

Case Study 2

<p>1. Title of Case Study: Clean semiconductor behaviour of perovskite solar cells probed by simultaneous current-voltage and GIWAXS measurements</p>
<p>2. Grant Reference Number: XMaS</p>
<p>3. One sentence summary: Employing simultaneous <i>in situ</i> grazing incidence wide angle x-ray scattering (GIWAXS) and <i>operando</i> current-voltage measurements on metal-halide perovskite interdigitated-back-contact (IBC) solar cells, the remarkably clean semiconductor behaviour of perovskites films is shown to emerge in the earliest phase of conversion from the as-coated precursor film.</p>
<p>4. One paragraph summary: Metal-halide perovskites show remarkably clean semiconductor behaviour, as evidenced by their excellent solar cell performance, in spite of the presence of many structural and chemical defects. This study shows how the clean semiconductor performance sets in during the earliest phase of conversion from the metal salts and organic-based precursors and solvent, using simultaneous <i>in situ</i> synchrotron x-ray scattering and <i>operando</i> current-voltage measurements on films prepared on interdigitated back-contact substrates. At the first stages of conversion from the precursor phase, at the percolation threshold for bulk conductance, high photo-voltages are observed, even though the bulk of the material is still present as precursors. This indicates that at the earliest stages of perovskite structure formation, the semiconductor gap is already well-defined and free of sub-gap trap states. The short-circuit current, in contrast, continues to grow until the perovskite phase is fully formed, when there are bulk pathways for charge diffusion and collection. This work reveals important relationships between the precursors conversion and device performance and highlights the remarkable defect tolerance of perovskite materials.</p>
<p>5. Key outputs in bullet points:</p> <ul style="list-style-type: none">• Photovoltaic device performance improvement• Simultaneous <i>operando</i> current-voltage and <i>in situ</i> x-ray scattering measurements• PhD of M. Alsari• Collaboration between XMaS and Dr. Samuele Lilliu
<p>6. Main body text:</p> <p>Perovskite photovoltaics (PV) is one of the fastest growing opto-electronic technologies with device efficiencies currently exceeding 23% in single solar cells and 27.3% in tandem devices [1]. To further improve device performance, researchers are exploring a variety of optimisation strategies, such as thermal engineering. For most solution-processed perovskite materials, annealing temperature and duration are critical factors for optimised conversion of the as-coated precursor material into a functional polycrystalline perovskite film. In this work, Alsari and co-workers [2] employ a new investigation method illustrated in Fig. 1 that can significantly reduce the workload required in thermal engineering of perovskite solar cells and, at the same time, establish a direct correlation between their opto-electrical and structural properties during <i>in situ</i> annealing. This is achieved by exploiting the concept of interdigitated back-contact (IBC) solar cells. Here the electron (TiO₂) and hole (PEDOT)</p>

selective electrodes are co-positioned on the backside of the cell in an interdigitated fashion (**Fig. 1b**)[3].

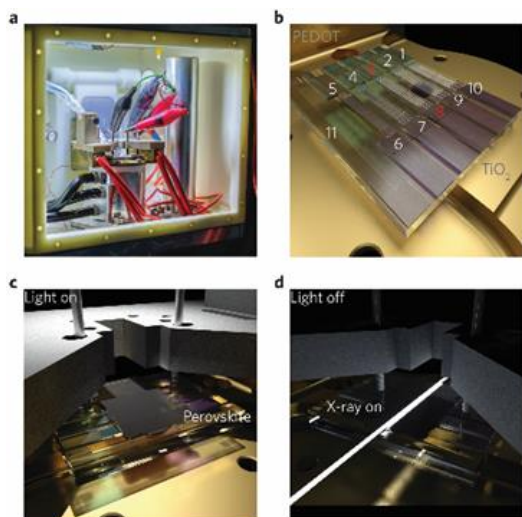


Figure 1: Illustration of the measurements setup: a) annealing chamber; b) illustration of ITO integrated substrate electrodeposited with PEDOT (electrode 1-5) and TiO₂ (electrodes 6-10); c) illustration of the experimental setup for current-voltage sweeps performed in situ without x-rays; d) illustration of the setup for diffraction pattern measurements (light off) using grazing incidence geometry.

