Monitoring Stability of Metal-Halide Perovskites Under Combined Stressors of Ion-Beam and Heat

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Rapid progress has been achieved in perovskite solar cells, improving the efficiency from 3.8 % to 25.7 % in less than a decade. However, the stability of perovskites still needs to be improved before commercialization. This study reports the thermal stability of perovskites exposed to an ion beam irradiation. Such combined stressors are seen in atomic/nanoscale microscopy, where a perovskite lamella is characterized using a controlled heating/cooling stage. Focused ion beams (FIBs) are frequently used to section perovskites of interest. Previous studies proposed that high-energy electron beams could cause unexpectedly fast thermal degradation. Alternatively, the perovskite surface may be already altered during FIB processes, accelerating the deterioration.

We use a grazing angle argon ion (Ar^+) beam directly irradiated on methyl-ammonium lead iodide ($MAPbI_3$) to test the impact of ion beams to degradation mechanisms. This perovskite film was spin-coated on a stack of glass / FTO (fluorine-doped tin oxide; 200 nm) / SnO_2 (35 nm). A 4 kV Ar^+ ion beam was injected into a part of the $MAPbI_3$ sample at an angle of 3° for 10 minutes. A strong photoluminescence (PL) peak was observed near 765 nm (1.62 eV) for both samples, attributed to the bandgap emission. However, the PL intensity decreased by 40 % after the Ar^+ polishing. A finite difference time domain (FDTD) simulation estimates an approximately 40 % of the PL excitation (244 nm laser) can be absorbed within ≈15 nm of the $MAPbI_3$ subsurface. This result agrees with the ion-beam penetration depth, calculated by Monte Carlo simulations. The PL analysis and the numerical simulations indicate that the 4 kV ion beam irradiation at an incident angle of 3° introduces an optically inactive “dead layer (≈15 nm)” on $MAPbI_3$. We performed x-ray photoemission spectroscopy (XPS) to investigate possible surface compositional changes of $MAPbI_3$ under Ar^+ polishing. Quantitative XPS analysis shows an apparent reduction of the organic components (e.g., C, O, and N) after the ion beam irradiation. In contrast, XPS signals of the inorganic species (e.g., Pb, I) significantly increase with introducing the doublet metallic Pb (0) near the bonding energy of 137 eV and 142 eV. Overall, the I/Pb ratio decreases from 2.6 (pristine) to 2.1 (polished), suggesting the ion beam irradiation modifies the subsurface of $MAPbI_3$ to be a lead-rich, iodine-deficient layer (< 10 nm).

The impact of the modified subsurface of $MAPbI_3$ on thermal deterioration was qualitatively investigated using a heat lamp at 150 °C. Owing to the partial surface decomposition, we observed the ion-beam exposed $MAPbI_3$ shows a faster decay than the control under the heating. Apparent deterioration of $MAPbI_3$ (yellow color) on the Ar^+ polished section after applying the heating stressor for 20 minutes. At this stage, the color of the pristine area remains unchanged (dark-brown color). The deterioration of the pristine area began at around 40 minutes. Both sample sections fully deteriorated at 70 minutes. Our experiment confirms that subsurface modification (≈15 nm) can significantly influence the deterioration mechanisms of $MAPbI_3$. This talk will discuss a new method of monitoring the deterioration of perovskites in real-time. A prototype design consists of a patch antenna (≈ 3 cm × 4 cm) and an array of four $MAPbI_3$ solar cells (1 cm × 1 cm). The distance of the adjacent solar cells is set to 1.4 cm in width and 0.6 cm in length. Computer Simulation Technology (CST) simulations display the resonance frequency of the patch antenna changes from 7.13 GHz to 7.07 GHz as the $MAPbI_3$ film decomposes to volatile species and PbI_2. While the shift is small, our pilot design demonstrates the feasibility of wireless monitoring the deterioration of perovskite solar cells. Tailoring antenna design and experimental validations are in progress.

