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Passivating contacts: unlocking the full potential of silicon solar cells

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INTRODUCTION

In 2016, approximately 1.5% of global electricity demand – representing less than 0.25% of total global energy consumption – was met by electricity generated by photovoltaic (PV) modules, the vast majority of which are comprised of crystalline silicon (c-Si) solar cells.[1] These modest statistics belie a transformational change that is occurring in electricity generation worldwide: in the same year photovoltaics became the fastest growing electricity generation source with more PV capacity installed globally (74 GW) than any other renewable (52 GW for wind power) or fossil fuel source (57 GW, net for coal; 29 GW net for natural gas).[2] According to the International Renewable Energy Agency, an additional 94 GW of PV was installed in 2017.[3]

In order to facilitate this rapid pace of change the PV industry has undergone an extraordinary expansion in recent years, with PV module production capacity estimated to be over 130 GW_p at the end of 2017, more than doubling in two years.[4] Crystalline silicon, with a current share of over 90% of the PV market, has been, and is forecast to remain, the dominant technology for the coming decades owing to its scalability; chemical, thermal, and temporal stability; and its demonstrated ability to consistently reduce costs through the experience curve.[4] It is widely recognised that the ongoing success of the PV industry, and so a more meaningful impact on energy generation globally, is predicated on the continuing increase in cell and module power conversion efficiency (PCE), coupled with an ongoing decline in production costs.[5]

Currently, however, over 70% of c-Si PV production capacity is vested in the fabrication of a low performance cell design in which the entire rear silicon surface is alloyed with aluminium to form the positive terminal of the device (see text box 1).[4] This cell structure, called the Al-BSF (aluminium back surface field), has a practical limit on its PCE of only ~20%, compared to the theoretical maximum efficiency of 29.4%.[4,6] An

additional ~20% of the current market, employing the more complex PERC (passivated emitter and rear solar cell) design, is similarly limited to efficiencies of around 23-24%.[4,7]

The most salient common feature of the Al-BSF and PERC cells is the direct application of the contacting metal onto the light-absorbing silicon wafer. Unfortunately, this intimate metal-silicon contact leads to recombination losses of the photo-excited electrons and holes due to a high density of electronically active states at the silicon-metal interface that lie within the silicon bandgap.[8] The use of high temperature functional-impurity doping beneath the metal terminals (the phosphorus and aluminium dopants at the electron and hole contacts of the Al-BSF and PERC cells; see text box 1) partially alleviates this effect, improving both the contact recombination and dramatically lowering the contact resistance. However, absorber doping induces its own fundamental optoelectronic energy losses, further constraining device performance.[9-12]

To mitigate these deleterious effects, so-called 'passivating contacts' are being developed, which reduce contact recombination losses via the insertion of passivating thin films (commonly silicon oxide, SiO_x; or hydrogenated amorphous silicon, a-Si:H) between the silicon wafer and the overlying metal terminals. In addition, some passivating contact technologies remove the dopants from the absorber material altogether, incorporating them into a contact structure that is external to the crystalline silicon wafer. Following this approach a spate of record efficiencies, the first to match or surpass the long-held 25% record set by a high efficiency PERC cell design,[13,14] were achieved in 2014/15 on devices fabricated on large area wafers: by SunPower (25%; now 25.2%),[15,16] Kaneka (25.1%),[17] and Panasonic (25.6%).[18] Sharp also exceeded the 25% efficiency mark in 2014 with a 25.1% cell measured through a 3.7 cm^2 aperture;[19] they have now achieved a similar result (25.09%) on a full area 6 inch wafer.[20] On the laboratory scale, research at

Fraunhofer ISE in 2015 yielded a small area device (4 cm^2) featuring a rear-side passivating contact with an efficiency of 25.1%,[21] now 25.7%,[22] and ISFH recently reported a 26.1% device.[23] Kaneka, after moving to an interdigitated back contact (IBC) cell architecture to maximise light coupling into the crystalline silicon absorber, reported a device with a confirmed efficiency of 26.7% – the current high watermark for crystalline silicon solar cells.[24,25]

