PEROVSKITE PHOTOVOLTAICS

# Embrace your defects

Control of electron and hole concentrations in semiconductors is a longstanding challenge. Now, by managing defect populations, a p-n homojunction solar cell has been fabricated, opening a new avenue for metal halide perovskite devices.

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The semiconductor industry is built upon junctions formed between p-type (hole rich) and n-type (electron rich) materials. The concentration of charge carriers in a crystal can be managed in a variety of ways including ion implantation and solid-state diffusion of dopants. For example, the addition of phosphorus and boron to a sample of silicon produce n-type and p-type regions, respectively.[1] On the other hand, many compound semiconductors exhibit an innate doping preference that gives rise to n-type or p-type conductivity in the absence of extrinsic doping.[2] For instance, native point defects in a crystal, in the form of missing atoms (vacancies) or surplus atoms (interstitials), can result in the generation of electron and hole carriers. This is the case for most transparent conducting oxides, which are n-type due to oxygen sub-stoichiometry as in the cases of $ZnO_{1-x}$ and $SnO_{2-x}$, whilst the photovoltaic absorber CdTe is naturally p-type owing to Cd deficiency.[3] The concentration of defects, and hence charge carriers, can be varied through the growth environment and used to tune the carrier mobility and electrical resistivity of the host semiconductor.

Unexpectedly though, lead halide perovskites simultaneously have high defect concentrations but low carrier concentrations ($<10^{14}$ $cm^{-3}$).[4] This arises from efficient charge balancing between positive and negative point defects. This ionic self-compensation of charges makes it difficult to dope lead halide perovskites. The Fermi level of as-grown methylammonium lead iodide ($CH_3NH_3PbI_3$) is often closer to the valence band than the conduction band, indicative of a weakly p-type behaviour, as is also observed in Hall effect measurements. However, the corresponding hole concentrations can be as low as $10^9$ $cm^{-3}$ (fewer than one carrier per-billion crystallographic unit cells),[4] which is insufficient to form an effective p-n junction. It has been shown that the Fermi level can be tuned by selective control of defect concentrations through varying the processing conditions. For example, annealing $CH_3NH_3PbI_3$ in iodine vapour enhances the electronic conductivity and can shift the Fermi level by 0.15 eV closer to the valence band, leading to a more pronounced p-type doping effect that has been attributed to a reduced concentration of positively charged iodide vacancies.[6] Despite this, the current generation of efficient perovskite solar cells are based on a p-i-n architecture, which combines an intrinsic perovskite layer with non-perovskite n- and p–type charge extraction layers such as $TiO_2$ and spiro-MeOTAD, respectively.

Now, writing in *Nature Energy*[7], Peng Cui, Dong Wei and colleagues in China report on a homojunction between p-type and n-type $CH_3NH_3PbI_3$ which is achieved by carefully controlling the stoichiometry of the perovskite precursors as illustrated in Figure 1a. The variation in carrier density is realised by self-doping rather than extrinsic doping. First, the n-type layer is deposited in an iodine-poor environment, where the formation of iodine vacancies is favoured. The iodine vacancy level is shallow with respect to the conduction band,

so the point defects readily ionise at room temperature and act as positively charged electron donors. The p-type layer is then deposited under iodine-rich conditions, where iodine vacancies are supressed and cation vacancies (electron acceptors) are favoured. By altering the $PbI_2$:$CH_3NH_3I$ precursor ratio from 0.90 to 1.15, a hole concentration of $10^{10}$ $cm^{-3}$ is converted to an electron concentration of $10^{13}$ $cm^{-3}$. Remarkably, Cui, Wei and colleagues show that the contact between the p-type and n-type perovskite is stable and results in an efficient homojunction solar cell with a power conversion efficiency of 21% (see device structure in Figure 1b). This is important progress as the existing p-i-n architecture limits the choice of materials and approaches to further enhance performance. A homojunction p-n architecture, instead, can benefit from internal electric fields within the perovskite absorber layer, thereby enhancing electron-hole separation.

This initial demonstration of a halide perovskite homojunction may require further developments for long-term durability. It has been established that halide perovskites are mixed ionic-electronic conductors with ions and electrons being mobile at room temperature and even more mobile under illumination.[8,9] Therefore, any gradient in doping profile (stoichiometry) could be removed by mass transport in response to current-voltage cycles of a solar cell under illumination or even in the dark over longer timescales. Therefore, even though Cui et al report no changes in device performance over the course of one month, an ultra-thin interfacial barrier layer between the p-type and n-type regions may be needed to impede ion redistribution across the p-n junction over time.

These findings open the way for perovskite solar cells to adapt device configurations from mature technologies such as silicon[10] which rely on homojunctions. Some of these will require higher n and p concentrations, which could be achieved by extrinsic doping; a task which has not yet proved successful. Approaches to next-generation perovskite solar cells include back surface fields for better selectivity in charge carrier extraction; inter-digitated back contacts for lateral control of doping density and the removal of metal grids from the top contact; and heterojunction with intrinsic thin layer (HIT) cells for interface passivation following the success of thin intrinsic layers for power efficiencies greater than 26% in silicon solar cells.

Additionally, the control of charge carrier concentrations and distributions in halide perovskite semiconductors illustrated by Cui, Wei and co-workers has wide ranging impacts beyond solar cells, including emerging applications in light emission (high current regime) and neuromorphic computing (low current regime). The time has come for lead halide perovskites to embrace their defects.

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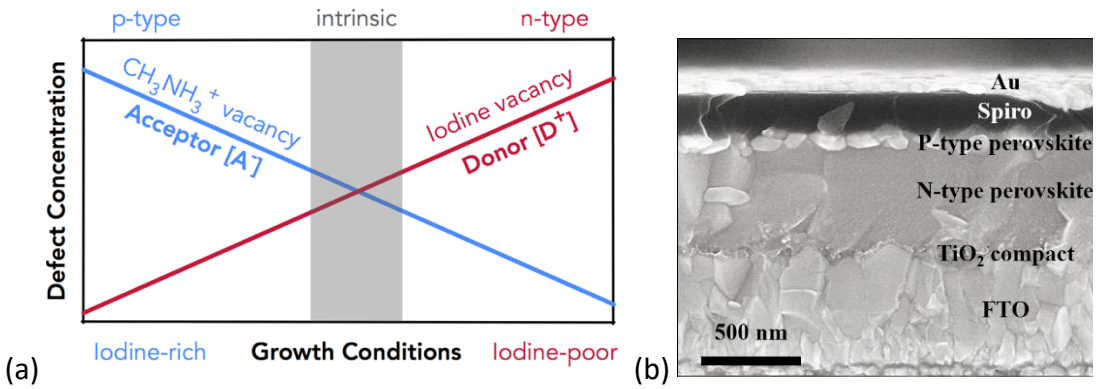



**Fig. 1 Control of defect concentrations in metal halide perovskites. (a)** *Three regimes of charge compensation in $CH_3NH_3PbI_3$ leading to n-type (electron rich), p-type (hole rich), and intrinsic ($[A^+]\approx[D^-]$) behaviour. These can be accessed by controlling the chemical potentials during crystal growth and annealing. The assignment of the majority donor and acceptor species is taken from Ref. 5.* ***(b)*** *Cross-sectional scanning electron microscopy image of the p-n homojunction-based perovskite solar cell fabricated by Peng Cui, Dong Wei and colleagues. Panel b is adapted from ref [7], Springer Nature.*

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