

Carrier population control and surface passivation in solar cells

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Abstract

Controlling the concentration of charge carriers near the surface is essential for solar cells. It permits to form regions with selective conductivity for either electrons or holes and it also helps to reduce the rate at which they recombine. Chemical passivation of the surfaces is equally important, and it can be combined with population control to implement carrier-selective, passivating contacts for solar cells. This paper discusses different approaches to suppress surface recombination and to manipulate the concentration of carriers by means of doping, work function and charge. It also describes some of the many surface-passivating contacts that are being developed for silicon solar cells, restricted to experiments performed by the authors.

1 Introduction

Maintaining a high concentration of electrons and holes in a photon-absorbing semiconductor is a premise for the conceptual design of a solar cell. This is because the electrochemical energy of electrons and holes is directly linked to their concentration, and so is the eventual voltage produced by the device. Although they may be referred to as a gas, simplifying the statistical relationships that govern their population density, electrons and holes do not leak out of the surfaces of the semiconductor; rather, they recombine with each other at surface defects, with the same net effect of being lost and of causing a reduction of the electrochemical energy of the system. Hence, it is important to envelop the semiconductor absorber with a “skin” that passivates those surface defects [1]. Intuitively, passivation can be envisaged as the covalent bonding between atoms present in the “skin” material and the surface atoms of the semiconductor. An example is the bonding between oxygen and silicon that results from thermally growing a SiO₂ layer. The oxidation process still leaves a fraction of silicon bonds unsatisfied and it is usually complemented by supplying hydrogen, whose small size facilitates its diffusion towards those dangling silicon bonds.

While the concept of chemical passivation is intuitively clear and widely accepted, the term “passivation” is sometimes used to refer to other mechanisms that also result in a reduction of

the recombination rate between electrons and holes. Generally, such mechanisms involve a large imbalance between the populations of electrons and holes near the surface, which indeed leads to a lower recombination rate, as described below. To preserve the intuitive meaning of passivation as chemical bonding, we will refer to other, non-chemical mechanisms as “carrier population control”.

Another premise for a semiconductor absorber to become a solar cell is that it should be able to deliver electrons to an external circuit. For that to occur, each carrier type must flow separately towards each of the two metallic terminals attached to the solar cell. This implies that each of those metallic terminals must be in contact with a region in the semiconductor where the conductivity for one carrier type is much greater than for the other carrier type [2]. Those two regions could be appropriately called selective electron and hole conductors, but given that they need to be at the surface and in contact with the metal terminals, they are frequently referred to as selective contacts.

The ability to manipulate the conductivity is, therefore, essential to construct a solar cell. Of the two components that determine the conductivity, mobility and charge carrier concentration, only the latter can be varied to a sufficient extent in practice. In silicon technology that is usually achieved by doping, but other methods can be used, for instance by depositing materials with a work function significantly higher or lower than that of the silicon absorber, as discussed in this paper.

The conceptual premises are clear, but their experimental implementation can be challenging. Metallic terminals are essential, but when a metal is directly deposited on silicon it causes a very high density of recombination centres, which draws to the surface both carrier types, thus undermining the objective of achieving single-carrier transport. Hence, it is important to find ways of implementing a highly asymmetric conductivity to each of the two metallic terminals while minimising recombination. In conventional silicon solar cells surface passivation and selective conductivity are implemented “in parallel”, which leaves the surface regions contacted by the metallic terminals de-passivated. An awareness of the limitations that recombination at the metal contacts cause has prompted the development of comprehensive contact systems where selective conductivity and surface passivation are implemented “in series”. Indeed, the most effective contact systems developed so far combine several layers of different materials, each of them performing one of the required functions of selective conduction, surface passivation and contact formation to the external metal.

This paper summarises the main results of our work during the last five years on non-traditional surface passivating materials and carrier-selective passivating contacts. Please note that a substantial part of that work has been in collaboration with other researchers, as mentioned in the Acknowledgement. Given that this paper is intended for a special issue on surface passivation and passivating contacts, no attempt has been made to include the outstanding work done by other researchers on those topics, in order to avoid excessive repetition. It is expected that companion articles of the same issue will give the interested reader a more comprehensive overview of the topic.

2 Pathways to reduce surface recombination

2.1 Surface passivation by chemical bonding

Surface passivation refers, in its purest form, to the chemical attachment of atomic or molecular species to the unsatisfied “dangling” bonds of silicon atoms at the surface of the semiconductor. Usually, a certain amount of interface defects remains after an oxidation process or after depositing a dielectric material on a silicon wafer. The density of such defects, or traps D_{it} can be further reduced by means of a hydrogenation treatment. For example, Eades

et al. measured $D_{it} \sim 10^9 \text{ cm}^{-2}$ for *annealed* SiO_2 [3], a remarkably low number in comparison with the $\sim 7 \times 10^{14} \text{ cm}^{-2}$ density of bonds present at the (100) silicon surface. The application of a hydrogenation treatment, preferably in atomic form, is a common denominator of all the approaches that have led to high quality surface passivation, including semiconductors, like a-Si:H, and dielectrics like SiO_2 , SiN_x , Al_2O_3 , Ga_2O_3 , etc. For some of them it is difficult to measure accurately the density of interface traps, due to their non-negligible conductivity. This obviously applies to materials that are attractive for selective contact systems precisely because they are conductive. Figure 1, updated from the original version in [4], gives a qualitative summary of the approximate levels of D_{it} and fixed charge reported for a variety of passivating films, reflecting the substantial spread of the values reported in the literature. Note that this D_{it} corresponds to the middle of the energy bandgap of silicon and, although useful to compare the quality of chemical passivation by different materials, it should only be regarded as a proxy for the complex statistics of Shockley-Read-Hall recombination.

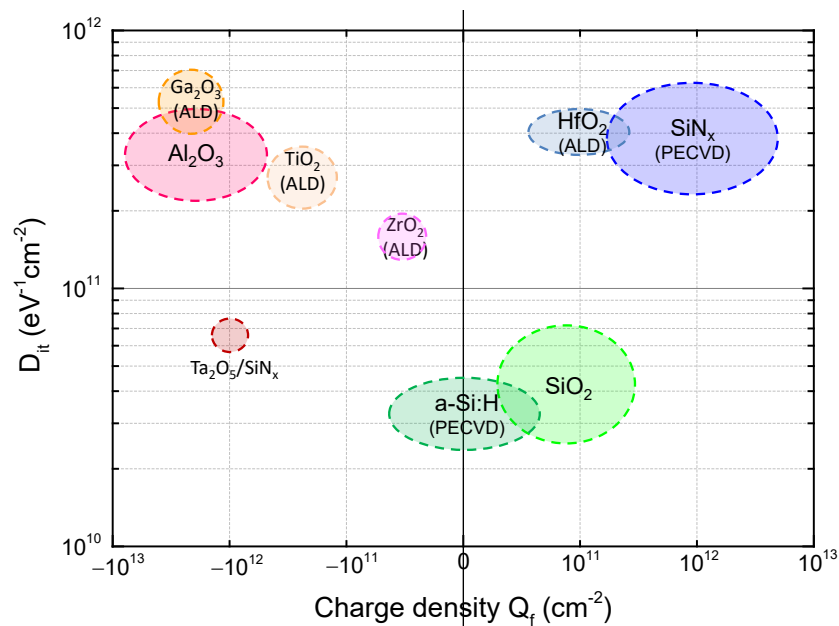


Figure 1. Qualitative summary of the approximate ranges for the density of interface defects and the charge measured experimentally for different materials deposited on the surface of crystalline silicon. The vertical axis indicates the level of chemical passivation, whereas the horizontal axis indicates the ability of charge (both polarities) to assist in controlling the carrier density at the interface.