Put into historical context, in the past four years crystalline silicon solar cell research has yielded an additional 1.7% absolute improvement in record device efficiency, compared to just 1.8% over the preceding *25 years* (see Figure 1).[13] Tellingly, all of the devices to surpass the 25% efficiency record have come from solar cells with passivating contacts. Indeed, the most successful devices have both their electron and hole contacts passivated. And while it is remarkable that these high performance devices have come from a variety of cell architectures (full-area, front and rear side contacted;[17,21,22] partial-area, all back contacted[15,16,18-20,23-25]), the common path to achieving high performance solar cells is clear: passivating the contact regions of the device.

This article reviews the various conceptual designs and material combinations used to fabricate passivating contacts on crystalline silicon, as well as solar cell architectures that incorporate passivating contacts. In doing so we will review the physics of contact formation and the historical progression that has led to this explosion in efficiency gains, and critically evaluate the manufacturing potential of these emerging technologies.

PART 1 - CONTACT FORMATION

In order for a solar cell to function there must be an internal physical mechanism that spatially separates photo-excited electrons and holes within the light-absorbing semiconductor, enabling their extraction at the device terminals.[26] This process of charge carrier selection implies

an asymmetric internal flow of charge carriers towards the solar cell's contact regions: *i.e.* a strong electron and weak hole current towards the electron contact, and *vice versa* for hole and electron currents towards the hole contact.[27] These internal currents are governed by both the conductivity, σ_e and σ_h, and the gradient in electrochemical potential, grad(η_e) and grad(η_h), for electrons and holes throughout the bulk material, leading toward the contact areas (Figure 2). Unfortunately, these parameters are difficult to extract experimentally and instead, in crystalline silicon devices, a pair of equilibrium parameters are typically used as proxies: the contact recombination factor J_{0c} to represent the flux of non-collected charge carriers (*e.g.* holes towards the electron contact), and the contact resistivity ρ_c to represent the interface resistance to collected charge carriers (*e.g.* resistive losses of electrons passing through the electron contact). It follows that an effective contact is one that minimises both recombination (J_{0c}) and resistive losses (ρ_c). The innovation of passivating contact technology is to apply materials within the contact structure that maintain a suitably low ρ_c while reducing J_{0c}, leading to a greater degree of charge carrier selectivity and so higher cell efficiencies.[28]

This asymmetry in conductivities at the solar cell's contacts can be achieved in a variety of ways. Conceptually the simplest method to achieve carrier selectivity is to apply metallic (or conductive layers, more generally) to the silicon wafer with asymmetrical work functions (ϕ) relative to the crystalline silicon conduction and valence band edges. In this way, the work function of the outer metal can manipulate the surface potential of the underlying silicon wafer, with electrons (holes) accumulating at the low (high) work function interface.[29,30] However, this facile modulation of the carrier concentrations (and so electron and hole conductivities) at the surface of the silicon wafer does not occur in practice, owing to the presence of both defect- and metal-induced gaps states (DIGS and MIGS, respectively), and their contribution to the phenomenon of Fermi level pinning (FLP; see text box 2), which

significantly hampers the influence of the outer metal work function.[8,31] For this reason, alternative methods for forming carrier-selective contacts to crystalline silicon have been adopted.

By far the most common method to achieve carrier selectivity is via the incorporation of a high concentration of dopant atoms directly into the silicon wafer, underneath the metal contact region – as in the Al-BSF and PERC cell designs. The process of heavily doping the absorber's sub-surface region at the contact (n^+ at the ETL, p^+ at the HTL) dramatically narrows the depletion width of the Schottky barrier that forms at the metal/silicon interface. When the doping concentration exceeds ~1×10^{17} cm^{-3} transport across the interfacial energy barrier becomes dominated by quantum-mechanical tunneling processes: first thermionic field emission, and then field emission when dopant density exceeds ~1×10^{19} cm^{-3}. In the case of thermionic-field emission, the barrier width narrows to the extent that only thermally excited carriers can tunnel through the Schottky barrier, unlike in field emission where free carriers in their ground state are able to pass through the contact. Another second order effect of heavy doping is image force lowering which reduces the barrier height with increasing dopant density, further lowering ρ_c. These tunneling-based carrier transport processes, which are dominant in all diffused junction solar cells, enable very low contact resistivities even in the presence of large Schottky barrier heights (Figures 5a and b).[32]

