity  $\sim 1 \Omega \text{ cm}$ ), 300–400  $\mu\text{m}$  thick, and typically have a minority carrier diffusion length of around 200  $\mu\text{m}$ . The solid lines in Figure 1 show the calculated dependence of the 1-sun efficiency of an  $n^+p$  Si solar cell fabricated on such wafers as a function of the wafer thickness and the rear surface recombination velocity parameters  $S_{0,\text{back}}$  ( $S_0$  will be defined below). It can be seen that the use of thin wafers (100–200  $\mu\text{m}$ ) leads to an unacceptably large efficiency loss if the rear surface is poorly passivated. On the other hand, for a well passivated rear surface and  $L_n = 200 \mu\text{m}$ , the efficiency improves by 3–7% on a relative basis if thin wafers are used, providing additional economic benefit. While today’s commercial c-Si solar cells feature poorly passivated rear surfaces, Figure 1 reveals that the use of thinner wafers necessitates a well passivated rear surface.

## FUNDAMENTALS OF SURFACE RECOMBINATION

In the surface recombination process, an electron from the conduction band recombines with a hole in the valence band via a defect level ('surface state') within the bandgap. Mathematically, the process is described by the Shockley–Read–Hall (SRH) theory.<sup>5</sup> The recombination rate  $U_s$  via a single-level surface state located at an energy  $E_t$  is given by

$$U_s = \frac{n_s p_s - n_i^2}{\frac{n_s + n_1}{S_{p0}} + \frac{p_s + p_1}{S_{n0}}}, \quad (1)$$

with

$$n_1 \equiv n_i \exp\left(\frac{E_t - E_i}{kT}\right), p_1 = n_i^2/n_1, S_{n0} \equiv \sigma_n v_{th} N_{st}, S_{p0} \equiv \sigma_p v_{th} N_{st}. \quad (2)$$

$S_{n0}$  and  $S_{p0}$  are the surface recombination velocity parameters of electrons and holes,  $n_s$  and  $p_s$  the electron and hole concentrations at the surface,  $\sigma_n$  and  $\sigma_p$  the capture cross sections for electrons and holes,  $N_{st}$  is the number of surface states per unit area,  $E_i$  the intrinsic Fermi energy,  $v_{th}$  the thermal velocity of the charge carriers ( $\sim 10^7$  cm<sup>-1</sup> s in Si at 300 K),  $k$  Boltzmann's constant,  $T$  the temperature, and  $n_i$  the intrinsic carrier density of the semiconductor. In analogy to the bulk expression  $U_b = \Delta n/\tau_b$  (where  $\Delta n$  is the excess carrier density in the bulk and  $\tau_b$  the bulk carrier lifetime), a surface recombination velocity (SRV)  $S$  can be defined as  $U_s \equiv S \Delta n_s$ , where  $\Delta n_s$  is the excess carrier density at the surface. For the case of flatband conditions at the surface and negligible carrier trapping, the excess densities of electrons and holes are equal ( $\Delta n_s = \Delta p_s$ ), giving<sup>1</sup>

$$S(\Delta n_s) = \frac{n_0 + p_0 + \Delta n_s}{\frac{n_0 + n_1 + \Delta n_s}{S_{p0}} + \frac{p_0 + p_1 + \Delta n_s}{S_{n0}}}. \quad (3)$$

This shows that the SRV not only depends on the properties of the surface states [i.e. their energy level (via  $n_1$  and  $p_1$ ), their density and their capture cross sections for electrons and holes (via  $S_{n0}$  and  $S_{p0}$ )], but also on the injection level  $\Delta n_s$  at the surface and on the wafer doping level (via  $n_0$  and  $p_0$ ). In practical devices there is usually a bending of the energy bands towards the surface. Hence, in contrast to the flatband case of Equation (3) there exists no analytical expression for the SRV. Instead, the surface recombination rate must be calculated from Equation (1), using numerically determined values for  $n_s$  and  $p_s$ .<sup>1</sup> Upon calculation of  $U_s$ , in analogy to the concept of effective recombination velocities of high–low junctions,<sup>7</sup> an effective SRV

$$S_{eff} = \frac{U_s}{\Delta n(x=d)} \quad (4)$$

can be determined at a virtual surface within the wafer positioned at the edge of the surface space charge region (located at  $x = d$ ).<sup>8</sup> If the sample features a  $p$ – $n$  junction, the electronic quality of the emitter is usually expressed via the emitter saturation current density  $J_{0e}$ . For an  $n^+$ -diffused emitter on a lowly injected  $p$ -type wafer with acceptor density  $N_A$ , the relation between  $S_{eff}$  and  $J_{0e}$  is

$$S_{eff} = \frac{J_{0e} N_A}{q n_i^2} \quad (5)$$

The relationship given by the SRH theory between the recombination rate and the properties of the surface states [see Equation (1)] shows that there are two fundamentally different technological possibilities to reduce the recombination rate at a semiconductor surface: (i) the reduction of the density of surface states, and (ii) the reduction of the concentration of free electrons or holes at the surface.

### *Reduction of the density of surface states*

According to Equation (1), the surface recombination rate is proportional to the defect density at the surface. Technologically, the density of surface states  $N_{st}$  can be drastically reduced by the deposition or growth of an appropriate passivating film on the semiconductor surface or by immersing the sample into polar liquids. These methods are discussed later.