2.2 Controlling the population of electrons and holes by means of doping

The product of the concentrations of electrons and holes drives the rate at which they recombine. It is intuitive to understand that this reaction rate is highest when the concentration of the two reactants is similar to each other. Therefore, it is possible to control electron-hole recombination by manipulating their respective concentrations, basically, by making one of the two much smaller than the other. To illustrate that, let us consider SRH recombination in silicon caused by a relatively high density of mid-gap defects. It is straightforward to calculate the net recombination rate for any combination of dopant densities in the semiconductor using the well-known SRH expression, plus the relationship between the pn product and the difference between the electron and hole Fermi energies E_{Fn} and E_{Fp} ,

$$(p_o + \Delta p)(n_o + \Delta n) = n_i^2 \exp\left(\frac{E_{Fn} - E_{Fp}}{kT}\right) \quad (1)$$

where p_o and n_o are the equilibrium hole and electron concentrations, $\Delta p = \Delta n$ their respective excess concentrations under illumination, n_i the intrinsic carrier density, k the Boltzmann

constant and T the temperature. In a moderately doped p-type semiconductor $p_0 \approx N_A$ and $n_0 \approx n_i^2/N_A$, where N_A is the concentration of acceptors. Fixing the difference $(E_{Fn}-E_{Fp})/q$ to a particular level, for example 600 mV allows us to determine the excess carrier concentration and, eventually, the recombination rate when we change the dopant concentration in the semiconductor. Figure 2 shows the recombination rate as a function of the ratio between the electron and hole concentrations for two different recombination centres, one that presents a capture cross-section for electrons 100 times greater than for holes ($k=\sigma_n/\sigma_p=100$) and another one where it is 100 times smaller ($k=0.01$). We have assumed two mid-gap defects, with a density three times greater for the first ($N_T=9 \times 10^{10} \text{ cm}^{-3}$) than the second. As expected, the maximum recombination rate occurs when $n\sigma_n \approx p\sigma_p$. For a defect with identical capture cross sections for electrons and holes the recombination rate is highest when $p=n$. Although the calculations presented in Figure 2 are simplistic, they are qualitatively similar to the measurements reported by Yablonoivitch et al. [5] for the interface between thermal SiO_2 and Si. In general, increasing the majority carrier concentration brings about a reduction of the minority carriers and the overall recombination rate. Therefore, to reduce recombination, the equilibrium carrier concentrations need to be very asymmetric, by eight or ten orders of magnitude ($n_0/p_0 < 10^{-8} \text{ cm}^2$), so that such asymmetry remains under excitation.

That doping can be used to reduce the impact of surface recombination can be and has been verified experimentally. For example, the effective carrier lifetime that can be measured in an unpassivated silicon wafer is in the range of 1-3 μs , depending on the thickness of the wafer and the diffusivity of the relevant minority carrier. When a dopant diffusion is added near the surfaces of the wafer, the effective lifetime increases to tens or even hundreds of μs . It is possible to reduce recombination even without an outer dielectric coating [6], but it is of course more complete with it. The ability of a diffused region to suppress recombination is compromised by recombination within its own volume; this is because although dopant diffusions are quite thin, the concentration of one of the two charge carriers is very high, which triggers the Auger process, leading to fast recombination of the minority carriers. Globally, recombination within the volume of the diffused region and at the outer surface can be encapsulated in a “recombination parameter” with dimensions of current density, J_0 , that is easily measurable using the method proposed by Kane and Swanson [7]. It is possible to translate such J_0 parameter into an equivalent surface recombination velocity, and vice-versa.

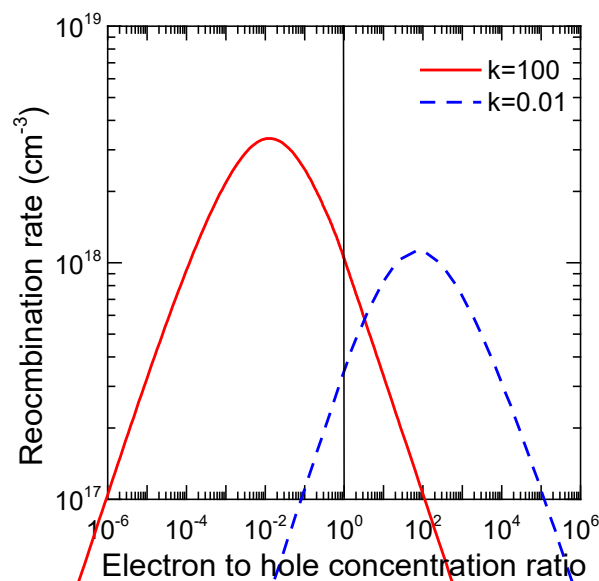


Figure 2. Recombination rate in silicon as a function of the electron to hole concentration ratio for a fixed separation between the electron and hole quasi-Fermi energies of 0.6 V. The two cases shown correspond to recombination centres with a capture cross-section for electrons ($\sigma_n=10^{-13} \text{ cm}^2$) 100 times greater than for holes ($k=100$) or 100 times smaller ($k=0.01$, $\sigma_n=10^{-15} \text{ cm}^2$). A density of defects 3 times lower for the second defect ($N_T=3 \times 10^{10} \text{ cm}^{-3}$) has been assumed.

2.3 Charge-assisted population control

Some insulators possess, or develop in contact with a silicon surface, a net positive or negative charge. In equilibrium, this has the consequence of attracting carriers having an opposite charge, which accumulate at the interface between the dielectric and the semiconductor. A common example is SiN_x, whose positive charge creates a very thin layer where the concentration of electrons is overwhelmingly greater than that of holes. For normal solar cell operation conditions (moderate illumination intensity), a large asymmetry between the concentrations of majority and minority carriers remains, which, as shown above, leads to a reduced recombination rate. Many people refer to this as “field effect passivation”, but the root cause of the lower recombination rate is the asymmetric population of electrons and holes caused by the charge. As Würfel has explained [8], an electric field established in equilibrium cannot exert a force on the excess carriers generated by an external excitation.