In addition to the much reduced contact resistance, the defect-assisted, or Shockley-Read-Hall (SRH), recombination rate at the silicon surface significantly reduces with the addition of dopants (see Figures 5c and d). At heavily doped contacts in thermal equilibrium a very low minority carrier concentration is established in the vicinity of the unpassivated surface defects due to the law of mass action ($np=n_i^2$). Under photo-excitation the vast asymmetry in the concentration of electrons and holes persists and the SRH recombination rate becomes

limited by the number of minority carriers reaching the surface, which can be additionally modulated by the depth of the doped region. However, increased doping leads to additional Auger recombination losses,[12] as well as band gap narrowing,[10,11] which increases the intrinsic, and so minority carrier density (n_i), and amplifies the recombination losses in the doped region (see Figure 5d). Therefore, the heavy doping approach to contact formation leads to an Auger-limited floor in J_{0c} at the metallized contact of > 200 fA.cm^{-2},[10,11,22,33] two orders of magnitude greater than state-of-the-art passivated, non-metallized surfaces (Figure 5c). In this way, heavy doping at the contacts contributes to an empirical limit in the V_{oc} of diffused junction based devices to around 700 mV, compared to ~750 mV achieved in some passivating contact cell designs. Since the contact resistivity of heavily doped contacts can be very low (less than 1 $\mu\Omega cm^2$ for controlled metallisation procedures like thermal evaporation), the strategy toward high efficiencies has long been to make the contact fraction (f_c) as small as possible, and to passivate the remaining un-metallised areas. An early example of this design approach is shown in the c-Si thermo-photovoltaic cell architecture of Swanson.[34] Further development of this design principle culminated in the first silicon cell to reach a PCE of 25% – a PERC cell – generally regarded as the optimum practically achievable performance of the heavily-doped homojunction architecture with both front and rear sides of the device contacted.[13,14]

PART 2 - PASSIVATING CONTACTS

Due to these inherent limitations of directly-metallised heavily-doped contacts, considerable effort has been devoted towards the alternative concept of passivating contacts. Rather than invoking the compromises implicit to heavy doping, passivating contacts directly address recombination losses and Fermi level pinning effects at the silicon surface. Of considerable importance is (i) the physical separation of the crystalline silicon absorber from overlying metallic layers which would otherwise induce energy states within the silicon bandgap (via MIGS) and (ii) the chemical passivation of crystalline silicon's surface dangling bonds

(DIGS), while at the same time allowing selective charge transport through the contact. Using this approach, de-pinning of Fermi level can, in theory, simultaneously reduce both the contact resistivity and contact recombination, compared to a directly metalized, Fermi level pinned surface. To demonstrate this effect, Figure 6 provides a simulation of the potential gains in ρ_c and J_{0c} at the electron contact of undoped silicon as a function of the metal contact work function with reduced pinning factors. In addition to the effect of the metal work function, a range of strategies have been proposed, and in some cases demonstrated, for achieving charge carrier selectivity within the passivating contact framework. These include the exploitation of asymmetries in band offsets, tunnelling probabilities and charge carrier mobilities at the contact interface, as well as the use of energy-selective defect bands.[26,29,30,35] These strategies all introduce some asymmetry in the conductivity to which the photo-excited electrons and holes at the contact interface are subjected.

