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Correlative Imaging of Mesoporous Perovskite Carbon Stack Solar Devices for Defect Evaluation.

Tom Dunlop[1], Harry Lakhiani[2], Peter Davies[3] and Cecile Charbonneau[4]

[1]SPECIFIC, Swansea University, Wales, United Kingdom, [2]SPECIFIC, Swansea University, United States, [3]AIM, Swansea University, United States, [4]SPECIFIC, Swansea unviersity, United States

Perovskite solar cells (PSCs) are a popular photovoltaic technology currently undergoing extensive development on the global research scene. Whilst their record efficiency now rivals that of silicon-PV in small scale devices, PSCs can only progress from laboratories to commercial manufacturing if we can establish stronger links between the complex multi-layered structure of these devices and their performance and stability. Here, we demonstrate how tailored sample preparation by broad beam ion milling sectioning and correlated SEM and Raman imaging techniques have been applied to study the impact of materials processing over structural defects and localized inactive areas in carbon-based mesoscopic perovskite solar cells.

Carbon-based mesoscopic perovskite solar cells (C-PSCs, Figure 1) are becoming one of the most promising perovskite solar cell architectures for addressing upscale challenges and stability issues[1]. These are extremely easy to manufacture with low-cost screen-printing techniques (devices up to 198 cm^2 of active area)[1] and exhibit promising long-term (>1000hrs) stability[2]. The fabrication of this particular PSC architecture includes a step where the perovskite precursor solution in infiltrated through a stack of three meso-porous layers. Optimizing the flow and pore filling of the precursor is critical to the functioning of the device, yet poorly understood. Indeed, previous work has reported a high spread of efficiencies across a population of devices prepared identically, indicating an underlying contributing factor[3]. Diagnosing manufacturing issues through this stack of layered materials has been a real challenge: the preparation of cross-sections via traditional breaking led to the formation of rough surfaces whilst affecting adhesion between the various layers, making electron imaging difficult.

In this study, Broad Beam Ion Milling (BBIM) was used to prepare cross sections of C-PSCs, a technique adapted from metallographic investigations. We demonstrate that a fine tuning of BBIM parameters enables the fast preparation of high quality cross-sections despite the great variety in chemical nature and mechanical properties of the stacked materials (Figure 1): FTO-coated glass, compact TiO_2, followed by 3 screen-printed mesoporous layers of TiO_2, ZrO_2 and carbon flakes, all infiltrated with perovskite (AVAI-$CH_3NH_3PbI_3$)[4]. Features identified using Raman and optical microscopy from the glass side were then matched and characterised using the SEM for cross sectional imaging. Using tailored BBIM sample preparation together with combined Secondary Electron (SE), Energy-Dispersive X-ray Spectroscopy (EDS), and Raman Microscopy, we were able to identify the nature and scale of a wide variety of features and defects within the cells. Raman Microscopy was used to identify cold spots of inactivity (low PL) within the cell under light and found these exhibited in a variety of sizes, SEM was then used to visualise and relate these spots to physical features within cross sections. These features include casting voids within the carbon (Figure 2a), contaminants within the mesoporous layers, and localized areas where perovskite is observed to decompose to PbI_2. Defects impacting the most on device performance were associated to carbon flakes orientation: when these were found to lie flat on top of the ZrO_2 layer, infiltration of the perovskite precursor was compromised, leaving areas of the mesoporous triple stack completely deprived with light absorber material. These infiltration defects, termed pin and plate defects (Figure 2 b and c respectively), were correlated to

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performance losses in devices[3], and found to cause complete inactivity over 10-100% of any section of the cell.

The preparation of high-quality cross-sections has proven particularly important to further developing C-PSC devices. Until now, the lack of consistency in C-PSC device performance was poorly understood. This work revealed important manufacturing bottlenecks that, if the printing industry can overcome, will allow these solar cells to fulfil their true potential at a commercial scale.

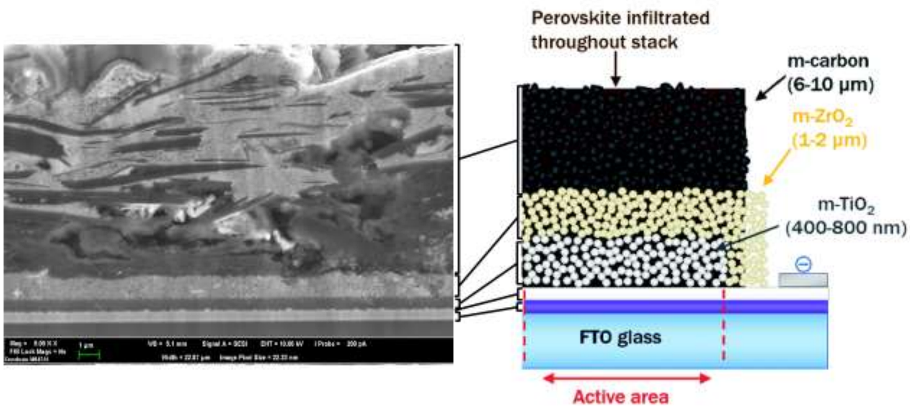

Figure 1. Image of the mesoporous carbon stack infiltrated with perovskite compared to the standard schematic [4].

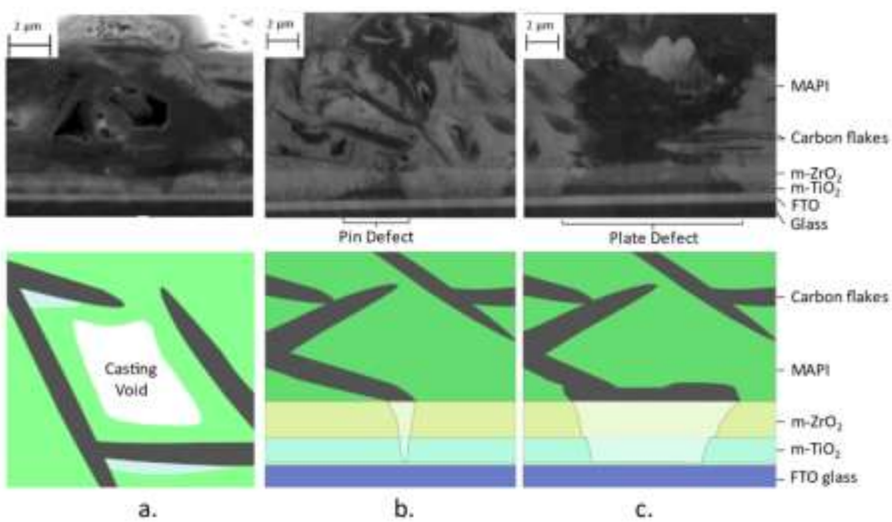

Figure 2. Schematic images of a. perovskite shrinkage cavity within the carbon layer, b. pin defects and c. plate defects within the mesoporous ZrO2 and TiO2 layers.

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