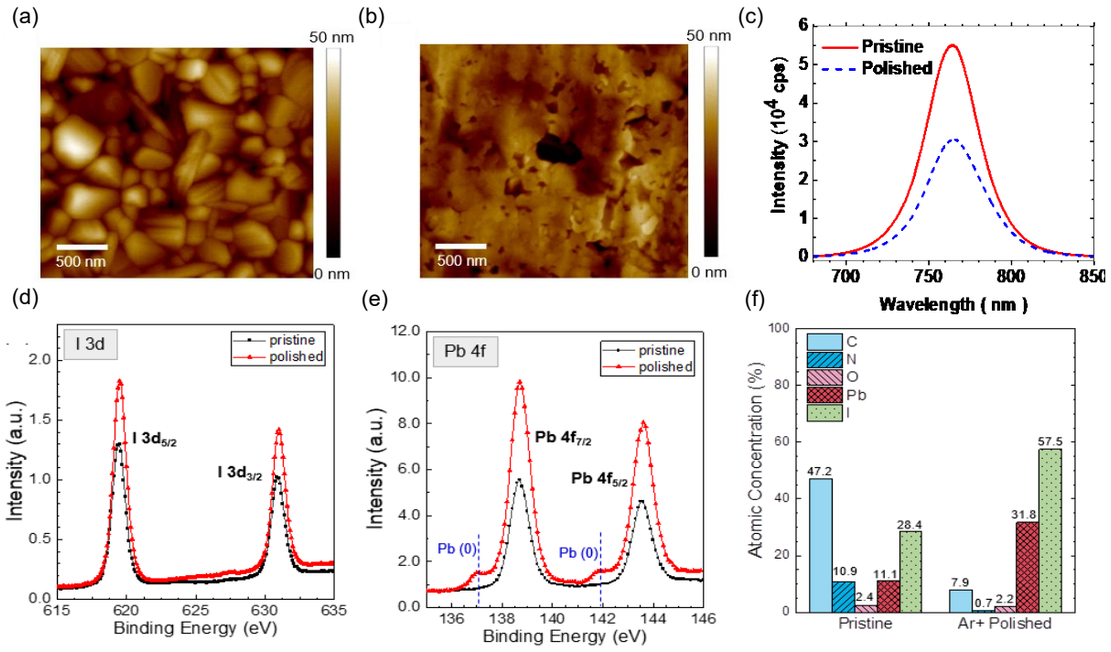

Figure 1. Surface topography of (a) pristine and (b) Ar^+ polished $MAPbI_3$. (c) PL responses (d, e) XPS comparison. (f) Summary of the compositional changes under the beam exposure.

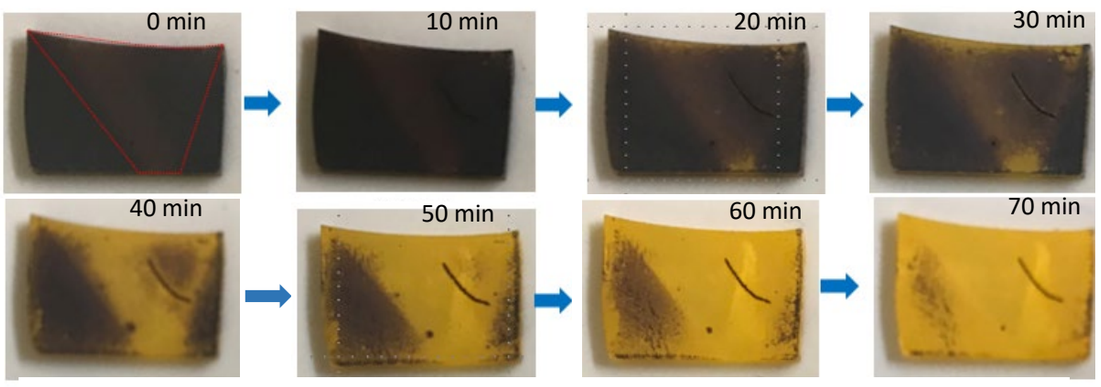

Figure 2. A series of photographs showing the thermal deterioration of $MAPbI_3$

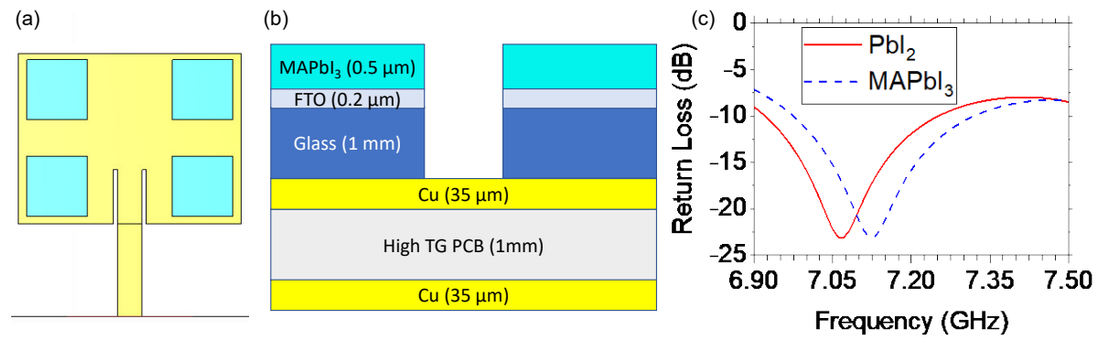

Figure 3. (a, b) Design of a patch antenna monitoring deterioration of $MAPbI_3$. (c) Simulated antenna resonance of $MAPbI_3$ "before" and "after" the deterioration