

Uppermost surface of MAPbI₃ perovskite studied by UPS and MAES

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In the perovskite solar cell, the interfaces play the crucial roles in the charge extraction, transfer and recombination. The properties of the interface should be strongly affected by the elements of the uppermost surface and thus determining it is crucial to the study of interfaces.

The general chemical formula for the perovskite is ABX₃. The most commonly used perovskite solar cell is the methylammonium lead iodide (MAPbI₃), where A, B, and X are methylammonium (MA), lead (Pb) and iodide (I), respectively, as shown in Fig. 1. Although the surface elements of the MAPbBr₃ single crystal were revealed using scanning tunneling microscopy (STM) by Ohmann et al¹, the surface elements of MAPbI₃ thin film prepared from the solution, which is practically used in the most of solar cells, is unknown. In this work, we examined the surface elements of MAPbI₃ prepared from the solution employing ultraviolet photoelectron (UPS) and metastable-atom electron (MAES) spectroscopies.

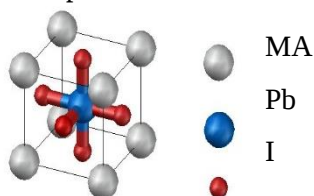


Fig.1 The crystal structure of MAPbI₃

UPS is an experimental technique to observe the valence electronic states; the ultraviolet photon excites the valence electron of the sample surface and the electron energy of the emitted photoelectron is analyzed. In MAES, the excitation source is replaced with the metastable atom. While the ultraviolet photon can penetrate into the sample, the metastable atom can only interact with the outer orbital of the sample. Therefore, by comparing intensities of related features observed both in MAES and UPS spectra, we can obtain information about the elements at the uppermost surface.

The MAPbI₃ film was prepared by the one-step method in N₂ atmosphere. Perovskite precursor solution in DMF was spin-coated on ITO or PEDOT-PSS coated ITO substrates, and toluene was added as a poor solvent during the spin coating. UPS and MAES measurements were performed using a He I α radiation light (21.22 eV) and a metastable He* (19.82 eV) atoms, respectively, at a pressure below 10⁻⁸ pa.

Figure 2 shows the UPS and MAES spectra of MAPbI₃ film. We assigned the features in the spectra based on the DFT calculations^{2,3}; the peak at 3.7 eV to the I *p* derived-states, and the small shoulder at 2.5 eV, and the peak at 4.6 eV to the Pb *s* and Pb *p* derived-states. The features at 9.0 and 11.1 eV, and the small shoulder at 6.9 eV are dominated by MA molecular states, with additional Pb *s* states at 9.0 eV.

The peaks assigned to the I *p* and MA derived-states are observed both in UPS and MAES spectra, while the Pb derived states are not observed in the MAES spectra. The results strongly indicate that the uppermost layer consists of MA and I.

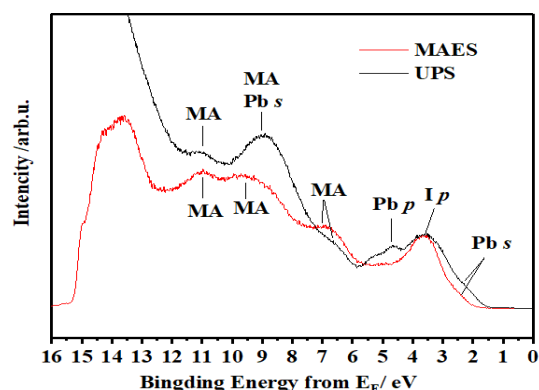


Fig.2 MAES and UPS spectra of the MAPbI₃ thin film on ITO

1. R. Ohmann, et al., *J. Am. Chem.* 137, 16049 (2015)
2. Yin, W et al., *Appl. Phys. Lett.* 104, 063903 (2014).
3. J. Endres, et al., *J. Phys. Chem. Lett.* 14, 2722 (2016)