A similar argument can be made for the case of a negative charge, which would create an induced layer where holes are in the majority and electrons in the minority. Irrespective of the bulk semiconductor being p-type or n-type, either an accumulation or an inversion layer have the consequence of altering the statistics of electron-hole recombination and, with some exceptions, they mitigate the influence of residual defects at the surface. The preference for a particular charge polarity may come from the knowledge of the capture cross-sections for electrons and holes of the dominant surface defects. More commonly the decision is made based on device structure considerations; for example, a positively charged dielectric like SiN_x, causes an inversion layer on p-type silicon, which then channels minority electrons towards locations where the recombination rate is high, such as those contacted by a metal or the edges of the device. Hence, to avoid the problem, a negatively charged dielectric like Al₂O₃ is commonly used to passivate the rear side of p-type Si solar cells with a localised metal contact.

Searching for alternatives to Al₂O₃, we have investigated other materials that could provide both a negative charge and effective chemical passivation. To achieve the latter, we have used hydrogen containing precursors in an ALD reactor. Table I shows a varying level of negative charge, high for Ga₂O₃, and lower, but still significant, for TiO₂ and Ta₂O₅. For HfO₂ we found a slightly positive charge, although other researchers have reported a negative one. The case of Ta₂O₅ is interesting, since hydrogenation did not occur to a sufficient degree until a second layer of hydrogen-rich SiN_x was deposited onto it and annealed; this shows that even a strong negative charge can be insufficient to reduce surface recombination. Capping with SiN_x and subsequent annealing frequently enhances the quality of passivation provided by other materials too; for example, the surface recombination velocity measured for GaO_x improved from 2.5 cm/s to 1.4 cm/s [9]. In addition, the well-known fact that high quality surface passivation can be achieved by a-Si:H or hydrogenated SiO₂, both of which have low or negligible charge density, indicates that chemical passivation can be effective even in the absence of carrier population control.

Material	Q_{eff}/q (10 ¹² cm ⁻²)	S_{eff} of undiffused wafers (cm/s)		J_0 of dopant diffusions (fA/cm ²)		Method/Reference
		<i>p</i> -type	<i>n</i> -type	<i>p</i> ⁺	<i>n</i> ⁺	
SiN _x	+0.6	1.6	<1.0		44	PECVD [10]
a-Si:H/SiN _x		3.0	2.0	87	47	PECVD [11]
HfO ₂	+0.5	9.9	3.3		23	ALD [12, 13]
Ga ₂ O ₃	-5.0	2.5		26		ALD [14]
TiO ₂	-0.8	9.8	2.5	19		ALD [15]
Ta ₂ O ₅ /SiN _x	-1.0	5.0	3.2	25	68	ALD/PECVD [16]
ZrO _x	-0.058	13.0	8.0			ALD [17]

Table I. Surface recombination parameters measured for various dielectric materials deposited on p-Si and n-Si wafers with a bulk resistivity of approximately 1-1.6 Ωcm , as well as onto boron or phosphorus diffused surfaces. The dopant diffusions had a R_{sheet} in the range of 85-120 Ω/\square . The corresponding charge density, obtained from C-V measurements is also given.

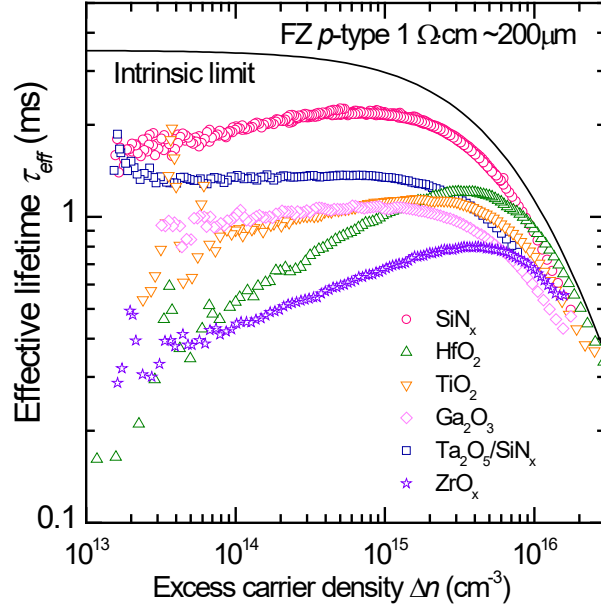


Figure 3. Effective minority carrier lifetime measured for p-type silicon wafers with a resistivity of about 1 Ωcm coated on both sides with various metal oxides. A sample coated with SiN_x is included as a reference.

2.4 Work-function control

According to the ideal Schottky-Mott theory, a difference between the chemical potentials, or work functions, of the deposited material and the semiconductor can result in a high concentration of one type of carrier near the surface and, consequently, a low concentration of the other type. As mentioned above, this asymmetry in carrier concentrations can help to reduce the recombination rate. The concentration of electrons and holes at the surface n_s and p_s is calculated from the electrostatic potential at the surface of the semiconductor ψ_s , which can be found by solving the electrostatic equations following the iterative approach of Girisch *et al.* [18]. The surface potential ψ_s is reduced when an excess concentration of carriers Δn is present in the semiconductor. However, a large asymmetry in the surface carrier concentrations can still exist at one sun illumination if the initial ψ_s is sufficiently large. Figure 4 shows calculations of the ratio p_s/n_s as a function of the work function $q\phi_m$ of materials deposited onto lowly doped n-type silicon ($N_D = 10^{14} \text{ cm}^{-3}$), assuming an ideal surface with zero recombination and no pinning of the Fermi level. Given that the excess carrier concentration in the semiconductor can vary widely depending on the electronic quality of the silicon wafer and also with the operating point of the solar cell, the calculations have been performed for a range of Δn . It can be observed that to maintain a strong predominance of holes over electrons of $p_s/n_s = 1 \times 10^{16} \text{ cm}^{-3}$ over the range of excess carrier densities typical of solar cell operation it is necessary to deposit a material with a work function of about 5-6 eV, even in the ideal case. Conversely, to achieve a strong predominance of electrons, with an asymmetry ratio of $p_s/n_s = 1 \times 10^{-16} \text{ cm}^{-3}$, it is necessary to deposit a material with a work function of about 3-4 eV.

Figure 4 also shows similar calculations for the case of a fixed charge density Q_f . A negative (positive) charge does cause accumulation of holes (electrons) near the surface, but the asymmetry ratio varies markedly with the excess carrier density Δn in the bulk of the wafer.

For example, a negative charge of $Q_f = -2 \times 10^{12} \text{ cm}^{-2}$ results in $p_s/n_s = 10^{16} \text{ cm}^{-3}$ if Δn is lower than 10^8 cm^{-3} but only about $p_s/n_s = 10^{10} \text{ cm}^{-3}$ if $\Delta n \approx 10^{14} \text{ cm}^{-3}$.

