In – depth chemical and optoelectronic analysis of triple-cation perovskite thin films by combining XPS profiling and PL Imaging

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Abstract

Today, perovskite-based solar cells have reached outstanding power conversion efficiencies (PCE) demonstrating a significant prospect for commercialization [1]. However, there are still principal challenges that need to be addressed to further enhance device efficiencies and especially durability. In particular, it is crucial to investigate the chemical and optoelectronic properties of perovskite layers and associated interfaces [2]. In-depth profiling is a powerful method to study the elements distribution and the chemical properties of perovskite layers at different scales from the surface to the bulk. The technique employs ionic argon beam abrasion that provides accurate determination of the in-depth elemental distribution toward buried interfaces. However, there is an urgent need to corroborate the reliability of data on chemical properties of halide perovskite thin films if we consider their fragility. In this present work, we address the question of the perturbation generated by ion beam on triple-cation mixed-halide perovskite surfaces from a chemical and optoelectronic point of view by combining X-ray photoemission spectroscopy (XPS) and photoluminescence (PL) spectroscopy. We investigate both, chemical and optical properties, for different sputtering times to solify our understanding of the sputtering process and the level of the perturbation eventually induced at the surface. For that purpose, we use XPS depth-profiling to assess the composition gradient while tracking the changes induced by the bombardment that could range deeper into the perovskite layer.

XPS profiling is performed by Ar^+ ionic bombardment on identical half-cells constituted of glass / FTO /c-TiO_2 / m-TiO_2 / triple cation Perovskite $Cs_{0.05}(MA_{0.14}, FA_{0.86})_{0.95}$ $Pb(I_{0.84}, Br_{0.16})_3$ for different sputtering times corresponding to successive 50 nm abrasion steps. The comparison of theses sequential depth profiles (Fig. 1) shows a very reproducible elemental distribution inside the perovskite layers. In addition, we observed that, for all the sputtering times, XPS profiling leads to a systematic reduction of Pb from Pb^{2+} to Pb^0 as well as to the degradation of the organic compounds constituting the perovskite layer. This highlights the homogeneity of the perovskite layer, also in its thickness, showing the exact same elemental distribution and the same degradation at the very surface.

In order to study the generated perturbation not only in the surface but also in the bulk, we performed PL measurements inside all the resulting craters. For all the residual perovskite thicknesses (i.e. different sputtering time), the obtained PL spectra show no peak shift nor phase segregation. This demonstrates that there is no cumulative effect of sputtering and that, after bombardment, the changes occurring at the surface such as the creation of metallic lead and the degradation of organic components, do not critically change the optoelectronic properties of the material at both bulk and surface level. These observations therefore validate the determination of the in-depth composition of halide perovskite films by XPS and sequential Ar^+ sputtering.

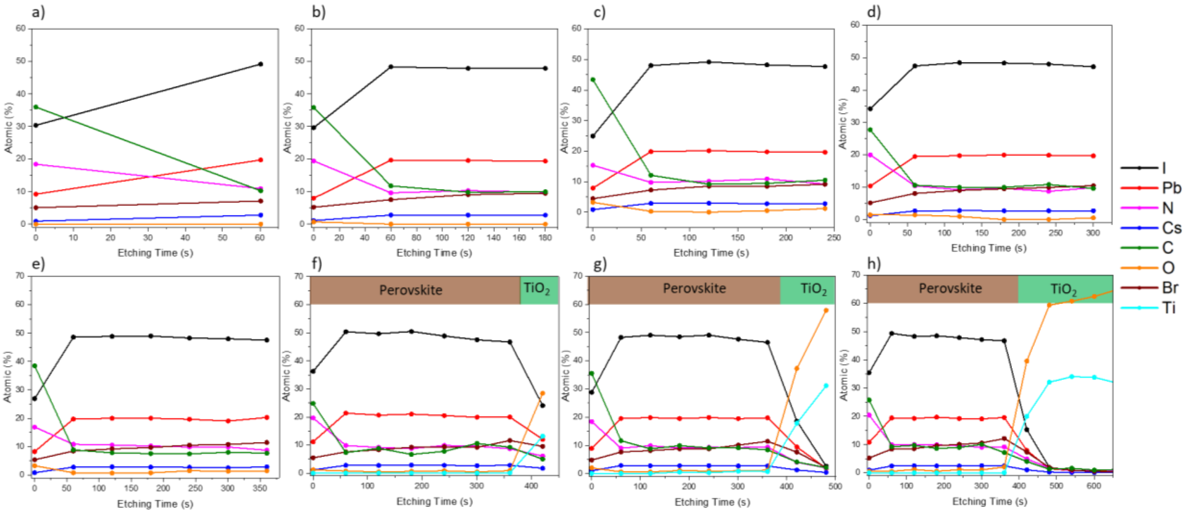

Figure 1: XPS depth profile (Ar$^+$,1000 eV)) of FAMACs perovskite for the a) crater 1 (350 nm), b) crater 2 (250 nm), c) crater 3 (200 nm), d) crater 4 (150 nm), e) crater 5 (100 nm), f) crater 6 (50 nm), g) crater 7 (Perovskite/TiO$_2$ interface) and h) carter 8 (Perovskite/TiO$_2$ interface). Quantification has been made peak fitting in the Br 3d, Cs 3d, I 3d, C 1s, N 1s, Pb 4f, O 1s and Ti 2p regions. Lateral bars on the top of panels f-h indicate the transition from the perovskite layer to the TiO$_2$ substrate.

References

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