Passivating contacts also have several practical advantages over conventional dopant-diffused contacting schemes. Compared to directly-metallised, heavily-doped contacts, passivating contacts are typically characterized by a very low contact recombination parameter J_{0c}. Hence they can be applied in simple full-area configurations, in contrast to heavily doped contacts which are ideally applied in small contact fractions, as described above.[28] This is shown in the simulation of Figure 7, which compares the optimum contact fraction and resultant idealized efficiency of directly metalized heavily doped contacts and passivating contacts. The ability to apply passivating contacts in a large area configuration not only simplifies device fabrication but also means that a higher ρ_c can be tolerated; values as high as ~100 mΩcm^2 can result in no significant PCE loss for full area contacts (Figure 7). Such architectures also simplify the current flows in the device to 1 dimension, eliminating lateral resistive losses,[21] and permitting the use of a broader range of dopant type and concentration in the silicon wafer itself. Finally, the high temperatures (750°C and above) required to make diffused-junction

devices, and the associated necessity for cleanliness throughout the fabrication process,[36] are relaxed when dealing with many passivating contact technologies, some of which can be deposited at or below 100°C.[37] In practice, however, finding passivating contact materials that achieve levels of charge carrier selectivity that exceed that of heavily doped contacts is not trivial and is an ongoing research challenge. This is particularly true given that such layers must not only be incorporated into the device without leading to optical losses or excessive fabrication complexity, but must also be stable, compatible with back-end processing and module integration, and ultimately be cost-competitive with conventional mass-produced solar cell manufacturing processes.

PART 2.1 – MIS passivating contacts

Early attempts at contact passivation on c-Si solar cells took the form of metal-insulator-semiconductor (MIS) contacts. During the 1970s and 80s a range of different structures were proposed for electron and hole contacts featuring different metals and passivating insulator layers.[30,38-43] A particularly striking example is that of the MISIM (metal-insulator-semiconductor-insulator-metal) cell proposed by Green[30] and later realised by Tarr *et al.*[39] This cell design mimics the simple contacting arrangement described above – using two metals with asymmetric work functions as electron and hole contacts – though with a thin silicon oxide interlayer to physically separate the metal from the silicon wafer and passivate surface defects. Such an arrangement can alleviate FLP, inducing favourable surface potentials at the cells' contacts. A lack of affordable, suitably high work function metals (for the HTL) with good adhesion properties limited the applicability of the MISIM cell structure and the simpler electron-collecting MIS cell received more attention.

The most successful of the MIS electron collectors was the combination of Al and a tunnelable (~15 Å) thermally grown SiO_2 layer used as the front contact in a p-type cell, commonly known as the MIS-IL

(MIS-Inversion Layer) cell.[44] The benefits of the MIS approach were demonstrated through improvements in V_{oc}, as highlighted by Godfrey and Green in 1979, who reported a V_{oc} of 655 mV, 20 mV higher than any previously reported c-Si device.[41] These MIS cells relied on a silicon monoxide anti-reflection coating (ARC), deposited in the non-contacted areas, with a positive fixed charge density to form an electron inversion layer at the surface. In this way, the fixed charge density in the non-contacted areas performs a similar role to that of the metal work function in the contacted areas. The effect of the fixed charge density was later enhanced by Hezel *et al*.[45] with the application of PECVD silicon nitride SiN_x, and later Cs^+ ion incorporation, to increase the magnitude of positive charge, aiding in the formation of the induced inversion layer.[46,47] After reaching a peak efficiency of 19.6% in 2001,[48] further development of this architecture was slowed as other contact approaches garnered more research attention. One such example is the 'metal-insulator n-p' (MINP) cell concept. MINP cells utilized a hybrid front contact, with an MIS contact formed on top of a lightly dopant-diffused surface, providing benefits in terms of lateral resistance and recombination.[49,50] Using a Ti / SiO_x /c-Si(n^+) front MIS electron contact, this cell structure held the world record for a short time in the 1980's becoming the first silicon device with an efficiency over 18%.[51] Since then, the use of MIS contacts on lightly diffused surfaces has been explored with different metals and insulators being featured in both n and p-type cells with efficiencies above 21%.[52-54]