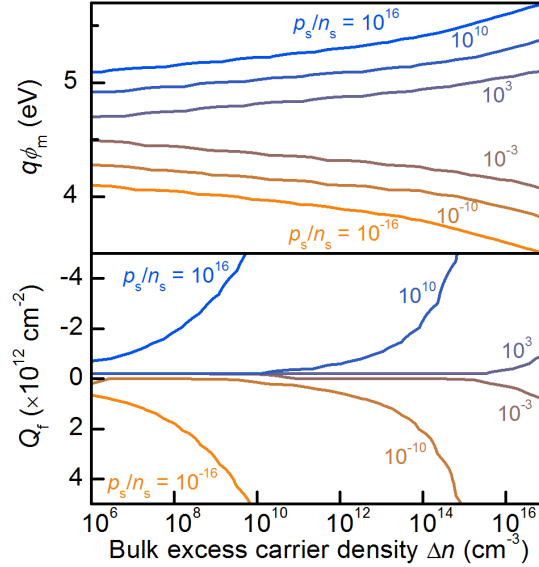


Figure 4. Surface hole to electron concentration ratio p_s/n_s calculated as a function of the excess carrier density in the bulk of a lowly doped ($N_D = 10^{14} \text{ cm}^{-3}$) n-type *c*-Si wafer with an applied work function (top) or fixed charge density (bottom). Figure from J. Bullock, PhD thesis, The Australian National University, 2016.

3 Combining surface passivation and carrier-selective conductivity

As mentioned in the introduction, it is clear that to support a high concentration of excess electrons and holes in the semiconductor and to separate them towards the two terminals of the solar cell it is essential to suppress recombination everywhere in the device. In particular, surface passivation should be incorporated into any electron or hole contact system, in order to make it more selective. The reason for this is that the fate of charge carriers (for example holes) that may flow into the contact structure designed to predominantly transport the other type of carriers (i.e. electrons) is to recombine.

Historically, chemical passivation from dielectrics has been incorporated to doped (hence asymmetrically conductive) regions of the silicon wafer in parallel. This is because dielectric materials are poor conductors and they need to be locally removed to make contact to the silicon with a metal. The dielectric is usually removed from just 1-5% of the surface area, but even such a small fraction of de-passivated dopant diffusion can represent the largest loss of the whole carrier-selective conductor system. This points out the importance of keeping under the metal terminals a layer (or layers) that permits the flow of current while passivating the surface of the silicon, that is, of incorporating chemical passivation and selective conduction “in series”. Below we describe different approaches to do that, but first let us discuss how to evaluate the quality of a given carrier-selective contact structure.

3.1 Performance parameters for carrier-selective contacts

It is straightforward to evaluate the ability of a carrier-selective contact structure to pass electric current by means of its contact resistivity ρ_c , an intuitive parameter that can be measured using well-known test structures and methods. On the other hand, the best way to evaluate the selectivity, that is, the ability to hinder the transport of one of the two carriers, is by assessing the recombination loss within the contact structure, including its interface with the metallic terminal. A suitable metric to evaluate recombination within a specific region of

the device is the recombination current parameter J_{0c} , which can also be easily measured. The sub-index zero indicates that this would ideally be a recombination-generation current extrapolated to equilibrium conditions, whereas the second sub-index indicates that we are referring to contact structures. A simple way to combine in a single parameter the limitations imposed both by recombination and resistance in an ‘upper-limit’ voltage given by [19],

$$V_{UL} = \frac{kT}{q} \ln \left(\frac{J_{ph}}{J_{0c}} \right) - J_{ph} \rho_c, \quad (2)$$

Although it would be desirable to do the calculation at the maximum power point, it varies from cell to cell. Hence we propose to evaluate V_{UL} using a well-established reference value for the current, such as the photogenerated current $J_{ph}=43.31$ mA/cm² calculated in Ref. [20] for an ideal silicon solar cell. The resulting upper limit voltage is, therefore, unattainable, and its calculation combines an open-circuit assumption to evaluate the cap imposed by recombination, together with a pessimistic evaluation of the voltage drop due to contact resistance. Nevertheless, it is precisely the assumption of these extreme conditions that makes its calculation robust, subject only to the specific J_{0c} and ρ_c parameters of the contact. It is, in fact, a suitable and easy to quantify metric to assess carrier-selectivity, and it remains relevant at the maximum power conditions. This is demonstrated in Figure 5, where contours of V_{UL} are overlaid on simulations of the achievable solar cell performance, showing near perfect alignment with the efficiency contours. The slight departure between the numerical simulation using Quokka [21] and the analytical calculation of V_{UL} in the low J_{0c} range arises from the influence of Auger recombination in the bulk of the wafer, which Equation 2 does not account for, given that it is only possible to do that for every particular case (wafer thickness and doping).

Figure 5 (a) confirms the intuitive expectation that the influence of ρ_c on a silicon solar cell with a full-area contact is minimal below ~ 0.15 Ωcm^2 , whereas the impact of the recombination parameter J_{0c} on cell voltage and efficiency is very strong. Nevertheless, there will be diminishing returns from reducing J_{0c} below the limitations imposed by band to band and Auger recombination in the volume of the semiconductor absorber. For a 100 μm thick silicon wafer such limitation can be approximately established as $J_{0\text{bulk}} \approx 5 \times 10^{-15}$ A/cm², which imposes a limit to V_{oc} of 761 mV [20].

Geometric restriction of the contact area provides an additional design tool to optimise the trade-off between recombination and resistance losses. Partial-area contacts can tolerate higher values of J_{0c} , but place greater demands on ρ_c , as well as creating more complexity in device fabrication. The V_{UL} metric can be modified to approximately take into consideration the contact area,

$$V_{UL} = V_t \ln \left(\frac{J_{ph}}{f_c J_{0c} + (1-f_c) J_{0\text{pass}}} \right) - J_{ph} \frac{\rho_c}{f_c} \quad (3)$$

where additional terms for the rear contact fraction f_c and recombination in the non-contacted, surface passivated regions $J_{0\text{pass}}$ are included. Contour plots for the case of partial-area contacts, are shown in Figure 5 (b). A detailed description of the modelling assumptions, can be found in Ref [19]. Similar calculations and graphs have been independently published by Brendel and Peibst. [22].

