

XPS depth profiling of advanced solar cells with femtosecond laser ablation

Introduction

Perovskites are an emerging class of materials in the solar cell industry, exhibiting a number of promising properties, such as improved efficiency and weight, compared to traditional silicon-based devices. X-ray photoelectron spectroscopy (XPS) is an established tool in solar cell research due to its ability to provide extremely surface-sensitive information about elemental composition along with chemical and electronic states.¹ XPS is ultimately a surface analysis technique, however, and in order to assess the full composition of complex, multi-layered structures such as solar cells, a technique known as depth profiling is necessary, which performs multiple rounds of successive material removal and analysis.

This application note explores a recent study by Chandler *et al.* that focuses on solar cells designed for aerospace applications,² where accurate determination of the “true” starting composition of the stacks is essential for tests that simulate space conditions, such as radiation exposure. Without a reliable baseline, it becomes impossible to distinguish between changes induced by the experimental conditions and artifacts introduced during analysis. Conventional ion beam sputtering methods used for depth profiling are known to distort chemical information for perovskites; femtosecond laser ablation (fs-LA) is presented as a novel, alternative method that helps to preserve vital chemical information.

Experimental

A halide-perovskite-based solar cell was fabricated on an ITO/SnO₂ substrate using a spin coating method; the structure of the layers is shown in Figure 1.

Analysis was performed with the Thermo Scientific™ Hypulse™ Surface Analysis System, which is equipped with both traditional ion-beam sputtering and femtosecond-laser ablation capabilities. XPS data was collected in SnapShot acquisition mode using an X-ray spot size of 30-200 μm, depending on the method of depth profiling.

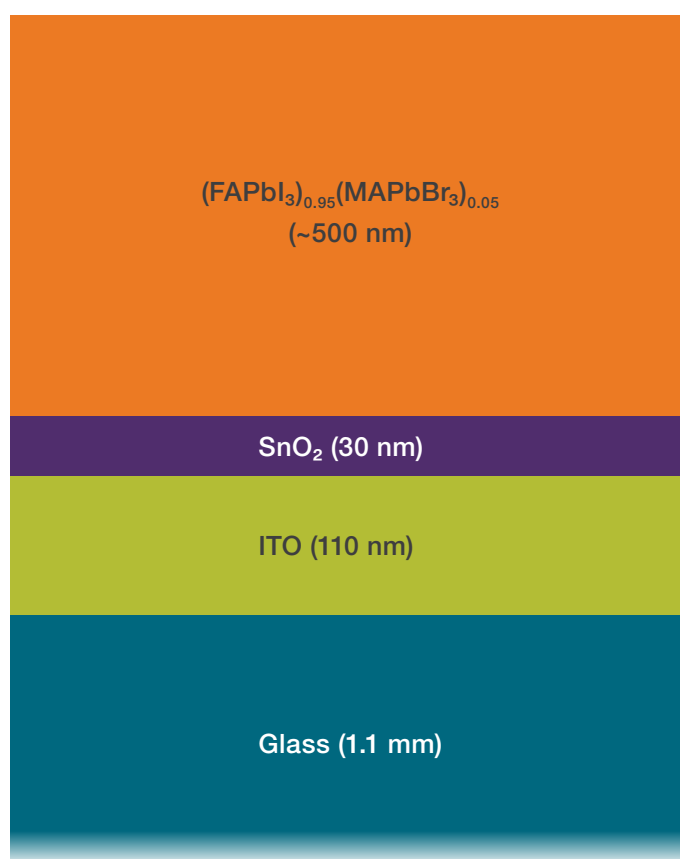


Figure 1. Device structure of the (FAPbI₃)_{0.95}(MAPbBr₃)_{0.05} solar cell analyzed with depth profiling in this study.

A MAGCIS ion gun was employed for the sputter depth profiles, generating either a 500 eV monatomic Ar⁺ beam or 8 keV Ar₁₅₀⁺ clusters. The fs-LA depth profiles were generated using a 1,030 nm wavelength laser operating at a 160 fs pulse length. The pulse energy was increased from 42 μJ to 167 μJ when transitioning from the perovskite layer into the substrate structure. A flood gun was employed for charge neutralization during profiling.