PART 2.2 – The external doping approach

A parallel stream of research initiated in the 1980s involved the development of passivating contacts with polycrystalline silicon (poly-Si),[55,56] and semi-insulating polycrystalline silicon (SIPOS) based material systems.[57,58] These inherited strongly from earlier research into microelectronic devices,[59] and were typically composed of a thin SiO_x layer sandwiched between the heavily-doped silicon-based outer layer and the c-Si wafer. In this conceptual arrangement, the work function of the outer silicon layer, manipulated by the dopant density and type, performs a

similar role to the metal in the MIS cells described above. The doped layer also provides a vertical conductive pathway for the collected carrier toward the metal, and since the dopant atoms are, *in principle*, outside of the absorber, the deleterious effects of bandgap narrowing and Auger recombination within the silicon wafer are effectively eliminated, allowing for very high open circuit voltages. Indeed, in the mid-1980s doped poly-Si and SIPOS contacts with thin chemically and thermally grown interfacial SiO_x layers were found to provide excellent contact recombination and contact resistivity on crystalline silicon,[60] suitable for solar cell contacts to the extent that SIPOS based contacts were the first to demonstrate a V_{oc} above 700mV – a significant milestone at the time.[58]

Recent years have seen a revival in interest of poly-Si contacts for crystalline silicon solar cells. The current state-of-the-art polysilicon contacts can be deposited via a range of different deposition and doping techniques, exhibiting $J_{0c} < 5$ fA.cm^2 and $\rho_c < 2$ mΩcm^2 for both n-type and p-type contacts.[61,62] At the cell level, a 25.7% hybrid device using a full-area n^+ poly-Si rear contact and a boron diffused front hole contact,[22] and a 26.1% n^+/p^+ poly-Si contacted IBC device[23] have both been demonstrated since December 2017. It should be noted that due to the high temperature steps (>700°C) required for both SIPOS and poly-Si based contacts, the potential formation of pinholes in, and dopant diffusion through, the thin SiO_x layer can be important factors in determining the performance of poly-silicon based contacts.[63] It has been demonstrated, for example, that oxide thickness, preparation method and thermal budget all play a critical role in determining the contact properties: thin, less dense oxides and high thermal budgets lead to oxide breakup and excessive dopant in-diffusion, compromising J_{0c} through a reduction in surface passivation and high Auger component, but lowering ρ_c; thicker, dense oxides and lower thermal budgets can promote better surface passivation (a lower J_{0c}) but poor contact resistance (higher ρ_c).[64,65] Regardless of the structural integrity of the oxide, the diffusion of dopants through the SiO_x layer and into the silicon wafer surface is a likely a key

feature of the doped poly-Si contacts. This could potentially be exploited to facilitate lateral current transport within the silicon wafer between the outer metal fingers.

The early 1990s saw the development of a low temperature ($\leq$ 200°C) alternative passivating heterocontact utilizing a stack of intrinsic and doped hydrogenated amorphous silicon (a-Si:H) layers, now known as the silicon heterojunction (SHJ) contact. This structure was inherited from earlier research on a-Si:H/poly-Si tandem cells,[66] and the known surface passivation of crystalline silicon by thin films of a-Si:H.[67] Work on SHJ cells was pioneered by Sanyo (later acquired by Panasonic) and trademarked as the 'Heterojunction with Intrinsic Thin-Layer' or HIT cell.[68] Optimization of the SHJ structure over the following decade resulted in an efficiency increase from 14.5% to above 20% in the year 2000,[69] marking its competitiveness with conventional dopant diffused homojunction technologies. Conceptually, SHJ contacts operate in a similar way to the polysilicon contacts described above: a passivating interlayer (intrinsic a-Si:H) alleviates the Fermi-level pinning effect, allowing the outer doped layer (boron or phosphorus doped a-Si:H) to manipulate the silicon surface potential while providing a selective conductive pathway for the collected carrier. Physically, the major difference between the SHJ and polysilicon contacts is in the charge transport at the contact interface. For SHJ contacts, direct tunnelling from the silicon into the doped a-Si:H layer is not a possible transport mechanism owing to the relative thickness of the intrinsic a-Si:H layer, and so bulk current transport through the contact structure and thermal transport over energy barriers at the contact interface, dominate ρ_c.[70,71] In addition, unlike in the polysilicon contacts where a dopant tail is often present underneath the c-Si surface, the dopants in the SHJ contact structure are strictly confined to the outer a-Si layers, placing more stringent requirements on the surface passivation provided by the intrinsic a-Si:H. The induced surface potential in the c-Si wafer therefore plays a more prominent role in the SHJ structure. For this reason, it has been noted that the low doping efficiency of boron in a-Si:H