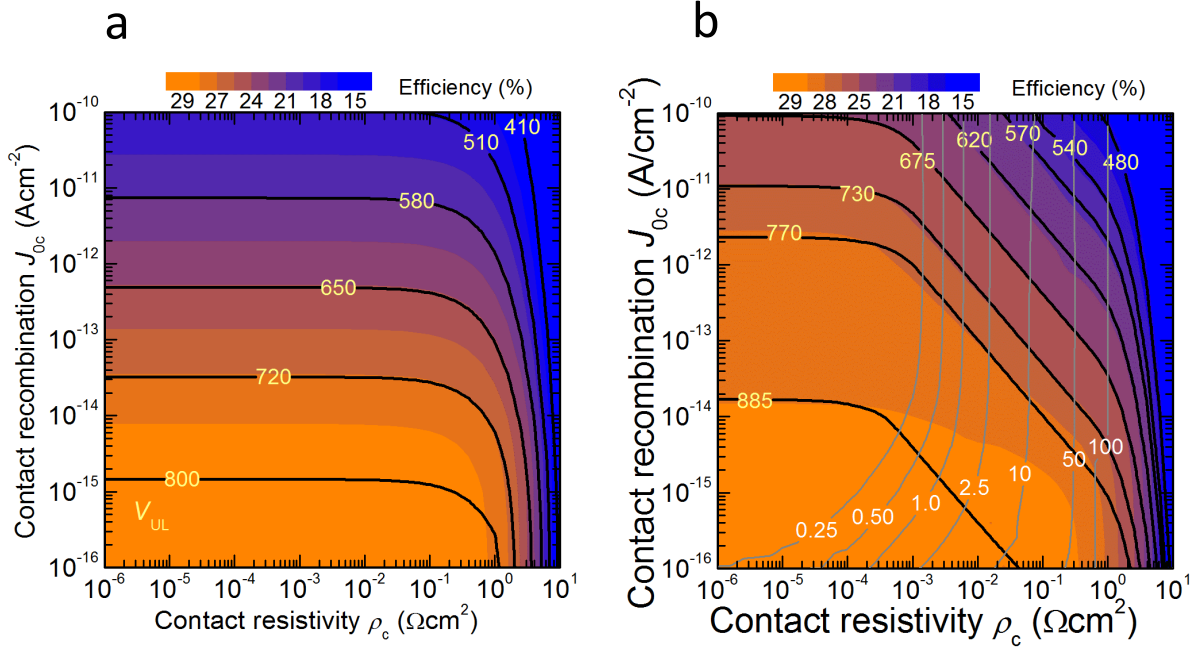


Figure 5: (a) Comparison between the selectivity parameter V_{UL} (black lines) and idealised simulations of solar cell performance using Quokka (colour contours), as a function of the rear contact J_{0c} and ρ_c for (a) a full area contact, or (b) a partial-area contact. In (b) the extra set of lines and lower numbers correspond to the optimum contact fraction. From J. Bullock, PhD thesis, The Australian National University, 2016.

3.2 Combining dielectrics and doping “in parallel”

The benefits of applying a passivating dielectric to the front dopant diffusion of a silicon solar cell were first reported by Fossum and Burgess in 1978 [23]. They showed that the open-circuit voltage of a p^+nn^+ solar cell increased by 30 mV when a very thin (5 nm) SiO_2 layer was thermally grown on the front boron diffusion and then coated with a silicon nitride antireflection layer deposited by PECVD, which may have provided atomic hydrogen to the interface. It took until 1986 to incorporate SiO_2 to the surface of phosphorus diffusions, and this permitted to make a 20% efficient n^+pp^+ solar cell [24]. The long delay can partly be attributed to the fact that common phosphorus diffused regions had a “dead layer” near the surface, where an excess concentration of electrically inactive dopant atoms caused very fast carrier recombination. The benefits of surface passivation can only be gained once phosphorus precipitates were avoided and the dopant profile optimised [25].

Figure 6, taken from [26] shows measurements of the recombination current density parameter J_0 measured for phosphorus and boron diffused regions having different dopant doses, as reflected in their respective sheet resistances. Un-passivated, metal-coated diffusions are shown on the left, indicating that the best way to reduce recombination in that case is to use a high dopant dose, either by making the diffusion deep or increasing the surface dopant concentration, or both. On the other hand, for well-passivated diffusions (with PECVD SiN_x for the n^+ and ALD Al_2O_3 for the p^+ surfaces), shown on the right of Figure 6, it is better to reduce the dopant dose. Doing that permits to keep Auger recombination at bay and achieve J_0 values in the range of 10 fA/cm², or lower. It is interesting to note that, for a given sheet resistance, passivated boron diffusions present a lower J_0 than phosphorus diffusions; this can be explained by the fact that the Auger coefficient [27] is lower for electrons in p-Si,

$C_p=0.99 \times 10^{-31} \text{cm}^6 \text{s}^{-1}$ than for holes in n-Si, $C_n=2.8 \times 10^{-31} \text{cm}^6 \text{s}^{-1}$. The result may be surprising if one considers that in moderately doped silicon the mobility for holes is smaller than that of electrons, which would mean that a heavier doping is required for p-type Si than n-type Si to achieve the same sheet resistance; nevertheless, this does not apply to high dopant concentrations, for which the difference between electron and hole mobilities is relatively small, both for majority and minority carrier mobilities, as shown in the inset.

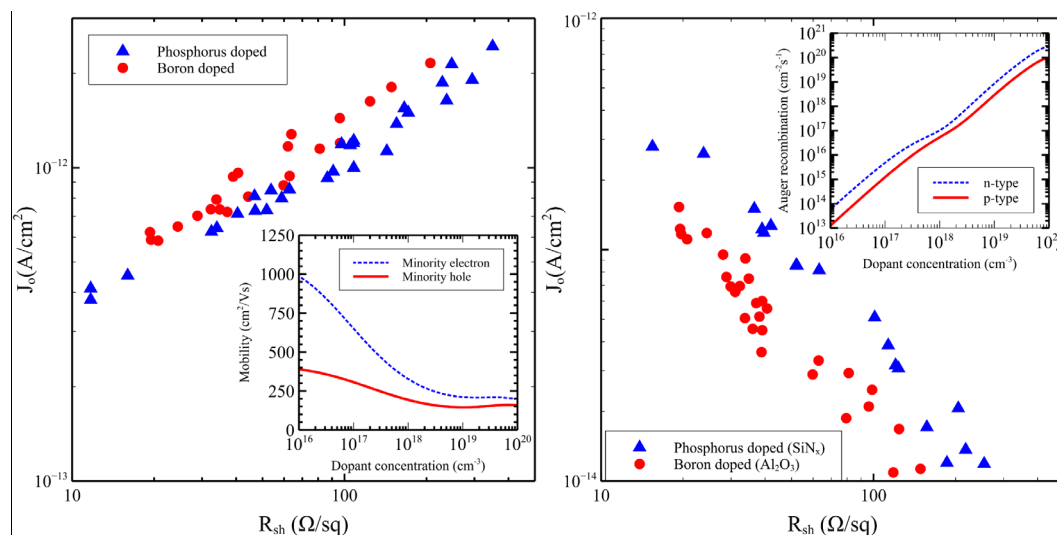


Figure 6. Recombination current density parameter measured for various phosphorus and boron diffused regions having different sheet resistances. Un-passivated, metal-coated diffusions are shown on the left, whereas well-passivated diffusions (with SiNx for phosphorus and Al₂O₃ for boron diffusions) are shown on the right. The insets show the minority carrier mobilities and Auger recombination rates corresponding to heavily doped n-type or p-type silicon. (From Di Yan, PhD thesis, The Australian National University, 2016)