Results

The 500 eV Ar⁺ monatomic and 8 keV Ar₁₅₀⁺ cluster-ion beam depth profiles are shown in Figures 2 and 3, respectively. In the case of monatomic sputtering, the observed elemental composition deviated substantially from the expected stoichiometry. Carbon and nitrogen were significantly depleted, and the I/Pb ratio dropped from the theoretical 3:1 to about 1.7:1. These all indicate preferential sputtering of carbon, nitrogen, and iodine. This distortion was accompanied by the appearance of a Pb⁰ (metallic lead) peak in the Pb 4f spectra through the perovskite layer, indicating beam-induced reduction. These findings clearly demonstrate that even at low energies, monatomic ion beams compromise the chemical state of the perovskite layer, thereby masking the true baseline composition.

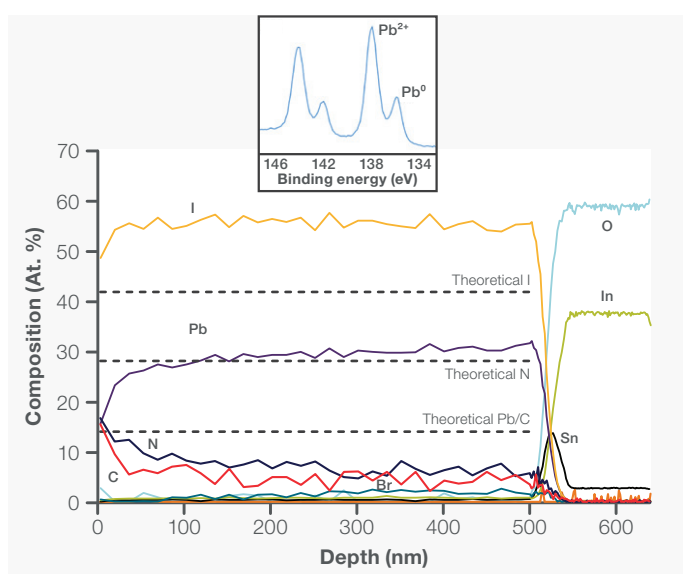


Figure 2. 500 eV Ar⁺ monatomic depth profile of the solar cell sample, showing relative atomic percentages down to the ITO layer. An example Pb 4f spectrum from a midpoint in the perovskite layer is inset.

Cluster ion beam profiling is generally considered to be better suited for organic materials because of a lower energy per atom beam. In this case, however, the damage was shown to be more extensive. Preferential sputtering of carbon and nitrogen was more pronounced, and the Pb⁰ signal was more intense than in the monatomic case. This suggests that thermal effects from the energy-dense surface interaction of the clusters contribute to greater chemical degradation, likely accelerating the conversion of FAPbI₃.

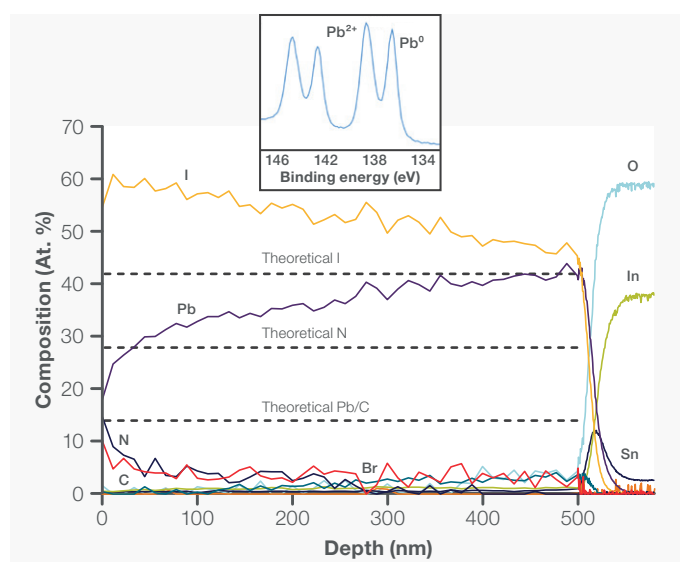


Figure 3. 8 keV Ar₁₅₀⁺ cluster depth profile of the solar cell sample, showing relative atomic percentages down to the ITO layer. An example Pb 4f spectrum from a midpoint in the perovskite layer is inset.