### *Reduction of the surface concentration of electrons or holes*

As the SRH recombination process involves one electron and one hole, the highest recombination rates are obtained for the case of approximately equal surface concentrations of electrons and holes. In contrast, if the concentration of one partner is drastically reduced, then the recombination rate reduces strongly. As electrons and holes carry electrical charge, such a reduction of the surface concentration of one charge carrier type (either electrons or holes) can most easily be realised by the formation of an internal electric field below the semiconductor surface. Technologically, two independent techniques exist for the formation of such a 'built-in' field:

- Implementation of a doping profile below the silicon surface.
- Field-effect passivation due to electrical charges in an overlying insulator (or on a gate electrode).

The fabrication of a doping profile below the surface of a silicon wafer is a standard processing step in the microelectronics and PV industry. In this case, the built-in electric field results from the spatially non-uniform concentration of the dopant atoms in the crystal lattice. The standard method is a diffusion process in a furnace tube kept at high temperature ( $\sim 850^\circ\text{C}$ ). If the dopants have the same polarity as the Si wafer, then this doping profile creates a high–low junction ( $p^+p$  or  $n^+n$ ). In c-Si solar cells, a  $p^+p$  high–low junction is widely used for the reduction of rear surface recombination losses (back surface field; BSF).<sup>9</sup> If the rear high–low junction of a BSF solar cell extends deep into the Si wafer, then the corresponding electric field will reduce both rear surface as well as bulk recombination losses (drift-field solar cells). Equivalently, if the high–low junction is located at the illuminated front surface, it is referred to as front surface field (FSF). In contrast, if the dopants have the opposite polarity as the background dopant atoms of the silicon wafer, then this doping profile will lead to a  $p-n$  junction. Usually this junction is contacted and then, in addition to passivating the surface, it also separates the light-generated charge carriers. If the  $p-n$  junction is not contacted, the resulting surface passivation scheme is referred to as floating-junction passivation.<sup>10</sup> The field-effect (or charge-induced) passivation method is brought about by a gate voltage or electrical charges within an insulator covering the silicon. Since, in practice, most insulator systems on silicon lead to the formation of electrostatic charges at/near the silicon–insulator interface, the field-effect passivation method is already exploited in a variety of c-Si solar cells.

In practical c-Si solar cells, the above-mentioned two fundamental passivation approaches are often combined to achieve minimum surface recombination rates. As an example, the surface passivation with a thermal  $\text{SiO}_2$  film greatly reduces the surface state density  $N_{st}$  and furthermore leads to a field-effect passivation due to fixed positive oxide charges.<sup>1,8</sup>

## ***SURFACE PASSIVATION METHODS FOR CRYSTALLINE SILICON***

When discussing surface passivation methods for crystalline silicon, it is useful to distinguish between the surfaces of homogeneously doped wafers and surfaces that are made on such wafers by adding dopant atoms into a narrow surface region by means of thermal diffusion, ion implantation, or other methods. The standard method in the PV community is the thermal diffusion process, and hence we distinguish in this paper between diffused and non-diffused silicon surfaces.

### Growth/deposition of a dielectric film

The standard method for the passivation of Si surfaces—both diffused and non-diffused—is the thermal oxidation at high temperature ( $\sim 1000^\circ\text{C}$ ). On high-resistivity silicon this method is capable of providing extremely low surface state densities of  $\sim 10^9 \text{ cm}^{-2} \text{ eV}^{-1}$ . Thermal  $\text{SiO}_2$  provides excellent surface passivation on high-resistivity ( $> 100 \Omega \text{ cm}$ ) *n*- and *p*-type Si wafers, as demonstrated by  $S_{\text{eff}}$  values below  $10 \text{ cm s}^{-1}$ .<sup>11,12</sup> However, for low substrate resistivities ( $\sim 1 \Omega \text{ cm}$ ) the passivation quality depends on the doping type: while *n*-Si is still well passivated,<sup>13</sup> the resulting  $S_{\text{eff}}$  on *p*-Si is significantly poorer. For example, the best  $S_{\text{eff}}$  value reported to date for  $0.7\text{-}\Omega \text{ cm}$  FZ *p*-Si is  $41 \text{ cm s}^{-1}$ .<sup>14</sup> Typically, the  $S_{\text{eff}}$  values for such substrates lie in the  $50\text{--}500 \text{ cm/s}$  range at injection levels of  $10^{14} \text{ cm}^{-3}$ .<sup>8,12</sup> Note that the SRV depends strongly on the bulk injection level.<sup>1,8</sup> The easiest way to reduce the SRV at oxidized low-resistivity *p*-Si wafers is to evaporate Al onto the oxide and then anneal the wafer for  $\sim 20 \text{ min}$  at  $400^\circ\text{C}$ . This so-called Alneal generates atomic hydrogen (formed during the oxidation of Al by residual water in the oxide), which effectively reduces the Si– $\text{SiO}_2$  interface state density. Furthermore, owing to work function differences, an Al capping layer drives the *p*-type surface towards inversion, reducing the surface recombination rate. Both effects are exploited at the rear surface of  $24.7\%$  record efficiency PERL Si solar cells made on  $\sim 1\text{-}\Omega \text{ cm}$  *p*-Si wafers (see below). With regard to illuminated oxide passivated surfaces, it is important to note that the high degree of surface passivation mentioned above can not be maintained when exposed to the UV photons of sunlight.<sup>1,15</sup> A detailed discussion of the recombination mechanism at non-diffused Si– $\text{SiO}_2$  interfaces is given by Aberle.<sup>1</sup>

Thermal  $\text{SiO}_2$  is also very effective in passivating diffused Si surfaces. Due to the built-in electric field caused by the doping profile, the defects at the surface have a much weaker impact on the total recombination of the entire sample. Furthermore, due to the large doping level at the surface ( $N_s \geq 5 \times 10^{18} \text{ cm}^{-3}$ ), the band bending at the surface is virtually independent of the operating condition of the sample and hence the SRV at diffused Si surfaces can be treated as being independent of the bulk injection level  $\Delta n$ . For forming gas annealed untextured oxide-passivated phosphorus-diffused Si surfaces, the following relationship between  $S$  and  $N_s$  was experimentally determined:<sup>16</sup>

$$S \approx N_s \times 10^{-16} \text{ cm}^4 \text{ s}^{-1} \quad \text{for } N_s \geq 10^{18} \text{ cm}^{-3}. \quad (6)$$

