PEROVSKITES

Unlocking Interfaces in Photovoltaics

Eliminating defects at interfaces enables perovskites to approach efficiency limits.

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Demand for energy in the context of climate change are driving rapid deployment of low-cost renewable energy and are accelerating efforts to deliver advanced photovoltaic (PV) technologies. In the past decade, the steeply rising solar-to-electrical power conversion efficiency of metal-halide perovskite solar cells (PSCs) make them a compelling candidate for next-generation PV, with interesting applications envisaged beyond traditional solar plants. These include building integrated PV, flexible solar-powered electronics, solar vehicles, and aircrafts. Metal-halide perovskites benefit from the low formation energy for crystallization, a consequence of their ionic nature, which enables close to ambient-temperature solution or vapor-phase deposition and a thin-film crystallization process. However, the ease by which rapid crystallization occur also introduces defects and local heterogeneities throughout the perovskite films, and at internal interfaces (*1*).

PSCs can deliver higher efficiencies with fewer fundamental losses than other polycrystalline PV technologies without the need for high-temperature crystallization or dedicated defect control. This phenomenon, often described as 'defect tolerance', is ascribed to the specific electronic structure and defect chemistry, where the predominant crystal defects have energy levels close to the conduction and valence bands and thus minimizing the negative effect on charge transport (*2*). However, despite the relatively benign nature of these defects, their presence has been correlated with long-term degradation, such as acting as mediation sites for ion migration that can initiate material decomposition. In order to reach efficiencies approaching thermodynamic limits, most of the defects in the bulk, grain boundaries, surfaces and interfaces need to be eliminated or well passivated.

A PSC is constructed with a solid perovskite thin-film, sandwiched between electron- and hole-selective charge transport layers (ETLs, HTLs or CTLs) and metallic contacts beneath and on-top of the CTLs, assembled in a layer-by-layer process (see the figure). The surfaces of the perovskite film, and the heterojunctions formed with the CTLs are the most detrimental regions for losses, which reduce the chemical potential of photogenerated carriers and in turn limit the achievable open-circuit voltage and efficiency. Because the surface represents the discontinuity of bulk perovskite, the unterminated bonds and vacancies become the main defect reservoir for charge trapping and non-radiative recombination. Over the last ten years there have been numerous attempts to realize single-crystal PSCs, with the perception that eliminating the polycrystalline grain boundaries and hence defects at the grain boundaries will lead to improved performance and stability (*3*). However, even without appropriate passivation, internal recombination losses in polycrystalline perovskite films are usually less important than charge trapping and recombination at the surfaces and heterojunctions. With surface passivation, recombination can just about be eliminated in polycrystalline thin films (*4*). Specifically, the most stable and efficient p-i-n PSCs use fullerene and its derivatives as the ETL. Recombination at this perovskite/fullerene interface dominates the bulk recombination by 1 to 3 orders of magnitude. The possible origin of the fullerene-induced interfacial recombination could be either the existence of charge transfer states or low-lying states due to the density of state broadening. Conclusively understanding the recombination loss mechanism still requires more exploration.

In addition to the top surfaces, the "buried heterojunction" is equally important while much less accessible. A key property of the buried interface is that the perovskite film is grown and crystalized upon the underlying layers. The underlying surface influences many properties, such as nucleation, crystal growth, and even the electrical "doping", or Fermi level, of the perovskite film (*5*). Therefore, comprehensively understanding the formation dynamics of the buried interface is important to effectively eliminate or passivate the buried defects. For solution-processed perovskites, poor wettability and less-controllable crystallization processes are speculated to relate to the local accumulation of small crystallites or amorphous species and lead to the generation of charge-traps at the interface (*6*). In addition, detrimental "voids" can form because of the delayed escape of low-volatility solvents entrapped at the buried regions, which jeopardize the film mechanical reliability (*7*). Macroscopic defects, such as delamination of the perovskite film from the underlying substrate, can be generated during the crystallization due to the inherent soft but brittle nature and high thermal expansion coefficients of perovskites that inevitably induce strain (*8*).

Perovskites as solar absorber layers are generally formed from a three-dimensional (3D) lattice structure with an "ABX_3" stoichiometry (A, B, and X denote monovalent cation, divalent cation, and anion, respectively). Furthermore, a whole range of "layered" or "two-dimensional (2D)" perovskites exist, incorporating larger A-site cations, which have wider band gaps than their 3D counterparts, but can have similar lattice constants in at least two of the three crystal planes. Forming 2D capping layers atop the bulk perovskite, and hence a 3D/2D heterojunction with lattice matching, is one successful passivation strategy for perovskites, and thin-film PV materials more generally (*9*). Insertion of an interlayer, such as few nm-thick LiF_2 or MgF_2, is another powerful method, which tends to reduce interfacial recombination, presumably due to the physical separation of perovskite and ETL. At the buried interface in p-i-n PSCs, substantial reduction in recombination losses has been enabled via the use of self-assembled monolayers (SAMs) (*10*). How or why they work so well is still not clear, but in some instances the losses at the buried interface can be almost eliminated. Non-charge transporting SAMs can also play a role at the buried interface. With the aid of one anchoring group and one functional group, SAMs can easily adhere to and be designed to modulate the subsequently grown perovskite surfaces (*8*).