The fs-LA depth profile is shown in Figure 4. In contrast to the ion beam profiles, the elemental distribution obtained with fs-LA closely matched theoretical values and remained stable throughout the entire perovskite layer. The relative intensities for carbon, nitrogen, lead, iodine, and bromine were consistent with the expected stoichiometry. Notably, no Pb⁰ peaks were detected in the core level spectra, indicating that the fs-LA process did not cause reduction of Pb²⁺ or degradation of the perovskite phase. Laser ablation also maintained the chemical integrity of the organic cations (FA⁺ and MA⁺) and halides in the structure. The slight increase in phosphorus, and accompanying decrease in nitrogen, at the beginning of the fs-LA profile is attributed to mild surface contamination or pre-analysis exposure, rather than a profiling artifact.

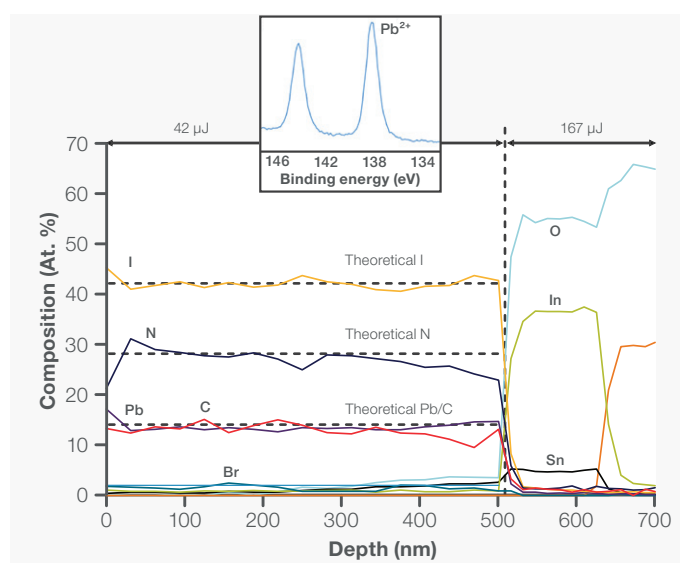


Figure 4. fs-LA depth profile of the solar cell sample, showing relative atomic percentages down to the ITO layer. An example Pb 4f spectrum from a midpoint in the perovskite layer is inset.

Summary

This study confirms the challenges associated with traditional ion sputtering (both monatomic and cluster) for the depth profiling of perovskite-based solar cells. These methods cause preferential sputtering, particularly of lighter elements like carbon, nitrogen, and iodine, which distorts elemental ratios in the profiles and results in artificial signals, such as the formation of metallic lead (Pb⁰). Depth profiling with femtosecond laser ablation represents a novel and robust alternative that preserves the original chemical composition and oxidation states throughout the perovskite layer. By avoiding preferential removal effects, accurate compositional information is maintained during the profile, and erroneous peak signals associated with chemical reduction are eliminated. These factors are vital in establishing a chemically undisturbed baseline before performing tests that simulate environmental effects on the solar cells.

With fs-LA depth profiling, any induced changes can be confidently delineated from analytical artifacts, and researchers can better understand and mitigate environmental effects on solar-cell performance, eventually leading to improved solar technologies for aerospace applications.

References

1. Hoffmann, V, et al. Accessing Elemental Distributions in Thin Films for Solar Cells. *Advanced Characterization Techniques for Thin Film Solar Cells: Second Edition* p523-567 (2016). doi: [10.1002/9783527699025.ch19](https://doi.org/10.1002/9783527699025.ch19)
2. Chandler, CW, et al. Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lead Halide Perovskite Thin Film Solar Cells. *Surface and Interface Analysis* 57:3 (2025). doi: [10.1002/sia.7374](https://doi.org/10.1002/sia.7374)

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