When passivating highly doped surfaces, it is important to pay attention to the charge that accompanies some passivating materials. Whereas SiO₂ and a-Si:H can be used on any surface, positively charged materials like Si₃N₄ and HfO₂ are preferable for phosphorus diffusions, and negatively charged ones, like Al₂O₃ and Ga₂O₃ for boron diffusions. A negatively charge onto a phosphorus diffused surface tends to deplete it of electrons and to increase the concentration of holes, hence reducing the asymmetry between both and increasing the recombination rate. Table I gives experimental values measured for several materials deposited by PECVD or ALD onto typical phosphorus and boron diffused regions having a sheet resistance of about 85-120 Ω/□. The different charge polarity of the dielectric materials is reflected in the difficulty to passivate boron diffusions with HfO₂, or phosphorus diffusions with GaO_x and TiO_x. To stress the quality of passivation achieved, it is worth noting that some of the measured $J_0 \approx 20-25$ fA/cm² can be almost completely attributed to Auger recombination within the doped layer.

3.3 Combining chemical passivation and doping “in series”

One approach to circumvent the poor conductivity of most passivating dielectrics is to make them extremely thin, so that carriers can tunnel through them. The idea, explored in the past for MIS and MINP solar cells, mainly using SiO₂, has been extended more recently to other materials. Using Al as the metal, Bullock et al. [28] found that Al₂O₃ deposited by ALD onto a phosphorus diffusion gave similar results to a thermally grown SiO₂, albeit with poorer stability upon annealing at low temperature. For an optimum Al₂O₃ thickness of ~2.2 nm they measured a $J_{0c} \sim 300$ fAcm⁻² on a ~100 Ω/□ phosphorus diffusion, together with a low contact resistivity of 0.3 mΩcm². In subsequent work [29] they achieved a very similar $J_{0c} \sim 300$ fA/cm² with a 1.9 nm SiO₂ layer, but a much higher $\rho_c \sim 200$ mΩcm². Attempts to apply a thin Al₂O₃ layer onto boron diffusions failed to produce satisfactory results.

Even though a $J_{0c} \sim 300 \text{ fAcm}^{-2}$ can be achieved without a thin interlayer under the metal, the dopant diffusion would need to be very deep and with a high dopant dose, as shown in Figure 6. In contrast, the MIS approach can achieve similar results with a light diffusion, which could be further passivated with SiN_x in the non-contacted areas. This would make it suitable for the front, illuminated side of the solar cell. In such scenario, although the metal contact itself would comprise doping and passivation in series, it would still be applied together with geometrical restriction and placed “in parallel” with the rest of the diffused region.

Selective contacts applied to the back do not need to satisfy the requirement of being transparent (unless the cell is bifacial). With that aim, Bullock et al. [30] developed an enhanced metal-insulator-silicon (MIS) structure based on a lightly diffused n^+ region passivated with a $\text{SiO}_2/a\text{-Si:H}$ stack, completing the contact formation by means of a thermally-activated alloying process between the $a\text{-Si:H}$ layer and an overlying aluminum film. The best MIS(n^+) contacts, with SiO_2 thicknesses of $\sim 1.55 \text{ nm}$, achieved a contact resistivity ρ_c of $\sim 3 \text{ m}\Omega\text{cm}^2$ and a recombination current density J_{0c} of $\sim 40 \text{ fA/cm}^2$, which remained stable at temperatures up to 350°C . This selective contact structure was uniformly applied to the rear of n-type silicon solar cells fabricated with a front boron diffusion, achieving a conversion efficiency of 21.0 %.

As an alternative to the above contacts, Bullock et al. [31] inserted an intrinsic hydrogenated amorphous silicon passivating film between the dopant-diffused silicon surface and the aluminium electrode. For phosphorus diffusions with a sheet resistance of $\sim 110 \Omega/\square$ they achieved $\rho_c \sim 0.05 \Omega\text{cm}^2$ and $J_{0c} \sim 40 \text{ fA/cm}^2$ for $a\text{-Si:H}(i)$ thicknesses in the 12–15 nm range. Such J_{0c} value was practically the same as that measured for the same n^+ diffusion passivated with a PECVD SiN_x layer, and 25 times lower than the value measured when the diffusion was coated with Al. This clearly shows that adding chemical passivation (by $a\text{-Si:H}$ in this case) to selective conductivity (from n^+ diffusion) can produce excellent passivating contact systems with a contact resistivity sufficiently low for full area applications. A similar experiment on p^+ boron diffusions produced $\rho_c \sim 0.1 \Omega\text{cm}^2$ and $J_{0c} \sim 200 \text{ fA/cm}^2$. Note that the ideal thickness of a passivating interlayer is approximately 10 times greater for a semiconductor like $a\text{-Si:H}$ than for a dielectric like Al_2O_3 .

3.4 Burying a dielectric under a doped semiconductor

The combination of a 1-2 nm buried SiO_x layer and a 20-200 nm thick phosphorus (or boron) doped silicon film is very effective at suppressing hole (or electron) recombination, and permitting electron (or hole) transport. Among the different methods available, we have used PECVD equipment and silane to deposit an intrinsic amorphous silicon layer ($a\text{-Si}$) and then dope it by conventional phosphorus or boron diffusion from POCl_3 or BBr_3 [32, 33]. Such doping step simultaneously serves to increase the crystallinity of the deposited silicon, and slightly in-diffuse the dopant into the silicon wafer, both of which are critical to achieve good contact and passivation properties. The process to form the interfacial oxide is very simple, either by thermal treatment of the wafers in oxygen or by immersing them in hot nitric acid. As shown in Figure 7, we have found that hole-selective contacts based on p^+ polysilicon usually present slightly worse parameters, $J_{0c} \approx 15 \text{ fA/cm}^2$ and $\rho_c \approx 10 \text{ m}\Omega\text{cm}^2$. Nevertheless, according to Figure 5, these parameters would still permit to achieve a high conversion efficiency. For the electron-selective contacts we have recently achieved $J_{0c} \approx 3 \text{ fA/cm}^2$ and $\rho_c \approx 4 \text{ m}\Omega\text{cm}^2$, which applied to the rear side of an n-type silicon solar cell have led to a 24.7% conversion efficiency [34]. In addition to the chemical vapour deposition approach, we have developed a physical deposition technique [35] and used it to form a hole-selective full area passivating contact on the rear of a p-type silicon wafer, achieving a 23.0% solar cell conversion efficiency [36].

