wildfire

APPLICATION NOTE

TEM & Objective lens

FEI Osiris ST

Holder / System

Wildfire S3

MEMS Device

Nano-Chip ST

Window: Through hole

Sample

Perovskite ($MAPbI_3$) solar cells

Sample Preparation Technique

FIB liftout

In Situ environmental parameters

Temperature range: RT - 350°C

TEM imaging parameters

200 kV, 700 pA probe current

Analysis techniques

HRTEM

Temperature-induced Degradation of Perovskite Solar Cells

Keywords

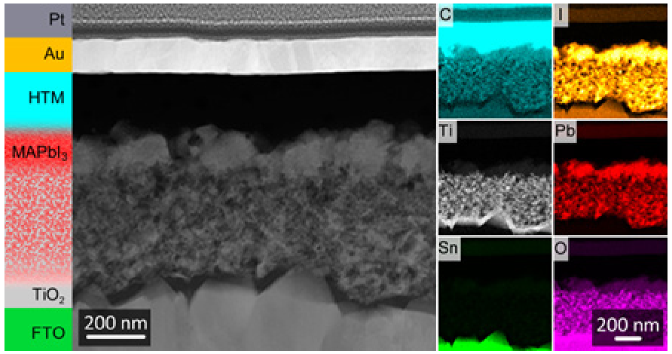
In Situ Heating, Transmission Electron Microscopy, Perovskite solar cells

Fields

Materials Science

Abstract

Poor thermal stability of perovskite solar cells is a drawback currently preventing their commercialisation. In situ heating in the transmission electron microscope is a valuable tool to understand the micro- and nano-scale processes correlated to performance degradation. Here devices are produced according to four common approaches in the literature, and the photovoltaic performance is characterised as they are heated within their operational range. The devices are then analysed using transmission electron microscopy as they are further heated in situ, to monitor changes in morphology and chemical composition using Energy-dispersed X-ray (EDX) elemental mapping. The authors identify mechanisms for structural and local chemical changes, such as iodine and lead migration, which can be correlated to the synthesis conditions.



Purpose

- Perovskite solar cells degrade upon ageing and heating; there is a need to understand the stability of the hybrid organic-inorganic perovskite and the organic hole transporting layers
- Identifying heat-induced degradation pathways for the devices
- Comparing the behavior of 4 devices produced with different approaches

Challenges

- Air-sensitive samples – need reliable FIB preparation and immediate TEM analysis after liftout
- Potential beam damage under repeated EDX mapping, need to limit dwell time
- Need to lower temperature during EDX analysis to pause sample dynamics

Results

In this experiment perovskite solar cells are manufactured employing four different approaches (Sample A – double-step conversion in vacuum, B – double-step in glovebox, C – double-step in air, D – single-step in glovebox) and prepared for in situ TEM heating using a focused ion beam (FEI Helios Nanolab).

The samples are heated at increasing temperatures for a time of 30' per step, followed by cooling to 50°C in order to freeze the degradation dynamics (Figure 1). After each heating step EDX spectrum images are acquired. The EDX data are then denoised using multivariate analysis to improve the signal to noise ratio.

The degradation dynamics are different among the samples (Figure 2), with A, B and D experiencing elemental migration of lead and iodine from the perovskite layer and their aggregation into particles, first appearing near the interface between the titania scaffold and the FTO and then migrating over the surface of the lamella.

In the case of sample C, which is exposed to air during the perovskite conversion, such aggregation is not observed; instead, elemental mapping (Figure 3) shows that iodine and lead infiltrate the hole transporting layer, diffusing towards the metal electrode of the cell.

In this work, the accuracy and the fast response of MEMS-based heating holders were vital in isolating the thermal stress from the analysis phase.

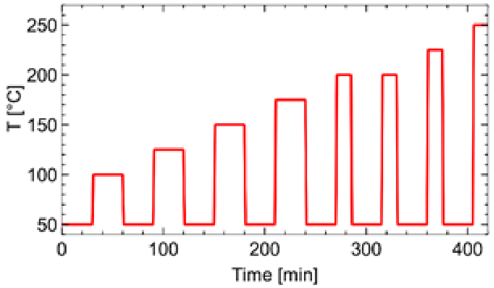


Figure 1. Thermal ramp applied to the samples.