can lead to fill factor issues attributed to injection-dependent recombination at the hole contact.[72]

The most commonly ascribed shortcoming of the SHJ approach in terms of its ultimate performance is the parasitic absorption occurring in the doped a-Si:H layers and transparent conductive oxide (TCO; typically ITO) that provide lateral charge transport.[73] For this reason, recent efficiency improvements have come from exploring the more complex IBC design, which places both contacts on the rear side of the cell, removing both the ITO and doped a-Si:H from the sun-facing side of the device. In 2014, Panasonic claimed the world record with an SHJ IBC cell at 25.6%,[18] a record which has since been improved on by Kanaka, also with an SHJ IBC cell at 26.7% in 2017.[24,25] Other strategies to reduce parasitic absorption without adopting the complex IBC design have focused on thinning the a-Si:H films,[74] diluting them with carbon and oxygen,[75,76] or crystallising the a-Si:H layers to micro- or nano-crystalline silicon,[70,77] as well as investigating alternatives to ITO.[78]

PART 2.3 – Towards dopant-free passivating contacts

A final passivating contact approach, which has gained momentum in recent years, is the integration of dopant-free passivating contacts. The term 'dopant-free' used here refers to the avoidance of doped silicon layers/regions, despite the fact that many of the dopant-free materials are doped either extrinsically or with native defects. These dopant-free materials include metal compounds and oxides, low dimensional semiconductors and organic polymers, such as those depicted in Figure 8. Driving the rapid growth of this research area is the potential to overcome several performance limitations of existing passivating contacts. For example, the use of heterocontacts that are not based on silicon opens a diverse materials space with a wider range of work functions outside of the confines of the silicon band edges, as well as more suitable optical characteristics for the front and rear sides of the device – wider bandgaps,

reduced free carrier absorption (FCA), and a range of refractive indices. In addition, such materials can generally be deposited using simple, low temperature, physical deposition or even solution-based processing techniques – introducing potential reductions in fabrication costs over doped poly- or amorphous silicon contacts.

The largest sub-group of these materials are the metal oxides. For the collection of electrons, a number of n-type metal oxides with favourable theoretical band alignments, and in some cases silicon surface passivation, are being explored, for example, TiO_x,[79,80] $NbOx$,[81] TaO_x,[82] GaO_x,[83,84] ZnO_x,[85] CsO_x,[86] some of which were previously identified during early semiconductor-insulator-semiconductor (SIS) research beginning in the 1970s.[87-89] Of particular promise is TiO_x, already demonstrating electron-selectivity on crystalline silicon both with and without additional passivating interlayers.[29,37,79,80,90] At the cell level, TiO_x based electron contacts have been integrated as full-area and partial-area rear contacts (PRC) with corresponding efficiencies of 22.1%[91] and 21.8%,[80] respectively. As for the hole contacts, while some attention has been paid to the p-type metal oxides in this application, for example, CuO_x,[92] most research in recent years has focused on the high work function n-type transition metal oxides MoO_x,[29,93-95] WO_x,[95,96] and VO_x,[97] also identified as useful for crystalline silicon solar cells in the past.[87] These films, which can exhibit work functions above 6.5 eV in the ideal case,[98] have been trialled as contact materials to crystalline silicon both with and without passivating interlayers. Molybdenum oxide in particular has recently been integrated into PRC and full-area contact cells attaining efficiencies of 20.6% and 22.5%.[99,100]