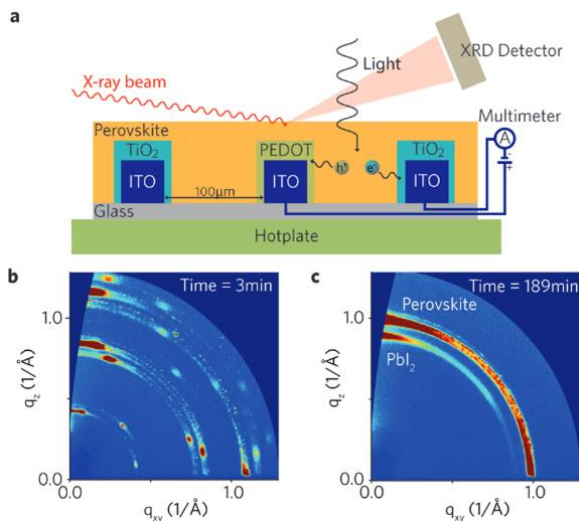


Figure 2: Simultaneous GIWAXS and current-voltage measurements of IBC solar cell during in situ annealing at 88.2°C at XMaS: a) Experimental geometry showing the grazing incident x-ray beam onto the sample and the detector for WAXS patterns recording. The electrodes connected to the current source and voltmeter are also shown; b) diffraction pattern after about 3 min of annealing showing only the precursor phase; c) diffraction pattern after about 3 h of annealing showing the perovskite and the lead iodide phases.

The main advantage of IBC solar cells is that the perovskite layer represents the final step of the device fabrication. Because the perovskite film is unobstructed by any top layer, *in situ* annealing can be performed without compromising the film formation. At the same time, the perovskite film is directly accessible by an x-ray beam, making IBC devices a great solution for simultaneous opto-electrical and grazing incidence wide angle x-ray scattering (GIWAXS) measurements performed *in situ* during annealing (**Fig. 2**). With the setup developed at the XMaS beamline, Alsari *et al.* demonstrate a high throughput thermal engineering route that can be used on a variety of perovskite materials, along with the possibility of establishing a direct correlation between the figures-of-merit of a solar cell and

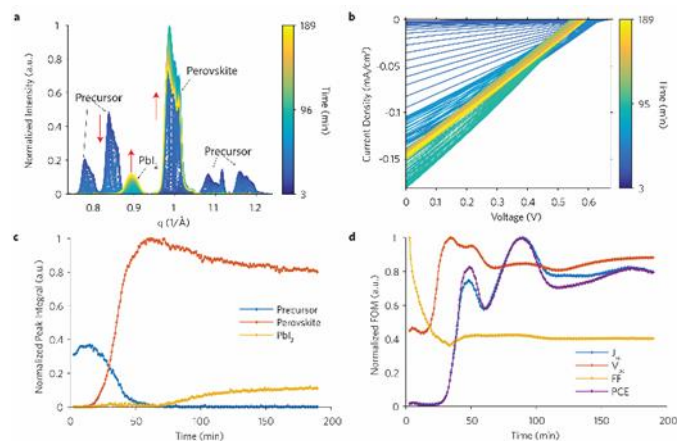


Figure 3: Structural and opto-electrical parameters extracted from simultaneous GIWAXS diffraction patterns (under dark conditions) and current-voltage measurement (under light conditions) of a perovskite (CH₃NH₃PbI₃) IBC solar cell during in situ annealing at 88.2°C [1].

its structural properties. **Fig. 3** shows a summary of the photovoltaic and structural measurements on CH₃NH₃PbI₃ perovskite IBC solar cells. The remarkably clean semiconductor behaviour of perovskites is evidenced by the high photovoltages measured at the first stages of perovskite conversion from precursors, at the percolation threshold for bulk conductance. The open circuit voltage (V_{oc}) reaches a maximum value before the precursor has fully converted into perovskite, when the fraction of precursor and perovskite crystals is comparable (**Fig. 3c-d**). The short circuit current (J_{sc}) and

power conversion efficiency (PCE) follow a trend similar to that of the perovskite peak intensity extracted from the GIWAXS measurements.

The measurement strategy followed by Alsari *et al.* is not limited to perovskite materials and is of interest for any solution processable photovoltaic technology requiring thermal annealing.

[1] H.J. Snaith and S. Lilliu, *SciVPro* (2018) 1, 1. doi:10.32386/scivpro.000004

[2] M. Alsari *et al.*, *Energy Environ. Sci.* (2018) 11, 383.

[3] L.M. Pazos-Outón *et al.*, *Science* (2016) 351, 1430.

7. Names of key academics and any collaborators:

Dr. Samuele Lilliu, Department of Physics and Astronomy, University of Sheffield

8. Sources of significant sponsorship (if applicable):

XMaS

The President of the UAE's Distinguished Student Scholarship Program (DSS), granted by the Ministry of Presidential Affairs, UAE

University of Sheffield DTG account

CDT in New and Sustainable PV, EP/L01551X/1

9. Who should we contact for more information?

Dr. Samuele Lilliu, Department of Physics and Astronomy, University of Sheffield,
s.lilliu@sheffield.ac.uk, +44 (0)114 222 3501