PERSPECTIVE

Interfacial fixed charges and dipoles to boost carrier selectivity for crystalline silicon solar cells

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With the rapid evolution of passivating contact, the carrier transport layer in crystalline silicon (*c*-Si) solar cells has expanded beyond the doped silicon films to non-silicon films with lower parasitic absorption and manufacturing cost. However, using the emerging carrier transport layers in direct contact with *c*-Si suffers from the insufficient carrier selectivity, which limits the efficiency of the device. Thus, to make such new strategies practical, it becomes particularly important to enhance the passivation quality and thus minimize the recombination losses at *c*-Si surfaces. By introducing interfacial fixed charges (Q_f) or dipoles on the *c*-Si surface, the local electric field can be tuned to affect the recombination and charge carrier transport dynamics. This perspective highlights the significance of interfacial Q_f and dipoles for carrier selectivity, and points out the challenges in a comprehensive understanding of the mechanism and precisely controlling the carrier behavior as well as the solar cell stability.

The critical aspect of crystalline silicon (*c*-Si) solar cells is the efficient separation and extraction of photo-generated electrons and holes at their respective electrical contacts.[1] In the era of *c*-Si homojunction solar cells, heavy doping and direct metal/semiconductor contact are employed to form the specific carrier transport channel. However, suffering from surface and Auger recombination, free carrier absorption, and band gap narrowing, *c*-Si homojunction solar cells have notable optoelectronic losses. In order to reduce the losses, a technique called passivating contact (also known as carrier selective contact or CSC) has been used, and the schematic diagram of passivating contact *c*-Si solar cells is shown in Figure 1A. This involves replacing the highly doped *c*-Si with other materials and avoiding direct contact between *c*-Si and metal. The goal of this technique is to passivate the *c*-Si surface while still allowing for the transport of carriers with the expected polarity. The passivating contact is commonly constructed by the passivation layer and carrier transport layer, and the process of charge-carrier selectivity indicates an internal flow of charge carriers towards the contact regions of solar cells. This flow is of an asymmetrical nature, where a strong electron and weak hole current move towards the electron contact. Similarly, vice versa for hole and electron currents towards the hole contact. The passivation and carrier transport layers in silicon heterojunction (SHJ) solar cells are intrinsic and doped hydrogenated amorphous silicon (*a*-Si:H) films, while that in tunnel oxide passivated contact (TOPCon) configuration is ultra-thin oxide and doped polycrystalline silicon (poly-Si) films. Benefiting from the significant carrier selectivity of the contact, SHJ and TOPCon solar cells have continuously broken world records for the efficiency of *c*-Si solar cells in recent years, and a new world record of 27.09% was achieved by LONGi with heterojunction back-contact architecture. However, the doped Si layers in SHJ and TOPCon solar cells remain certain parasitic absorption due to their relatively narrow bandgap. Besides, *a*-Si:H films in SHJ solar cells lack satisfactory thermal stability and need capital-intensive equipment, while a high temperature is required during TOPCon solar cell manufacturing to realize the desired doping level in poly-Si and high passivation quality.