The effectiveness of these $\text{SiO}_x/\text{polycrystalline silicon}$ contact structures is probably related, at least in part, to the fact that the doping process causes a “tail” of phosphorus (or boron) into

the silicon wafer. Typically, the measured electrically-active dopant profiles show a concentration above 10^{20} cm^{-3} in the polycrystalline silicon film followed by an abrupt drop at the location of the thin oxide, down to about 10^{19} cm^{-3} . The dopant “tail” into the wafer can, therefore, be expected to reduce the concentration of minority carriers at the interface, adding a level of carrier population control to its chemical passivation provided by the SiO_x . The physical mechanisms for majority carrier transport and minority carrier blocking are still being debated, and both tunnelling and pinholes in the oxide seem to be able to explain the experimental results. In any case, it is clear that the outstanding results achieved with polysilicon contacts would not be possible without the thin SiO_x layer since, as Figure 6 shows, ordinary doped regions present a much higher J_0 when contacted by a metal. Even compared to the MIS or MINP approaches discussed above, the results achieved by burying the SiO_x layer, rather than placing it onto the diffused region, can only be described as portentous.

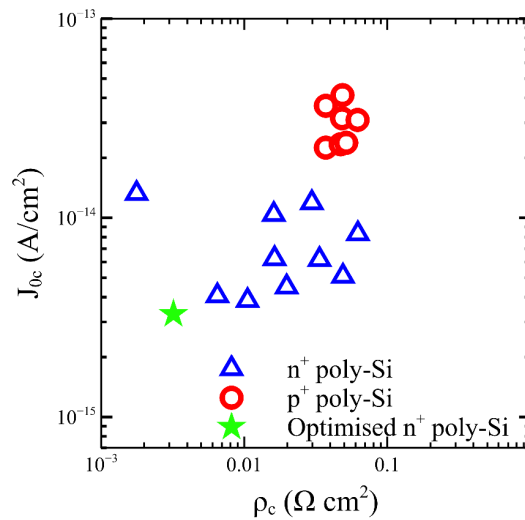


Figure 7. Pairs of contact resistance and recombination current density parameter measured for various polycrystalline silicon/ SiO_x passivating contacts formed by chemical vapour deposition and doped by thermal diffusion of either phosphorus or boron. (From Di Yan, PhD thesis, The Australian National University, 2016)

3.5 Carrier-selective contacts based on extreme work function materials

Some materials can be relatively good conductors at the same time as having an extreme work function. Such combination, together with some level of chemical passivation of the surface, makes them suitable as carrier-selective contacts. A sufficiently high, or low, work function can sustain either accumulation or inversion conditions under one sun illumination and thus maintain regions near the surfaces with highly asymmetric conductivities for electrons and holes. For example, the high work function of MoO_x (about 6 eV) produces an accumulation layer on p-type silicon and an inversion layer on n-type silicon. Bullock et al. [37] measured the sheet resistance of the inversion layer to be $R_{IL} \sim 12 \text{ k}\Omega/\square$. For selecting electrons, it is appropriate to use materials like LiF_x , which when capped with Al presents a very low work function of $\sim 2.8 \text{ eV}$.

In practice, it is difficult to achieve good chemical passivation with the same material that provides an extreme work function. This may be related to the method used to deposit it; for example, MoO_x deposited by evaporation in a vacuum results in some, but insufficient, reduction of surface recombination. Subsequent hydrogenation is difficult, because the material can only be annealed at temperatures below $150 \text{ }^\circ\text{C}$. To overcome such difficulties, extreme work-function materials are frequently used in conjunction with a good passivator, like a-Si:H. The risk of inserting an additional layer for chemical passivation is to further hinder the ability

to conduct electric current. It is therefore important to simultaneously optimise surface passivation and contact resistance of the complete selective contact structure. Contact resistance usually presents a minimum for very thin interlayers of the extreme work function material, as shown in Figure 8 (a). Nevertheless, this is not a general rule and, for example, the moderate conductivity of MoO_x ($\sim 2 \times 10^{-5} \text{ S/cm}$) and WO_x permits a low contact resistivity even with 10-20 nm thick layers, as can be seen in Figure 8 (b). Note that although Pd was used in this instance as the metallic terminal, less extensive tests revealed similar results using evaporated Ni and sputtered indium-tin-oxide (ITO) layers.

Another material that shows promise for hole-selective contacts is copper oxide, which is naturally p-type and has a work function of 4.8-5 eV. Zhang et al. [38] measured a low $\rho_c \approx 11 \text{ m}\Omega\text{cm}^2$ for an 8nm thick layer of $\text{CuO}_x\text{:N}$ deposited by sputtering. The layer was identified to contain a mix of CuO_2 and CuO , with some nitrogen doping and excess precipitated Cu. More work is, however, required to optimize this material in terms of surface passivation, or combine it with a passivating interlayer.

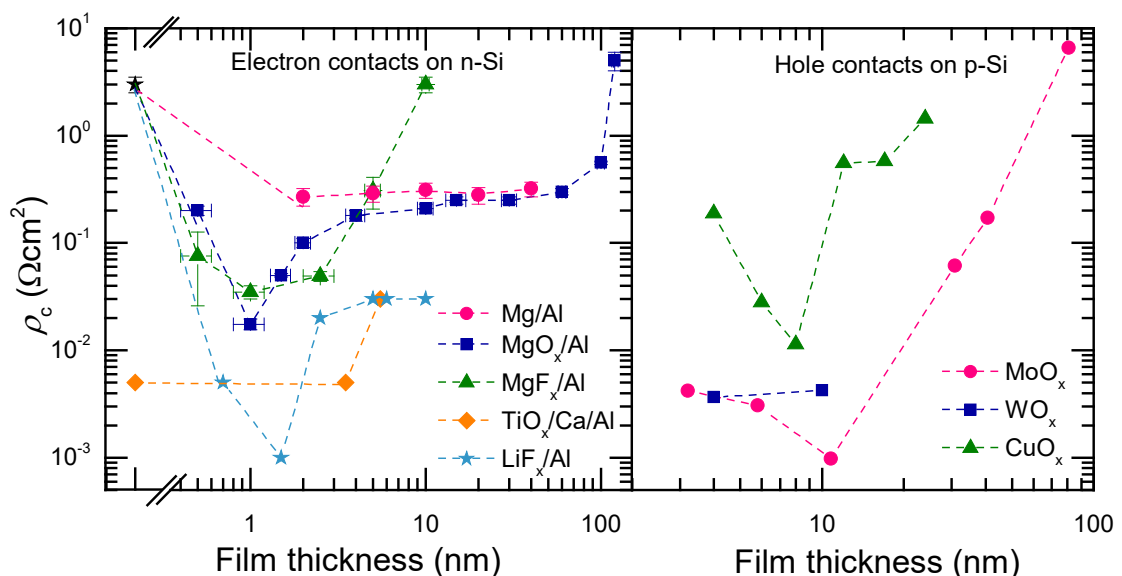


Figure 8. Contact resistivity measurements for various electron-selective and hole-selective contacts as a function of the thickness of the relevant low work-function material. An exception is the case of $\text{TiO}_x/\text{Ca}/\text{Al}$, where the thickness refers to the passivating TiO_x interlayer. In the case of MoO_x , WO_x and CuO_x palladium was used as the metal.

