Damage Mechanism and Defect Evolution of Hybrid Perovskite FAPbI₃ Under a Variable Dose Electron Beam

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Due to their excellent photovoltaic and optoelectronic performance, organic-inorganic hybrid perovskites (OIHPs) have attracted increasing attention since first applied in solar cells in 2009 [1]. The power conversion efficiency (PCE) of single-junction perovskite solar cells has increased remarkably to above 25% [2], reaching towards its detailed balance limit of 33% [3]. Despite the simple and low-cost fabrication of OIHPs, their long-term instability is still limiting the commercialization in solar cells. OIHPs have the chemical formula of ABX₃, where A site is organic cation such as methylammonium (MA⁺) and/or formamidinium (FA⁺), B site is occupied by group IVA metals Pb²⁺ or Sn²⁺, and X site is occupied by halides such as I, Br, or Cl. OIHPs undergo easy phase transformations under moisture at room temperature, where the highest symmetry cubic (perovskite) phase transforms into non-perovskite phases (such as tetragonal or hexagonal) through octahedral tilting [4]. Thus, OIHPs are subject to intragranular defects (e.g. twins or stacking faults) which are related to phase coexistence, impacting their performance in solar cells [5].

Nevertheless, the microstructures of OIHPs have not been adequately characterized due to their beam-sensitive characteristics under electron beam exposure. The rapid degradation of hybrid perovskites under beam irradiation makes high-resolution Transmission Electron Microscopy (TEM) challenging and also results in possible phase transformation of the pristine structure, further convoluting their structure-property correlations. Several low dose techniques have successfully captured the hybrid perovskite structures, including ultralow-dose electron diffraction patterns [5][6], atomic-resolution low-dose low-angle annular dark field (LAADF) STEM imaging [7], and aberration-corrected high-resolution TEM with exit-wave reconstruction [8]. However, some results and explanations are still contradictory regarding the observed structures being the intrinsic phases or due to beam damage.

In our study, low-dose TEM was used to visualize the rapid degradation and defect evolution of OIHP FAPbI₃ under the electron beam. Highly dense planar defects were revealed by Dark-field TEM (DFTEM) where the degradation is most likely to happen. A series of TEM images were recorded under continuous beam irradiation. Massive holes form at the intragranular planar defects and expand drastically as soon as the beam is exposed to FAPbI₃. In this study we explore the effect of the electron
dose on the nanoscale defect formation, such as the formation of cavities and their growth under the electron beam in the sample.

References:


[9] This work was supported by Department of Energy (DOE) (500000023786).