As an innovative approach to address these challenges, the dopant-free

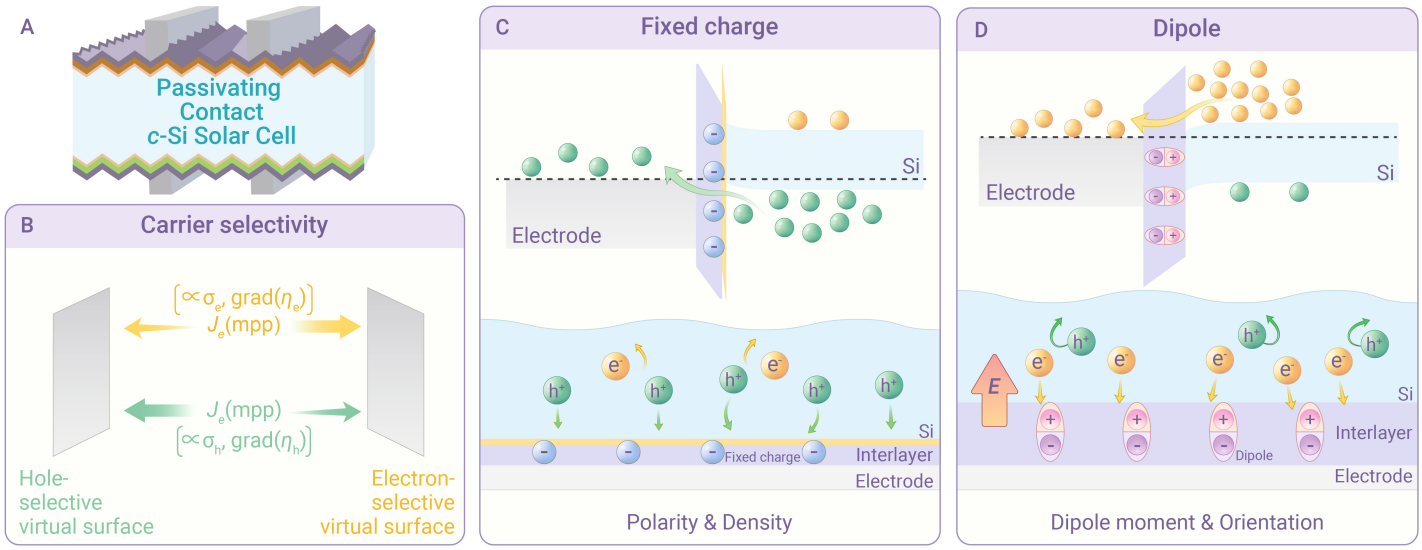

Figure 1. Carrier selective contacts in *c*-Si solar cells (A) Schematic of the passivating contact *c*-Si solar cells. (B) Carrier selectivity of electron- and hole-selective contacts. (C and D) Energy band alignments and schematic structures of passivating contacts with interfacial fixed charges and dipoles.

passivating contact (DFPC) has been proposed and rapidly developed.[1] By replacing the doped-Si layers, that are used in SHJ and TOPCon solar cells, with wide-bandgap semiconductors, the parasitic absorption loss can be reduced. Moreover, the cost-effective deposition techniques and low-temperature route exhibit great production potential, even for flexible photovoltaics.[2] Along the decade of progress, the efficiency of *c*-Si solar cells featuring dopant-free electron or hole selective passivating contacts has been continuously improved, and the state-of-the-art efficiency of 23.83% is achieved from MoO_x-based *c*-Si solar cells.[3] However, the efficiency of DFPC *c*-Si solar cells still lags behind that of SHJ and TOPCon solar cells. Indeed,

carrier selectivity (Figure 1B) is determined by both surface recombination and contact resistivity, while DFPC is more tolerant of contact resistivity (in particular when it is less than 100 mΩ·cm^2, carrier selectivity depends on surface recombination). Thus, surface passivation quality becomes a key factor in carrier selectivity, given that DFPCs generally exhibit sufficient low contact resistivity. Improving the passivation performance of DFPC *c*-Si solar cells is still a challenge, and one of the reasons for this is that the well-developed passivation strategies used in industrial technology are not directly applicable to DFPC solar cells. For instance, although the intrinsic *a*-Si:H in SHJ shows significant passivation, it still cannot avoid parasitic absorption and high equipment investment. Besides, the high-quality passivation of SiO_2 in TOPCon requires assistance in forming gas annealing and SiN_x as the reservoir for hydrogen, which is not suitable for most DFPC solar cells.

In order to reduce carrier recombination at the *c*-Si surface, it is possible to introduce a specific electric field orientation at its surface. This technique, known as field-effect passivation, can increase the concentration of one type of carrier while decreasing the concentration of the other one. To achieve the desired upward or downward band bending on the silicon surface, an interfacial fixed charge (Q_f) or dipole with a specific orientation in the passivation layer can be formed. Recent studies have demonstrated the feasibility and potential of this strategy in DFPC *c*-Si solar cells as well as thin-film solar cells.[4]

Some passivation materials have positive or negative Q_f that affect the charge carrier transport dynamics. To illustrate, when a passivation material that possesses negative Q_f, such as $A1_2O_3$, contacts with *c*-Si, it will induce an upward band bending of the Si surface, repelling electrons and reducing carrier recombination (Figure 1C). Li et al.[5] demonstrated ultrathin Al_2O_3 acted as a tunnel passivation layer in hole-selective contacts and took advantage of its negative Q_f to improve the field-effect passivation. Moreover, hydrogenation strategies were implemented in the Al_2O_3 process to promote electron transfer from *c*-Si to Al_2O_3, giving rise to more negative Q_f that further ameliorates the hole selectivity. In addition, the negative Q_f is also found in HfO_2 films determined by positive corona charging and surface photovoltage measurements. Murphy's team conducted extensive research on the electronic properties and negative Q_f of HfO_2, optimizing post-annealing conditions to obtain the best passivation quality on Si wafers.[6] On the contrary, some researchers believed that the as-deposited HfO_2 film consists of positive Q_f, which was confirmed by capacitance-voltage and conductance-voltage measurements. Constant voltage stress reveals whether the Q_f polarity changes depends on the post-annealing ambient, which will change in the nitrogen ambient but not in the hydrogen ambient.[7] Therefore, one can adjust post-annealing conditions to form positive/negative Q_f in the HfO_2 passivation layer, thus improving the corresponding electron/hole selectivity of DFPC *c*-Si solar cells.