In addition to the problems with low-resistivity *p*-Si wafers and the UV stability, there are other problems arising from the high temperatures during the thermal oxide growth. These can severely degrade the bulk carrier lifetime and are undesirable from production cost and throughput considerations. Hence, significant effort has been devoted in recent years to the development of low temperature ( $< 500^\circ\text{C}$ ) surface passivation schemes as an alternative to the high-temperature oxidation of Si. The most successful of these approaches turned out to be the plasma-enhanced chemical vapor deposition (PECVD) of silicon nitride ( $\text{SiN}_x$ ).<sup>17–19</sup> Record-low effective SRVs of  $4 \text{ cm/s}$  have been obtained on  $1\text{-}\Omega \text{ cm}$  *p*-Si wafers using remote PECVD or high-frequency ( $13.56 \text{ MHz}$ ) direct PECVD.<sup>19</sup> Note that the surface state density at Si– $\text{SiN}_x$  interfaces is much larger ( $>$  factor 10) than in the case of thermally grown Si– $\text{SiO}_2$  interfaces. As shown in Aberle,<sup>1</sup> the excellent surface passivation of  $\text{SiN}_x$  is due to (i) the field-effect passivation provided by positive interface charges and (ii) the properties of the capture cross-sections of the dominant defects. Plasma  $\text{SiN}_x$  also very efficiently passivates diffused Si surfaces. On  $100 \Omega/\square$  phosphorus diffused emitters,  $J_{0e}$  values of  $100 \text{ fA cm}^{-2}$  were measured on  $1.5\text{-}\Omega \text{ cm}$  FZ wafers at  $300 \text{ K}$ .<sup>1,20,21</sup> These values are comparable to the  $J_{0e}$  values obtained by thermal oxide passivation of these emitters. The corresponding  $S_{\text{eff}}$  of these emitters is  $61 \text{ cm s}^{-1}$ . The UV stability of  $\text{SiN}_x$  passivated silicon surfaces (both diffused and non-diffused) is excellent.<sup>1</sup>

Plasma silicon nitride has two important additional advantages for *c*-Si solar cells. First, its refractive index can be strongly varied and adjusted to give excellent performance as a single- or double-layer antireflection (AR) coating on both encapsulated and non-encapsulated *c*-Si cells.<sup>22</sup> Second, plasma silicon nitride contains large amounts of hydrogen. During annealing at temperatures in the  $600\text{--}800^\circ\text{C}$  range, some of this hydrogen travels into the underlying silicon. In defect-rich multicrystalline Si materials such as the EFG ribbons made by ASE Americas (formerly Mobil Solar),<sup>23</sup> this hydrogen

leads to an enormous improvement of the bulk carrier lifetime ('hydrogen passivation of bulk defects').<sup>24</sup> Without this bulk passivation effect EFG cells would probably not be commercially competitive. Due to these two additional properties plasma  $\text{SiN}_x$  acts as a surface and bulk passivating AR coating on crystalline Si, a unique combination that is not met by other AR coatings for c-Si solar cells (Note: The standard AR coating on industrial c-Si solar cells is  $\text{TiO}_x$  prepared by atmospheric pressure CVD. This material does not provide any surface passivation,<sup>25</sup> and the possible variations of the refractive index  $n$  are too small to enable its use as double-layer AR coating). Importantly, the equipment industry now offers high-throughput in-line PECVD machines for silicon nitride,<sup>26</sup> and hence it is very likely that this material will rapidly find widespread use in the PV industry.

Another highly effective and UV-stable passivation method for non-diffused Si surfaces is a thermally annealed double-layer stack consisting of a thin silicon oxide (grown either in a conventional furnace or by means of rapid thermal processing or deposited by PECVD) and plasma silicon nitride.<sup>25,27</sup> The same double-layer stack also provides good and UV-stable surface passivation on phosphorus-diffused emitters.<sup>25</sup>

Another method should be mentioned that is very useful for carrier lifetime measurements on Si wafers. It is well known that the surface passivation provided by a dielectric film on a Si wafer can be substantially improved by depositing electrical charges onto the dielectric (for instance with a commercially available corona charger). As shown by Schmidt and Aberle,<sup>28</sup> a standard photoresist film can be used as dielectric. After corona charging,  $S_{\text{eff}}$  values in the  $30\text{--}70\text{ cm s}^{-1}$  range are achieved on  $n$ - and  $p$ -Si wafers with resistivities  $\geq 1\text{ }\Omega\text{ cm}$ .<sup>28</sup> In air, the corona charges are stable for a few hours. This method is attractive as, upon completion of the measurement, the photoresist can be etched off and the wafer can be used for further processing.

### *Chemical methods*

Immersion of Si wafers into specific liquids also leads to an excellent surface passivation, presumably due to the saturation of dangling Si bonds at the surface. For some acids (e.g. HF and  $\text{H}_2\text{SO}_4$ ), extremely low  $S$  values of less than  $1\text{ cm s}^{-1}$  were measured on  $n$ -type high-resistivity FZ wafers.<sup>29</sup> The most widespread chemical passivation method is an alcoholic iodine solution.<sup>30</sup> Although chemical passivation methods are not applicable to solar cells deployed in the field, they are very useful for characterisation purposes such as carrier lifetime measurements. Unfortunately, the degree of surface passivation provided by these chemical passivation schemes depends strongly on the applied wafer cleaning sequence.