In addition to metal oxides, a range of other metal compounds have been explored as contact materials for crystalline silicon solar cells, including sulphides,[101] nitrides,[102] phosphides,[103,104] iodides,[105,106] carbonates,[107] and fluorides.[29,108,109] Of note among these are the alkali and

alkaline earth metal fluorides utilized in electron extraction, including LiF, KF, CsF, and MgF_2. When these layers are integrated under a metal electrode, most commonly Al, work function values as low as ~2.5 eV can be obtained, promoting the collection of electrons from the adjacent crystalline silicon surface. The applicability of this technique to silicon solar cells has recently been demonstrated, in some cases with a-Si:H passivating interlayers. In particular, LiF has recently been integrated as an electron contact into full-area and PRC cells with efficiencies above 20%.[29,108]

Two less developed subcategories of passivating contacts for crystalline silicon solar cells are those formed by low dimensional materials and organic films based on both polymers and small molecules. Devices featuring low-dimensional carbon based contacts, namely graphene[110] and carbon nanotubes,[111] as well as the inorganic transition metal dichalcogenides (TMDC), such as MoS_2,[112] and have been demonstrated to some degree. However, the highest efficiencies demonstrated using these materials so far are 15%, with most falling below 10%, owing largely to a lack of surface passivation. The formation of organic/crystalline silicon contacts, most commonly for the collection of holes, has been achieved using a variety of organic HTLs including 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC),[113] poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) (PEDOT:PSS),[37,114,115] and 2,2′,7,7 - Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9′-spirobifluorene (Spiro-OMeTAD).[116] PEDOT:PSS remains the most promising candidate, with demonstrated efficiencies over 20% when implemented as the hole contact in p-type crystalline silicon cells, and slightly lower for n-type.[115] Another interesting, yet nascent approach, is the use of small organic molecules or self-assembled monolayers (SAMs) with strong interface or molecular dipole moments to counter the effect of FLP. Prominent examples in the organic electronics literature include polyethylenimine ethoxylated (PEIE) and branched polyethylenimine (PEI) to reduce the work function of electron extracting and injecting layers in OPV and

OLEDs, replacing low work function materials like Ca or LiF/Al.[117] On silicon, materials like poly (ethylene oxide) (PEO)[118] and 8-hydroxyquinolinolato-lithium (Liq)[119] have been shown to reduce barrier heights and facilitate improvements in electron collection. More recently, monolayers of polar amino acids have also been shown to facilitate electron collection following direct Al metallisation on silicon, with an efficiency of 17.5% having been demonstrated.[120] Generally, in all of these applications poor surface passivation compromises device efficiencies thus far. The application of these materials to surfaces passivated with tunnel oxides or amorphous silicon – mimicking the approach in MIS, polysilicon and SHJ contacts – could be a promising route to improving device performance.

Other means of manipulating the Schottky barrier height, like approaches taken in silicon microelectronics research where device scaling imposes strict contact resistance requirements, also remain largely unexplored in silicon PV applications. The use of high k dielectric bi-layers to generate interfacial dipoles that assist in charge collection, for example, could also offer promising means to counter the effects of FLP at the crystalline silicon or amorphous silicon surface.[121]

PART 3 – CONCLUSION AND OUTLOOK

While the incorporation of passivating contacts has enabled considerable gains in record efficiencies in recent years, most of the passivating contact cell designs described above rely on processing schemes that considerably differ from the current industrial mainstream silicon PV technology. This can be a significant roadblock towards rapid, large-scale industrial adoption. In this context, what is needed in the immediate future is a low-threshold upgrade of industrial silicon PV manufacturing that only marginally affects existing production facilities, in order to minimise the cost-of-ownership, learning, and retooling related risks. The most straightforward way to do so is by following the same philosophy

that underlies the current shift from Al-BSF to PERC cells: address the recombination losses at the hole-collecting rear contacts in industrial silicon solar cells. For this, a simple hole-collecting passivating contact that can withstand the firing of screen-printed metal contacts, as applied in industry, is currently sought after. To this end, p-type polysilicon or silicon-rich silicon carbide are promising material candidates, though issues related to the compatibility with conventional high temperature Ag screen print metallisation still remain.