Similarly, at the contact interface, dipoles can also be induced to fulfil suitable energy level matching and reduce the energy barrier for carrier transport. Researchers have proved that some wide-bandgap inorganic compounds and polymers can form and orientate dipoles to provide adequate surface passivation and high carrier selectivity simultaneously (Figure 1D). A common example in DFPC *c*-Si solar cells is the use of LiF/Al as an electrode for electron-selective contacts. Besides the two explanations for enhanced performance: (i) forming Al/Li alloys with low work function and (ii) protecting Si surface from evaporated Al damage, a reasonable one is that oriented dipoles with a large dipole moment are spontaneously formed in LiF and result in a vacuum level offset between Si and Al, thus sweeping electrons to Al and lowering contact resistivity.[8] For organic polymers, polyethylenimine (PEI) was used as a valid electron-selective layer for *c*-Si solar cells because the interfacial dipoles point outward the Si surface, indicating a hole-blocking property and a small barrier for electrons.[9] Through a sole interlayer PEI, efficient electron selectivity was successfully achieved by high-quality field-effect passivation. Kang et al.[10] prepared a self-assembled copolymer, poly (vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), as the passivation layer in DFPC *c*-Si solar cells and realized the high efficiency and stability of the devices. They proposed that different polarities or magnitudes of the corona polling voltage applied to P(VDF-TrFE) can adjust the orientation of dipoles at the interface, so that P(VDF-TrFE) can be modified for higher carrier selectivity, even act as an ambipolar passivation layer.

As a promising strategy, the application of interfacial Q_f and dipoles to DFPC *c*-Si solar cells can potentially enhance the chemical and field-effect passivation of the Si surface simultaneously, thus improving solar cell efficiency. These materials not only act as a barrier layer between Si and carrier transport layer or electrode to inhibit the interface reaction and reduce interfacial trap states, but also provide Q_f and dipoles to alter the band bending and carrier distribution on the Si surface, reducing the carrier transport barrier and further boosting the carrier selectivity. Nevertheless, challenges remain in a comprehensive understanding of the mechanism and precisely controlling the carrier behavior. For instance, the physical portrait of the selectivity improvement by LiF, MgF_2 and other similar materials has not been clearly described. Besides, for dipoles, the influence of the external electric field cannot be ignored, because it may change the dipole orientation in solar cell operation, which leads to the attenuation of surface passivation and carrier selectivity. However, device stability testing is rarely mentioned in the above literature, which may require further research and corresponding strategies. Fortunately, advances in material science and characterization techniques have allowed researchers to delve deeper into the intricacies of Q_f and dipoles, leading to improved DFPC designs. The strategy and theory demonstrated in this perspective can be used as a general way to achieve high carrier selectivity not only for *c*-Si-based device platforms but also for organic, perovskite, and tandem photovoltaics. As researchers continue to refine the understanding of interfacial Q_f and dipoles and develop advanced materials, the future holds promising prospects for achieving higher-performance solar cells.

REFERENCES

1. Allen, T. G., Bullock, J., Yang, X., et al. (2019). Passivating contacts for crystalline silicon solar cells. Nat Energy **4**: 914–928. DOI: 10.1038/s41560-019-0463-6.
2. Liu, W., Liu, Y., Yang, Z., et al. (2023). Flexible solar cells based on foldable silicon wafers with blunted edges. Nature **617**: 717–723. DOI: 10.1038/s41586-023-05921-z.
3. Cao, L., Procel, P., Alcañiz, A., et al. (2022). Achieving 23.83% conversion efficiency in silicon heterojunction solar cell with ultra-thin MoO_x hole collector layer via tailoring (i)a-Si:H/MoO_x interface. Prog Photovolt Res Appl **31**: 1245-1254. DOI: 10.1002/pip.3638.
4. Li, M., Xie, Y., Lin, F. R., et al. (2023). Self-assembled monolayers as emerging hole-selective layers enable high-performance thin-film solar cells. The Innovation **4**: 100369. DOI: 10.1016/j.xinn.2022.100369.
5. Li, L., Ying, L., Lin, Y., et al. (2022). Effective hydrogenation strategies to boost efficiency over 20% for crystalline silicon solar cell with Al_2O_3/Cu_2O passivating contact. Adv Funct Mater **32**: 2207158. DOI: 10.1002/adfm.202207158.
6. Wratten, A., Pain, S. L., Walker, D., et al. (2023). Mechanisms of silicon surface passivation by negatively charged hafnium oxide thin films. IEEE J Photovolt **13**: 40–47. DOI: 10.1109/jphotov.2022.3227624.
7. Tomer, S., Devi, M., Kumar, A., et al. (2020). Silicon surface passivation by atomic layer deposited hafnium oxide films: trap states investigation using constant voltage stress studies. IEEE J Photovolt **10**: 1614–1623. DOI: 10.1109/jphotov.2020.3022686.
8. Zhang, Y., Liu, R., Lee, S.-T., et al. (2014). The role of a LiF layer on the performance of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)/Si organic-inorganic hybrid solar cells. Appl Phys Lett **104**: 083514. DOI: 10.1063/1.4866968.
9. Yang, X., Ying, Z., Yang, Z., et al. (2021). Light-promoted electrostatic adsorption of high-density lewis base monolayers as passivating electron-selective contacts. Adv Sci **8**: 2003245. DOI: 10.1002/advs.202003245.
10. Kang, S. B., Park, W. J., Jeong, M. H., et al. (2020). Ambipolar passivated back surface field layer for silicon photovoltaics. Adv Funct Mater **30**: 2004943. DOI: 10.1002/adfm.202004943.

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DECLARATION OF INTERESTS

The authors declare no competing interests.