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FIB Sample Preparation of Hybrid Organic-Inorganic Perovskite (HOIP) Solar Cells

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Hybrid Organic-Inorganic Perovskites (HOIPs) are a class of photoactive semiconductor compounds which have garnered much attention as candidates for high conversion efficiency solar cells, and have shown a remarkable increase in conversion efficiencies from ≈3.8% in 2009, when they were first reported, to over 25% in 2021, but are nevertheless below the theoretical ≈31% efficiency limit for a single-junction photovoltaic device [1,2]. Further improvements will require an intrinsic understanding of the microstructures, interfaces, composition along with the atomic-scale defects present in the material and the electrochemical behaviour of the device.

Scanning Transmission Electron Microscopy (STEM) is uniquely capable of studying many of these features but has strict sample geometry and preparation requirements, which require the use of Focused Ion Beams (FIBs) to prepare cross-sections of the thin-film devices [3-5]. Two damage mechanisms are likely to dominate the effects of the ion-beam on the HOIPs - radiolysis and localized heating, followed by degradation of the organic cations [6]. This damage appears most evidently as small (<50nm) voids evenly distributed across the particles, and an overall shrinkage of the perovskite layer due to evolution of volatile organohalide decomposition products and formation of nanoparticles of PbI_2 in the case of lead-based metal-halide perovskites, as shown in **Figure 1**. Radiolysis effects tend to be amplified at lower accelerating voltages and thus the final low-voltage polishing steps commonly used in FIB preparation procedures appear to introduce a significant portion of the damage observed. Modified procedures were explored by performing the bulk of the polishing and the final polishing steps at voltages other than the 1-2keV commonly used, with smoother faces on the finished lamella and samples thin enough for high-resolution low-dose STEM analysis as demonstrated in **Figure 2**. In this study a preparation procedure of samples for high-resolution STEM analysis from whole thin-film HOIP solar cells via Ga^+ FIB-SEM in-situ lift-out was studied with a focus on identifying what ion beam-damage looks like and what steps can be taken to minimize it [7].

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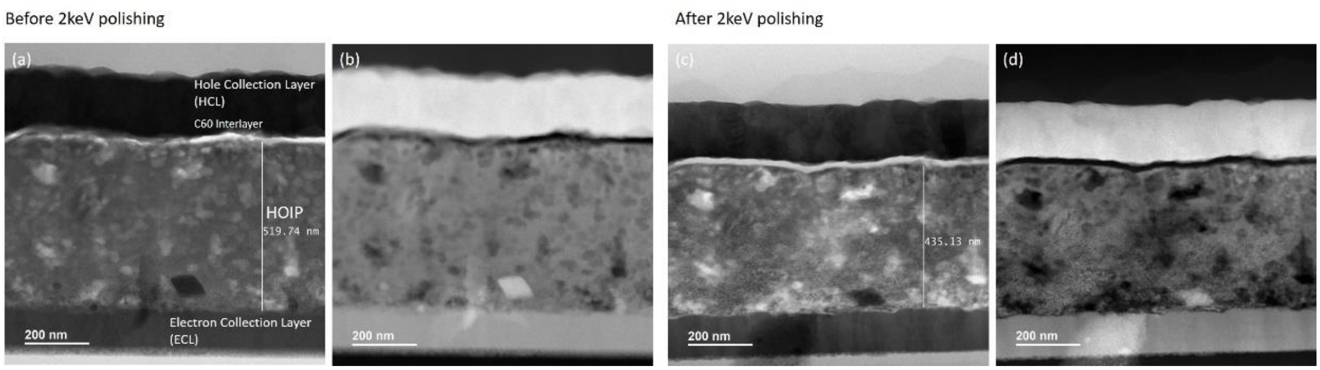

Figure 1: STEM BF/DF images of FIB-prepared lamellae of whole thin-film HOIP solar cells (a,b) before the final 2keV polishing step and (c,d) after the 2keV polishing step. The perovskite layer already shows the onset of beam-induced damage prior to the final 2keV polishing step, with voids visible in the ADF image (b) and the precipitation of small particles near the ECL interface. These effects are amplified after further thinning, with enlargement of the pores, more particles precipitating, and a ≈15% reduction in layer thickness.

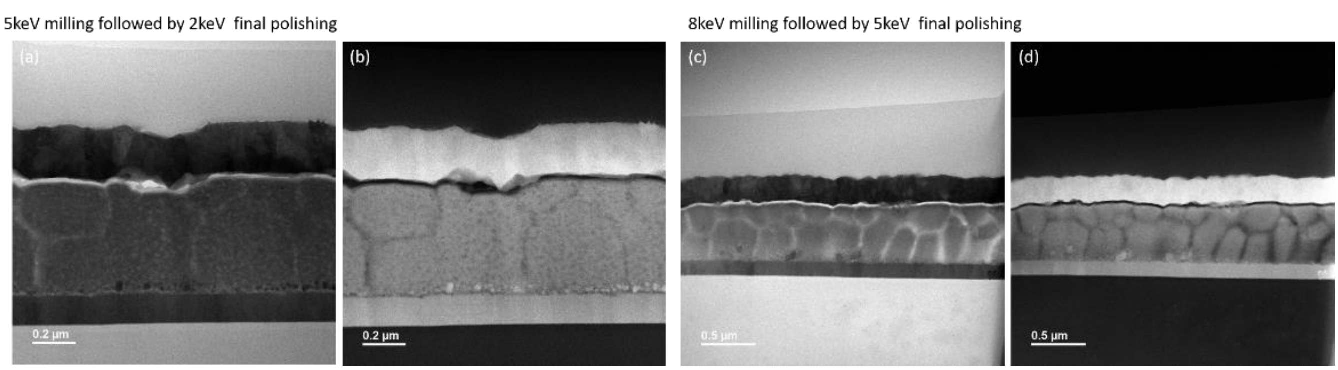

Figure 2: STEM BF/DF image pairs of two HOIP solar cell lamellae from the same device prepared at (a,b) 5keV milling and 2keV final polishing step and (c,d) 8keV milling and 5keV final polishing step. Of note is the significantly smoother appearance of the particles when the milling and polishing is conducted at higher voltages.

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