From a longer perspective, a shift in the cell production from p-type to n-type wafers is predicted, due to the higher defect tolerance of phosphorus-doped silicon to oxygen and common metallic impurities.[4] This transition is likely to prompt greater adoption of passivating contact technologies both due to the departure from conventional p-type silicon solar cell processing procedures, especially the Al alloying process, and the increased benefit of passivating contacts on high lifetime n-type wafers.

Further, passivating contact technologies naturally provide greater flexibility in cell architecture. Full-area passivating contacts can easily be formed into bifacial designs where light is collected from both sides of the absorber, improving the energy yield and thus potentially lowering the levelised cost of energy for a given installation. The lower surface recombination also allows greater flexibility in the junction position. For example, an n-type rear junction cell with a front electron passivating contact can utilize a more resistive, but more transparent, TCO on the front surface since the wafer can act as a lateral conductive channel for majority carriers (in this case electrons). The parasitic absorption can be further lowered by introducing wide bandgap metal oxides to replace the doped silicon ETLs. So far, no suitable fully transparent electron contacts have been reported, however.

Alternatively, placing both passivating contacts at the rear-side of the device in an IBC configuration, is arguably the ultimate cell design for high performance silicon photovoltaics. However, to become an industrial reality, process and patterning simplification are of critical importance. Since passivating contact materials are typically fabricated by chemical or physical vapour deposition, or via solution processing, interesting new routes can be found to this end, enabling bottom-up concepts such as the tunnel-junction IBC cell.[122] Fully-passivating contact silicon technology is also anticipated to be the most attractive choice for the high insolation, hot-climate market, as such cells feature the lowest temperature coefficient and so can result in higher energy yields.[123]

Finally, to overcome the fast approaching 29.4% single-junction theoretical PCE limit of crystalline silicon PV, we anticipate that passivating contact silicon cells will be the key driver as a bottom cell technology in a tandem cell configuration. This is thanks to the fact that such cells feature the highest operating voltages, even under reduced illumination conditions, such as in tandems; the passivating contacts can be tailored to provide excellent internal light reflection;[124,125] the top cell filters out the short wavelength light, relaxing constraints on the bottom cell's blue response; and the top contacts can easily be adapted into tunnel junctions, which are needed for monolithic 2-terminal tandem integration. This point has been already demonstrated using expensive III-V top cells, both for 4 terminal[126] and monolithic 2-terminal tandem cells.[127] For true industrial adoption, it is likely that a cheaper top cell technology is needed. For this, perovskite solar cells, having excellent tuneable optoelectronic properties, are attractive candidates, with the first monolithic silicon-perovskite tandems already demonstrated using silicon bottom cells with passivating contacts.[128,129]

Through the increasing trend towards passivating contacts, crystalline silicon photovoltaics joins a larger group of optoelectronic devices which

separate carriers via contact interfaces rather than with absorber doping. Many existing technologies, such as organic solar cells and light emitting diodes, which cannot easily implement impurity doping approaches, have already developed a suite of charge carrier selective contacts. Interestingly, highly efficient perovskite solar cells also increasingly feature passivating contacts, which prove to be effective in not only increasing the operating voltages, but also quenching the hysteresis effects in the current-voltage response.[130] Crystalline silicon stands to inherit knowledge form these fields, assisting to expedite the rapid uptake within mainstream photovoltaics. In addition, the materials and accumulated knowledge relating to surface and contact passivation in silicon can be of potential benefit to other material systems, as already demonstrated in CdTe[131] and CIGS devices.[132]

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