### *Gate voltage*

Using a  $\text{SiO}_2$ -passivated gate-controlled  $p$ - $n$  junction diode, Grove and Fitzgerald<sup>31</sup> performed the first investigations of surface recombination rates in surface space charge regions. The first successful experimental attempts to reduce surface recombination losses in c-Si solar cells by means of a gate voltage were performed in the period 1976–1982 by Schwartz *et al.*<sup>32</sup> and Kim *et al.*<sup>33</sup> This later led to the development of the gate-enhanced solar cell by Aberle *et al.*<sup>34</sup>

### *High–low junctions*

As discussed above, the electric field associated with  $p^+p$  or  $n^+n$  high–low junctions provides a passivation of Si surfaces. The standard procedure is the fabrication of a  $p^+p$  high–low junction at the rear (back surface field; BSF) of the cells by means of aluminium alloying or boron diffusion. The first c-Si solar cells exceeding 20% 1-sun efficiency (PESC cells)<sup>2</sup> had an alloyed Al BSF. Depending on the wafer doping level, the energy barrier associated with a high–low junction is typically around 0.2 eV.

This is much smaller than in the case of a  $p$ - $n$  junction (see below), and hence high-low junctions additionally require the reduction of the surface state density by a suitable dielectric to minimise recombination. By combining a boron diffused full-area BSF layer with thermal oxide passivation, 1-sun cells with efficiencies above 24% are now routinely processed at the University of New South Wales (UNSW).<sup>35</sup> A good example for solar cells featuring a front surface field (FSF) high-low junction are the rear-junction concentrator cells developed at Stanford University.<sup>3</sup> In these cells, in order to ensure a good UV stability, the illuminated front surface of the  $n$ -type high-resistivity Si wafers receives a phosphorus-diffused, thermal oxide passivated  $n^+$  layer.

The effective SRV provided by an alloyed Al BSF typically lies in the range 200–2000  $\text{cm s}^{-1}$ . In the case of very lightly boron or phosphorus diffused high-low junctions with additional surface passivation with  $\text{SiO}_2$  or  $\text{SiN}_x$ ,  $S_{\text{eff}}$  values well below 50  $\text{cm s}^{-1}$  are achieved.

### $p$ - $n$ Junctions

With regard to surface passivation, the operational principle of a  $p$ - $n$  junction is similar to a high-low junction. However, due to the involvement of  $n$ - and  $p$ -type dopant atoms (and the corresponding shifts in the Fermi energy), the resulting energy barrier within the silicon is much greater ( $\sim 0.9$  eV) and hence a  $p$ - $n$  junction provides a much better surface passivation than a high-low junction. When the junction is contacted (i.e. is not floating), it not only passivates the surface but simultaneously separates the light generated charge carriers. As in the case of a high-low junction, the surface passivation can be further improved by growing/depositing a suitable dielectric film on the surface. The latter method is routinely used in the non-metallised (i.e., illuminated) front surface regions of  $c$ -Si solar cells. Using ultrathin tunnel dielectrics, this approach is also used below the metal grid lines of various  $c$ -Si solar cell structures.<sup>36,37</sup> A more efficient method, however, is the introduction of a deep and sufficiently heavy dopant profile below the metal contacts ('selective' emitter). Selective emitters are a key feature of most existing high-efficiency  $c$ -Si cell concepts. Note that, as a result of heavy doping effects such as bandgap narrowing, the dopant profile below the metal contacts needs to be properly adjusted (very heavy diffusions do *not* provide optimum performance!).<sup>1,38</sup> The excellent degree of surface passivation provided by a floating junction has been demonstrated at UNSW in 1994. By introducing an  $n$ -type floating junction at the rear surface of PERL cells (forming so-called PERC cells), record high open-circuit voltages of 720 mV have been achieved under standard test conditions.<sup>39</sup> Assuming ideal diode theory with unity ideality factor, this  $V_{\text{oc}}$  corresponds to a total  $J_0$  of 25  $\text{fA cm}^{-2}$ . Assuming negligible bulk recombination and equal  $J_{0\text{e}}$  for the front and rear emitter, the upper  $J_{0\text{e}}$  limit of each emitter is 12.5  $\text{fA cm}^{-2}$ . According to Equation (5), this is equivalent to an upper limit for the  $S_{\text{eff}}$  of these emitters of 8  $\text{cm s}^{-1}$ . Hence, these emitters provide about the same surface passivation as the  $\text{SiN}_x$  films mentioned above. The impact of surface recombination, when quantified in terms of the  $V_{\text{oc}}$  limit it imposes upon a cell, on the limiting efficiency of  $c$ -Si solar cells is given by Green<sup>40</sup> as a function of the cell thickness. These simulations show that with the present state of the art of surface passivation, 1-sun efficiencies of 20% are possible for  $c$ -Si cell thicknesses as low as 1  $\mu\text{m}$ .

Related to the  $p$ - $n$  junction surface passivation concept are metal-insulator-semiconductor inversion-layer (MIS-IL) silicon solar cells.<sup>41–43</sup> In the non-metallised front surface areas of these devices an inversion-layer emitter is induced by electrical charges within an overlying insulator. In many respects this inversion-layer emitter is equivalent to the doped emitter of a  $p$ - $n$  junction cell. The best insulator system developed to date for Si inversion-layer solar cells is a cesium-treated combination of a thin thermal oxide and plasma silicon nitride.<sup>44</sup> This scheme features both an excellent surface passivation and an excellent UV stability.<sup>1</sup> Below the metal contact of a MIS-IL cell, the inversion-layer emitter is generated as a result of work function differences between the metal electrode and the Si substrate.