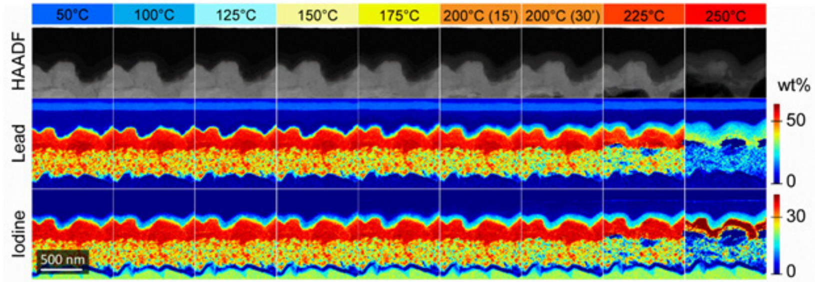


Figure 2. Changes in the HAADF signal at the perovskite / hole transporter interface and corresponding elemental maps for Pb and I after heating of sample C at different temperatures.

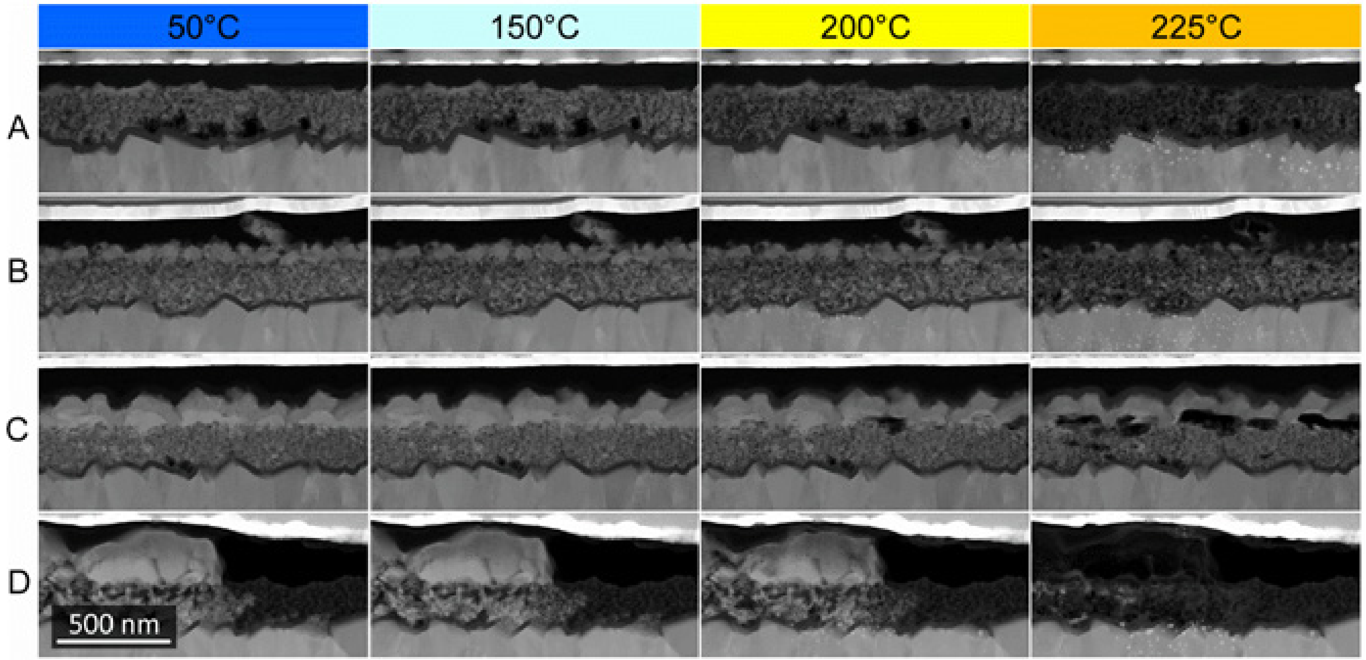


Figure 2. Comparison of the four samples after heating at different temperatures. Visible degradation of the perovskite layer nucleates from the perovskite/TiO2 interface; bright particles appear in A, B and D, whereas only a decomposition of the perovskite layer is visible in sample C.

Reference: G. Divitini, S. Cacovich, F. Matteocci, L. Cinà, A. Di Carlo and C. Ducati, Nature Energy 15012 (2016)

doi:10.1038/nenergy.2015.12

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