Advances in characterization methods have expanded understanding and enabled more insightful analysis. Multimodal microscopy reveals crystal orientation variations and correlates the sub-grain misorientation with local strain, pointing out the structural sources of nonradiative recombination (*11*). Depth-resolved spectroscopic measurements as well as in-situ and operando techniques emerge as critically important assessment tools for buried interfaces and their impact on device operation. The emerging "lift-off" techniques,

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where the perovskite layers are peeled off the substrate, allows the buried interfaces to be exposed, enabling direct microscopic mapping and surface-sensitive probing of the underlying surface (*12*). Notably, similar lift-off methodologies have proven effective and useful in other thin-film PV materials, such as CdTe, and insights gained from different materials should lead to more rapid advances in characterization methodologies (*13*).

With the substantial progress on interfaces, a growing consensus is forming about the requirements for an ideal perovskite interface: (i) the elimination or repair of surface/interface defects; (ii) the design of a rational energy landscape to satisfy selective carrier collection; (iii) the minimization of strain/stress; and (iv) the improvement of physical robustness and adhesion.

Numerous passivation strategies aim to reduce the interfacial defect densities, while the detailed atomistic nature of defects and the electronic influence of differing defect types at the interface remains uncertain. What is easy to overlook is that the "passivators" employed are also foreign species, which may induce complex electronic states at the interfaces.

The fabrication of 2D/3D perovskite heterojunctions need to form a rational energy landscape at the interface for smooth charge transportation of one carrier type and reflection of the other. Most of the large-organic-spacer-involved 2D perovskites present more of a p-type nature than the 3D counterparts. This makes inserting this layer most favorable at the interface of perovskite/p-type CTL, specifically on top of the perovskite layer for n-i-p cells and buried underneath the perovskite for p-i-n cells. If the distribution of multiple quantum wells in 2D or quasi-2D layers can be further controlled, the energy landscape can be tuned to enable high electron selectivity at the top interface (*14*).

Challenges remain for the selection of CTLs, especially when targeting both high efficiency and high stability (*15*). Spiro-bifluorene derivatives, along with a host of ionic additives and p-dopants, seem essential for HTL in high-efficiency n-i-p devices, but suffer from serious ion migration and thermal instabilities. Fullerene derivatives are commonly used as ETLs in p-i-n cells, but show severe recombination losses at the perovskite interfaces and are a weak point for delamination. Substantial improvements of p-i-n device performance and stability are expected with the development of new "non-fullerene" ETLs. Some archetypical "non-fullerene acceptors" from organic PV such as "ITIC" and perylene derivatives do result in operational PSCs. However, competitive performance with alternative ETLs has not been achieved. Once a pathway emerges for this improvement, we expect that rapid combinatorial modifications to the organic structures will results in progress towards realizing ideal perovskite/ETL heterojunctions.

In comparison with the perovskite top interface, deeper understanding the "buried secrets" under the perovskite film requires more powerful characterization techniques. High-resolution electron microscopic and near-field techniques could be responsible for clarifying nanoscale crystallographic, chemical, and electrical information at the buried interfaces. Visualization of local carrier behavior at the buried interface will also benefit from dedicated high-resolution, ultrafast fluorescence mapping techniques.

Beyond borrowing characterization methodologies, other synergies exist between the different PV technologies, from crystalline silicon to organic PV materials. Many of the materials used in organic PVs find use in perovskites, and CTL configurations can often be applied in a sandwich structure device with both perovskite and organic bulk heterojunction absorber layers. Key challenges in traditional thin-film PV are centered around enabling improved charge contacts. For silicon PV, passivated contacts have proven to deliver the highest efficiencies, with amorphous silicon or a thin silicon oxide layer being used in silicon heterojunction and tunneling oxide passivated contact (TOPCon) cells respectively. However, a vast range of other heterojunctions have been explored for silicon. If appropriately applied, some of the material deposition methodologies and passivation strategies developed for perovskites may find success when applied to silicon wafers as well.

The huge progress made in last decade pushes PSCs forward to be among the most efficient PV technologies, substantial advances in operational stability have also been achieved, positioning perovskites on the brink of industrialization. Revealing the remaining mysteries at the interfaces could unlock the full potential of perovskites.

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Fig. 1 Roadmap for perfecting the interfaces in perovskite solar cells.