Another approach related to the  $p$ - $n$  junction concept is based on a heterojunction formed by the deposition of doped amorphous silicon (a-Si) on a doped crystalline silicon substrate. As shown by Sawada *et al.*,<sup>45</sup> excellent surface passivation is achieved if a thin intrinsic a-Si layer is incorporated

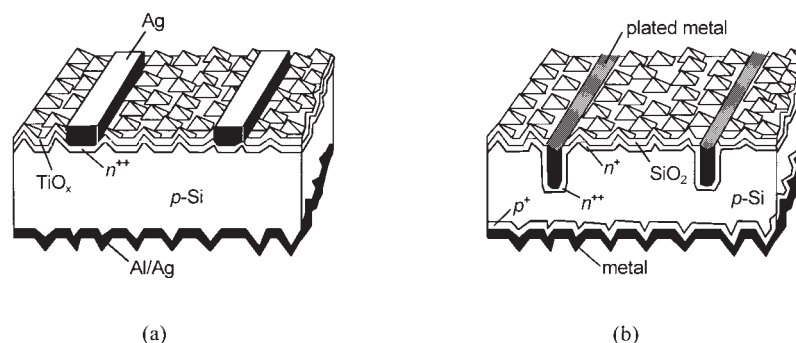


Figure 2. Schematic representations of (a) a standard screen-printed c-Si solar cell and (b) a buried-contact c-Si solar cell

between the c-Si wafer and the doped a-Si film. This scheme has been used by Sawada *et al.* to fabricate 20% efficient a-Si/c-Si heterojunction solar cells on *n*-type 1-Ω cm CZ wafers (see below). Using *n*-type a-Si, the same group also fabricated a hetero-type high–low junction on *n*-type 1-Ω cm CZ wafers giving an  $S_{\text{eff}}$  of below  $50 \text{ cm s}^{-1}$ .<sup>45</sup> Due to the thinness of the a-Si layers, the light-induced degradation effect ('Staebler–Wronski effect') is negligible compared to standard a-Si cells.

## SURFACE PASSIVATION OF c-Si SOLAR CELLS

Every c-Si solar cell fabricated to date features some degree of surface passivation. In the following we discuss several types of c-Si solar cells that were developed in the last 30 years and that are good representatives of specific surface passivation methods.\*

### Screen-printed cells

Figure 2(a) shows a standard screen-printed  $n^{++}p$  Si solar cell. This cell was developed in the 1970s and has dominated the terrestrial PV market in the last 25 years. The structure is still attractive today, as can be seen from the fact that Shell Solar presently builds a large new production plant for screen-printed multicrystalline Si cells in Germany. The key feature of screen-printed cells is a front metal grid that is fabricated by squeezing a silver containing paste through a wire mesh ('screen') and subsequently 'fire' this paste for a few minutes at  $\sim 750^\circ\text{C}$ . This metallisation method is robust, reliable and of rather low cost; however, it requires a very heavily doped Si surface ( $\geq 10^{21} \text{ cm}^{-3}$ ) and a rather thick  $n^+$  emitter ( $\geq 0.4 \mu\text{m}$ ). This emitter thus features a dead layer at the surface that significantly reduces the blue response of the cells. Furthermore, screen printing is not capable of achieving finger widths well below  $150 \mu\text{m}$  under industrial conditions. The resulting large shading losses ( $\sim 10\%$ ) substantially limit the achievable cell efficiencies.

With regard to surface passivation, the key feature of this cell is a very heavily diffused  $n^{++}$  emitter ( $p$ – $n$  junction passivation method). This enables respectable open-circuit voltages despite the large front surface metallisation fraction. However, due to the dead layer along the top surface, these cells are rather insensitive to a passivation of the non-metallised cell areas with  $\text{SiO}_2$  or  $\text{SiN}_x$ . The  $\text{TiO}_x$  film does not provide any surface passivation and hence merely acts as an AR coating. The poor blue response, in conjunction with the large metallisation fraction, explains the modest short-circuit currents of screen-printed cells. For instance, the CZ cells fabricated by Siemens Solar typically have a  $J_{\text{sc}}$  of  $34$ – $35 \text{ mA/cm}^2$ .<sup>46</sup> In order to improve the cell efficiency, various groups/companies presently investigate

\* Due to space constraints and/or the author's ignorance, it is possible that an interesting cell concept is not considered.

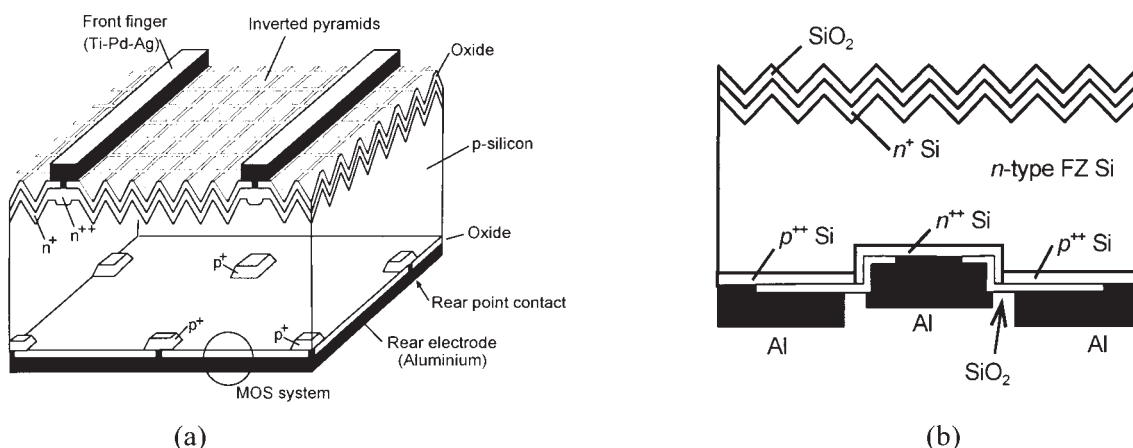


Figure 3. Schematic representations of (a) a PERL 1-sun solar cell and (b) a backside-contact concentrator solar cell (after Verlinden *et al.*<sup>53</sup>)