4 Incorporating carrier-selective conductors into solar cells

The ultimate proof that a given material, or a combination of them, can function as a carrier-selective conductor is to apply it to a solar cell. We have done so for a number of them, seeking such a proof-of-concept, with a relatively lower priority given to optimising cell performance. Table III summarises the performance of various solar cells fabricated in our laboratory (some steps were performed in some cases at collaborating institutions) using a combination of dopant diffusions, generally at the front side of the device, and a carrier-selective contact system, usually at the rear. For materials that so far have not provided sufficient passivation when deposited directly on silicon we have fabricated solar cells with a partial rear contact, that is, with most of the surface passivated by a conventional material, such as SiN_x for n-type wafers or Al_2O_3 for p-type wafers, while the selective conductor itself makes contact on a small fraction, in the range of 1-6%. With some materials (TaO_x , MgO_x and MoO_x), we attempted a

full-area contact, achieving relatively modest open-circuit voltages in the range of 630-640 mV. The benefits of adding an a-Si:H interlayer are clearly demonstrated by the much higher voltages, in the range of 690-710 mV, that can be achieved. An exception is the case of metallic Mg deposited onto the a-Si:H, which seems to have affected the passivation, possibly due to a chemical reaction between the two.

All the cells in the table, except two, were made with n-type silicon wafers, and all the selective conductors, but two, are for electrons. The first hole-selective conductor in the table is MoO_x, which we applied directly on 5% of the rear surface of a p-type silicon wafer to replace the customary localised p⁺ region based on Al or B doping. Thanks to its transparency, MoO_x, can also be used at the front side, and the table shows an example where it was combined with ITO at the front and a phosphorus diffused polysilicon conductor at the rear of an n-type wafer. This device was not optimised, and it did not have a textured surface, which explains its relatively low efficiency of 16.7%. Nevertheless, it proves that a MoO_x conductor does provide a sufficiently low contact resistance on n-type silicon [37].

The table also includes two of the solar cells that we have made recently on both n-type and p-type silicon using a SiO_x/polySi conductor for electrons or holes at the rear. The design and fabrication sequence of these devices is considerably more sophisticated than the others in the table. The carrier-selective conductor at the front side was made with two different boron (for the n-type cell) or phosphorus (for the p-type cell) doses, heavier under the metal grid and lighter under the Al₂O₃/SiN_x (just SiN_x for the p-type cell) passivation. The metal bus bar, which surrounds the periphery, does not make contact with the silicon. Thanks to such complexity, it was possible to combine high voltage, current and fill factor, achieving an efficiency of 24.7% with an n-type silicon wafer and 23.0% with a p-type one, which proves the electronic quality of the polysilicon contacts. It can be expected that if a similar level of technological sophistication is used for other selective conductors, higher efficiencies than those reported in the table should be achievable.

	Selective conductor system	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	Eff. (%)	details	Ref.
Partial Rear Contact	MoO _x /Ag	658	39.8	77.8	20.4	15 nm MoO _x p-Si, 5% contact	Bullock [39]
	Ca/Al	652	39.6	78.6	20.3	30 nm Ca n-Si, 1.2% contact	Allen [40]
	TiO _x /Ca/Al	681	39.6	80.9	21.8	3.5 nm TiO _x , 30 nm Ca n-Si, 6.2% contact	Allen [41]
	LiF _x /Al	676	38.9	78.3	20.6	1.5 nm LiF _x n-Si, 1% contact	Bullock [42]
Full-area Rear Contact	MgO _x /Al	629	39.5	80.6	20.0	1 nm MgO _x	Wan [43]
	TaO _x /Mg/Al	638	37.8	79.3	19.1	6 nm TaO _x 10 nm Mg	Wan [44]
	a-Si:H/Mg/Al	637	38	78.4	19.0	6 nm a-Si:H, 10 nm Mg	Wan [45]
	a-Si:H/MgF _x /Al	687	37.8	77.3	20.1	6.5 nm a-Si:H, 1 nm MgF _x	Wan [46]

	n ⁺ c-Si/SiO _x /a-Si:H/Al	666	39.3	80.5	21.0	1.5 nm SiO _x , Al alloyed to a-Si:H	Bullock [30]
	SiO _x /n ⁺ polySi	705	42.4	82.6	24.7	n-Si, selective boron diffusion	Yan [34]
	SiO _x /p ⁺ polySi	701	41.1	79.9	23.0	p-Si, selective phosphorus diff.	Yan [36]
Front and rear contact	MoO _x /ITO SiO _x /n ⁺ polySi	637	35	0.75	16.7	n-Si wafer, not textured	Bullock [47]
	a-Si/MoO _x /ITO a-Si:H/TiO _x /LiF _x /Al	706	38.4	76	20.7	DASH solar cell	Bullock [48]

5 Conclusion

A better understanding of the physics of solar cells has prompted a fresh look at how they can be constructed. Leaving behind deeply entrenched misconceptions, a plethora of previously disregarded materials are being put to good use. Materials that possess a very high work function, like MoO_x, or a very low one, like LiF_x/Al, which when deposited on silicon create near the surface a thin layer where either electrons or holes are concentrated. That is, a layer that preferentially conducts one or the other type of charge carrier. Such selectivity can then be complemented by chemical passivation, that is, by bonding foreign atoms onto the dangling bonds of the silicon surface.

Surface passivation and carrier population control are inextricably linked in the pursuit of two fundamental premises of solar cell operation: to prevent the recombination between carriers and to enable their separate flow towards different terminals. Their combination in what has come to be called “passivating contacts”, which may be applied uniformly across the silicon surface, offers the promise of high performance together with simplicity. Besides being vertically conductive, the materials used in such contact systems need to be transparent, if they are to be applied on the front, illuminated side, or even on the back surface, for bifacial cells. In such applications, the requirement for conductivity is exacerbated by the need to transport current laterally towards the metal grid. Those constraints are very difficult to satisfy with a single material, and all passivating contacts developed so far are composed of multiple layers, each of them performing a specialised function.

The new mentality has led to the development of silicon solar cells that no longer rely on doping for carrier separation. Significant progress has been made in a short period of time, yet there remain many challenges ahead and the journey is still fraught with obstacles. It is uncertain whether or not dopant-less materials and devices will offer advantages for mass production and be stable in the long term. What is clear is that they offer an opportunity to advance scientific understanding and explore new approaches to silicon photovoltaics. Unsurprisingly, the field of passivating selective contacts is expanding rapidly, and is giving silicon solar cell research a renewed impetus.

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