the benefits of replacing  $\text{TiO}_x$  by  $\text{SiN}_x$ , whereby the 'firing through the  $\text{SiN}_x$ ' process appears particularly promising. Also, research is under way to develop a cost-effective method of creating a selective emitter for screen-printed cells.<sup>47</sup> In combination with a surface passivating film such as  $\text{SiN}_x$ , this would strongly improve the blue response of the cells without sacrifices in the open-circuit voltage. Furthermore, the implementation of a diffused boron BSF is investigated.

#### Buried-contact cells

The most successful new solar cell structure developed during the last 15 years, in terms of product deployed in the field, is the buried-contact solar cell shown in Figure 2(b).<sup>48</sup> The key feature of this cell is the front metal grid which is made by scribing deep narrow grooves (width  $\sim 20 \mu\text{m}$ ) into the wafer (by means of a laser or mechanically) and subsequently filling these grooves with metal using electroless plating of nickel, copper and silver. Compared to screen-printed cells much narrower metal fingers are possible, reducing grid shading losses by about 50%. Furthermore, the cell features a selective emitter and thermal oxide passivation in the non-metallised front surface regions. The heavy diffusion along the metal–Si interface ensures that, despite the large metallisation fraction (equivalent to  $\sim 10\%$  of the illuminated front surface area), metal contact recombination losses remain low. The reduced shading losses, the superior passivation along the illuminated surface and reduced resistive losses are the reasons why buried-contact cells have significantly higher efficiencies than screen-printed cells (17–18% vs 15–16% for industrially produced CZ cells).

#### PERL (or LBSF) cells

The most advanced 1-sun c-Si solar cell developed to date is the so-called PERL (Passivated Emitter and Rear Locally Diffused)<sup>49</sup> or LBSF (local BSF)<sup>50</sup> cell shown in Figure 3(a). These cells are improved versions of the PERC (Passivated Emitter and Rear Cell) structure developed by Blakers *et al.* at UNSW.<sup>51</sup> The key features of PERL/LBSF cells are a phosphorus-diffused selective emitter with thermal oxide passivation, a front grid with a very small metallisation fraction ( $\sim 1\%$ ), a point-contacted rear surface (metallised fraction  $\sim 1\%$ ) with local boron diffusions (forming a local BSF), and thermal oxide passivation in the non-contacted rear surface regions. The rear oxide is covered with Al, further reducing surface recombination due to the Alneal effect and the band bending due to workfunction differences between the Al and the p-Si wafer. Numerical modeling indicates that the area-averaged  $S_{\text{eff}}$  value of

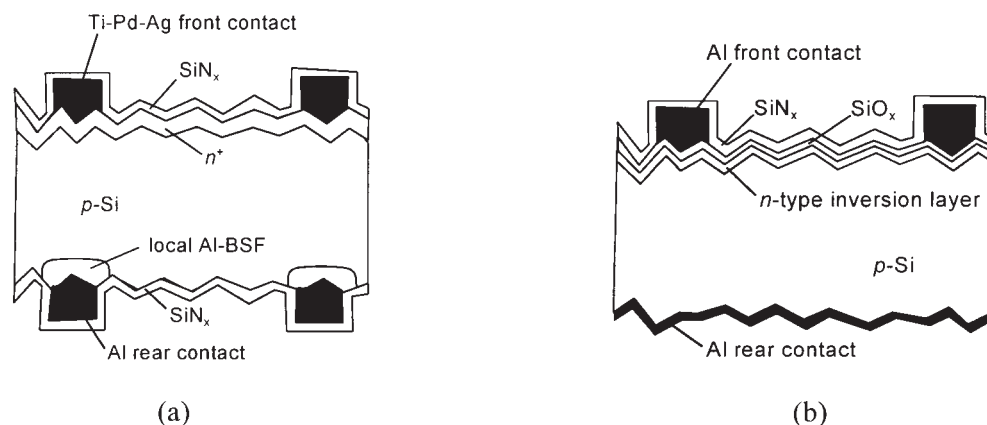


Figure 4. Schematic representations of (a) a high-efficiency bifacial c-Si solar cell passivated on both sides with SiN<sub>x</sub> and (b) the SiN<sub>x</sub>-passivated MIS-IL solar cells developed by Hezel *et al.*<sup>44</sup> in the 1980s

the rear surface of PERL cells fabricated on 1-Ω cm *p*-Si wafers is around 10 cm s<sup>-1</sup> at the maximum power point.<sup>52</sup> Using polished front surfaces, excellent  $V_{oc}$ 's of 717 mV have been obtained at UNSW with this structure. When fabricated with a textured front surface, PERL cells exhibit record high efficiencies of up to 24.7%.<sup>35</sup>

#### Backside-contact concentrator solar cells

Figure 3(b) shows a schematic of the most successful c-Si concentrator solar cell developed to date.<sup>3,53</sup> Both metal electrodes are on the back side ('interdigitated' metal grids), eliminating metal shading losses at the illuminated front surface and facilitating the interconnection of individual cells. The entire rear surface of these backside-contact cells is heavily diffused with either boron or phosphorus, and a large fraction of the heavily diffused rear surface areas are passivated by a thermal oxide. Contact to the  $n^{++}$ - and  $p^{++}$ -diffused regions is made via small openings in the rear passivating oxide (pitch ~ 50 μm), and hence these cells are often also referred to as point-contact cells. As already mentioned, the front surface of these cells feature a  $n^+n$  front surface field (FSF) and a thermal oxide to ensure a high-quality, UV stable front surface passivation. Under concentrated sunlight (100×, AM1.5D, 25°C) these cells show an efficiency of up to 26% if fabricated on thin (~ 150 μm) *n*-type high-resistivity FZ wafers.<sup>54</sup> When fabricated on doped (*n*- or *p*-type) FZ wafers with a dopant density of ~ 10<sup>16</sup> cm<sup>-3</sup>, the cells also achieve excellent 1-sun efficiencies of 22.7%.<sup>53</sup>

#### Silicon nitride passivated bifacial cells

As discussed above, recent years have seen a significant improvement of the passivation quality of low-temperature deposited plasma silicon nitride films. As a representative example, this has led to the bifacial *p*-*n* junction cell structure of Figure 4(a).<sup>55</sup> Both surfaces of the cell (i.e. the phosphorus-diffused front surface as well as the non-diffused *p*-type rear surface) are passivated with optimised plasma silicon nitride films. This simple cell structure exhibits efficiencies of up to 20.1% under front illumination and up to 18.1% under rear illumination.<sup>55</sup> Especially the high rear efficiency is a clear confirmation of the outstanding passivation quality provided by plasma SiN<sub>x</sub>. Another important advantage of plasma SiN<sub>x</sub> is the possibility to adjust a large refractive index in the 2.0–2.3 range, greatly minimising reflection losses.<sup>22</sup>

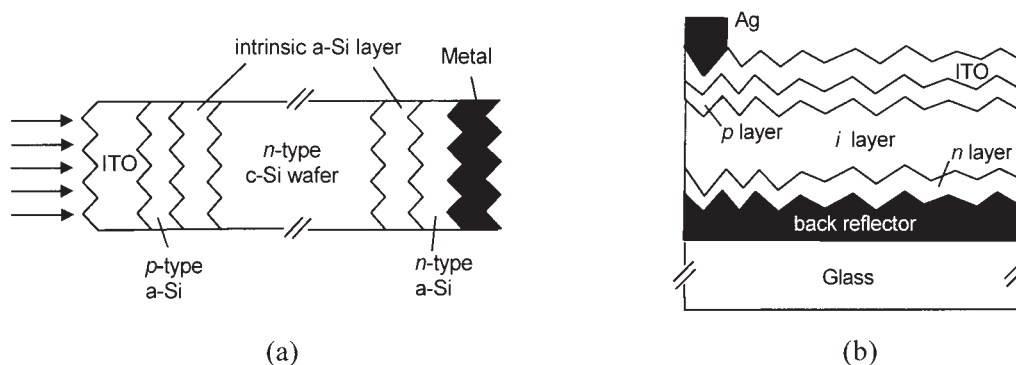


Figure 5. The HIT a-Si/c-Si heterojunction solar cell developed at Sanyo Corp.<sup>45</sup> (a) and the thin-film polycrystalline silicon STAR cell developed at Kaneka Corp. (b)<sup>58</sup>

#### Silicon nitride passivated MIS inversion-layer cells

The emitter of MIS-IL Si solar cells can be made at low temperature ( $< 500^{\circ}\text{C}$ ) and hence these devices are promising candidates for the cost-effective generation of PV electricity. Presently, the best MIS-IL cells are made on *p*-Si wafers using an  $\text{Al}/\text{SiO}_x/\text{p-Si}$  MIS tunnel contact and a  $\text{SiN}_x/\text{Cs}/\text{SiO}_x$  surface passivation and AR coating between the front grid lines.<sup>44</sup> The tunnel oxide is grown thermally at  $500^{\circ}\text{C}$  and has a thickness of  $\sim 10$  Å. The PECVD silicon nitride film is deposited at low temperature ( $< 400^{\circ}\text{C}$ ). The Cs-treated  $\text{SiN}_x$  based AR coating has a very high positive charge density of well above  $10^{12}$  elementary charges per  $\text{cm}^2$  under thermal equilibrium conditions (the charge density is lower<sup>1</sup> under illumination). These cells exhibit 1-sun efficiencies of up to 18.5% on FZ Si,<sup>56</sup> and even higher efficiencies are expected using advanced cell concepts.<sup>44</sup> Figure 4(b) shows the MIS-IL cell structure developed by Hezel *et al.* in the 1980s.<sup>44</sup>

#### Heterojunction cells using amorphous silicon

Researchers at Sanyo Corp. have shown<sup>45</sup> that crystalline Si wafers can be very efficiently passivated with a double-layer stack consisting of an intrinsic and a doped layer of amorphous silicon (a-Si). Application of this so-called HIT structure (Heterojunction with Intrinsic Thin layer) to both surfaces of an *n*-type  $1\text{-}\Omega\text{ cm}$  CZ wafer (creating an a-Si BSF and an a-Si/c-Si heterojunction at the front) led to excellent 1-sun efficiencies of 20.0%. This is a remarkable result considering that the junction is formed at a very low temperature of  $200^{\circ}\text{C}$ . The effective SRV of the a-Si BSF was reported to be below  $50\text{ cm s}^{-1}$ . Figure 5(a) shows a schematic of the 20% efficient HIT cell developed at Sanyo.

#### Thin-film polycrystalline silicon cells

If suitable light trapping and surface passivation is incorporated, c-si (despite being an indirect semiconductor) has the potential to achieve 1-sun efficiencies of up to 20% at thicknesses as low as  $1\text{ }\mu\text{m}$  (see, for instance, Green<sup>40</sup>). Furthermore, Figure 1 shows that for well passivated thin devices the electronic material quality is far less important than for thick devices. This behaviour has stimulated interest in the development of thin-film polycrystalline Si (poly-Si) solar cells on low-cost foreign substrates. At the US company Astropower this has led to the development of thin ( $\sim 20\text{ }\mu\text{m}$ ) poly-Si films (grain size  $\sim 1\text{ mm}^2$ ) on insulating ceramic substrates, able to withstand the high temperatures involved in obtaining good-quality silicon.<sup>57</sup> Devices with  $20\text{ }\mu\text{m}$  silicon thickness now feature a  $J_{\text{sc}}$  of  $26\text{ mA cm}^{-2}$ .<sup>57</sup> Also remarkable are the achievements at Kaneka Corp. in Japan. Yamamoto and co-workers<sup>58</sup> developed the so-called STAR (Surface Texture and enhanced Absorption with a back

Reflector) cell which is deposited at low temperature by means of PECVD onto glass coated with a conductor. For a poly-Si cell with a silicon thickness of only 2  $\mu\text{m}$ , an efficiency of 10.1% was obtained,<sup>58</sup> demonstrating both efficient light trapping and rear surface passivation. Figure 5(b) shows a schematic representation of the STAR poly-Si cell. In order to further improve the cell efficiency, present research efforts at Kaneka concentrate on the development of a-Si/poly-Si tandem cells or even a-Si/poly-Si/poly-Si triple cells. This has already led to devices with stable efficiencies of 12.0%.<sup>58</sup> An alternative approach would be the replacement of the poorly passivating ITO film on the top surface by  $\text{SiN}_x$  and the implementation of a BSF.

Other groups working on solid phase crystallisation of a-Si and/or the direct deposition of microcrystalline Si<sup>59</sup> have also made devices with about 10% efficiency. Another interesting cell is the multi-layer thin-film cell developed by Green and Wenham.<sup>60</sup> This cell is the focus of a large commercialisation effort at Pacific Solar in Australia; however, no device results have as yet been published.

## CONCLUSIONS AND OUTLOOK

In this work, the fundamentals of the surface recombination process at c-Si surfaces are reviewed. The surface recombination rate can be minimised by reducing the surface state density and/or the surface concentration of electrons or holes. The latter is achieved by implementing a doping profile below the Si surface or by the field-effect passivation due to a gate voltage or electrical charges in a dielectric film covering the silicon. Based on these two fundamental surface passivation principles, a number of technologically possible surface passivation methods are discussed, including the growth/deposition of a dielectric film, chemical passivation by liquids, the application of a gate voltage, and the formation of high–low junctions and  $p$ – $n$  junctions (both contacted and floating). Every c-Si solar cell fabricated to date features one or more of these surface passivation methods. With regard to solar cell applications, it is important that the surface passivation is long-term stable ( $> 20$  years) and stable against the UV photons of sunlight. The surface passivation features of major c-Si solar cell structures are reviewed, including screen-printed cells, buried-contact cells, highest-efficiency 1-sun cells and concentrator cells, silicon nitride passivated bifacial cells and MIS inversion-layer cells, a-Si/c-Si heterojunction cells, and thin-film polycrystalline cells.

The surface passivation methods available today are of such a high quality that surface recombination losses can, except for highest-efficiency ( $> 20\%$ ) cells, be reduced to negligible levels. The challenge for commercial cells is, of course, to find a low-cost, high-throughput method that is compatible with the other solar cell fabrication steps and the silicon material used. Due to these constraints, low-temperature passivation methods are becoming increasingly popular.

In order to reduce the cost of solar electricity, there is the clear trend in the c-Si PV industry towards lower-cost Si materials. In the area of ingot-based Si (CZ, block-cast multicrystalline Si) this is primarily achieved by the use of thinner wafers (100–200  $\mu\text{m}$ ). Such wafers can now routinely be fabricated using state-of-the-art wire saw techniques. In parallel, the electronic quality of non-ingot based Si materials (Si ribbons) improves continuously. Due to this and the kerf loss ( $\sim 200$   $\mu\text{m}$ ) associated with the cutting of Si wafers, Si ribbons will very likely displace ingot-based Si materials during the next decade or two. It appears also likely that during the same time period thin-film ( $< 10$   $\mu\text{m}$ ) polycrystalline Si solar cells on foreign insulating substrates (either standard glass or high-temperature compatible ceramics) will become competitive with the self-supporting wafer- and ribbon-based c-Si cells. Naturally, with reducing cell thickness the relative importance of surface recombination increases.

In order to avoid an unacceptably large efficiency loss when moving towards thinner silicon materials, the near-term challenge in the c-Si PV industry is to implement an effective passivation method for both cell surfaces. As discussed in this paper, there are several suitable passivation schemes available. While the efficiency potential of industrially produced thin-film poly-Si cells on foreign substrates can not yet reliably be predicted, it is clear that wafer-based c-Si solar cells will allow to maintain (or even improve)

today's efficiency levels while at the same time reducing the consumption of (expensive) crystalline silicon by up to 50%. The evolving lower-cost c-Si materials (ribbon Si, poly-Si films) inevitably feature rather high densities of electronic bulk defects. Given the trend towards these Si materials, the most promising surface passivation methods identified to date are the fabrication of a  $p$ - $n$  junction and the passivation of the resulting silicon surface with plasma silicon nitride as this material—besides reducing surface recombination and reflection losses—additionally provides a very efficient passivation of bulk defects ('surface and bulk passivating AR coating').

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