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Multi-Analytical Study of Degradation Processes in Perovskite Films for Optoelectronic Applications

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The combination of three instrumental techniques: optical spectroscopy/microscopy, X-ray diffraction and mass-spectrometry (ToF-SIMS with depth profiling) was used to analyze the time, temperature and light induced degradation in thin films of the perovskite-type materials. Hybrid perovskite (MAPbI₃) and inorganic perovskite (CsPbI₃) films were obtained by a thermal vacuum evaporation and subjected to illumination by the continuous and monochromatic light. Photoelectrical measurements were carried out on the multilayer devices, in which perovskite was sandwiched between CuI hole transporting and C₆₀ electron transporting layers.

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1. Introduction

Recently, we investigated the planar hybrid heterojunction p -CuI/ n -C₆₀ for the semitransparent photovoltaic cells [1]. In the present work, we introduced the hybrid perovskite in this junction, so that CuI and C₆₀ form an envelope of the hole- and electron-transporting layer, respectively. Perovskite (*e.g.*, MAPbI₃, CsPbI₃) itself is a widely used in the photovoltaics due to unique electro-physical properties, however, performance of the perovskite-based cells is dramatically affected by the perovskite layer structure that is, in turn, determined by the processing conditions (substrate temperature, deposition rate, under- and overlying functional layers, *etc.*) [2, 3]. Therefore, the challenging issue is the proper adaptation of functional layer materials to the deposition techniques used for fabrication of the multilayer structure in order to minimize the degradation. Hereinafter, the deposition technique is thermal vacuum evaporation for all the materials used.

2. Experimental procedures

The cuprous iodide CuI (99.999%) and buckminsterfullerene C₆₀ (99.9%) were used to form the charge transporting layers adjacent to the main perovskite photoabsorber. Glass substrates covered with a transparent indium tin oxide ITO (Aldrich, 25 Ω/sq) and thin-film (semitransparent) silver (99.9% SBRF) layer served as the bottom and top electrodes, respectively. Bathocuproine BCP and molybdenum trioxide MoO₃ were used as the buffer layers materials. The functional layers were deposited sequentially on various substrates

using a VUP-5M vacuum station in the thermal evaporation mode at the pressure $< 10^{-6}$ Torr in the following order: MoO₃ (3 nm)/CuI (15 nm)/MAPbI₃ (200 nm)/C₆₀ (35 nm)/BCP (8 nm)/Ag (20 nm). The thickness, density and morphology of the perovskite layers were studied by quartz crystal microbalancing, X-ray diffraction and reflectometry, XRD + XRR (Bruker D8 Discover diffractometer) and white-light interferometry, WLI (TalySurf CCI2000 profilometer). The time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiments were carried out in a TOFSIMS5 spectrometer as described previously [4]. The optical transmission of samples in the range of 350–900 nm was analyzed with a FireFly4000 spectrometer. The $J - V$ measurements were done using a Keithley SCS-4200 parameter analyzer. A mirror halogen lamp providing the average incident power of 25 mW/cm² and a MDR-41 LOMO monochromator were used for illumination. During measurements, the samples were kept into a shielded chamber filled with the ultra-pure Ar to minimize the atmospheric effects (O₂, H₂O).

3. Results and discussion

Figure 1a shows the dynamic $J - V$ plots of the multilayer cell under the white light illumination. In Fig. 1b, a KC-10 cut-off filter was inserted between the light source and sample, thus irradiation with wavelengths shorter than 520 nm was damped. In both cases, the prolonged illumination leads to the stepwise degradation of characteristics. However, while the filtered light causes rather a decrease in U_{oc} (by ~ 0.2 V after 2 h exposure), the continuous white light causes both a weak decrease in U_{oc} and dramatic drop of J_{sc} (by more than 2 orders of magnitude).

To prove whether the Joule heat produced by illumination or incident photons are responsible for these changes, the cells were exposed to a low-intensity monochromatic light of 497 ± 3 nm. As seen from Fig. 1c, the degradation picture in such a case is similar to that induced by

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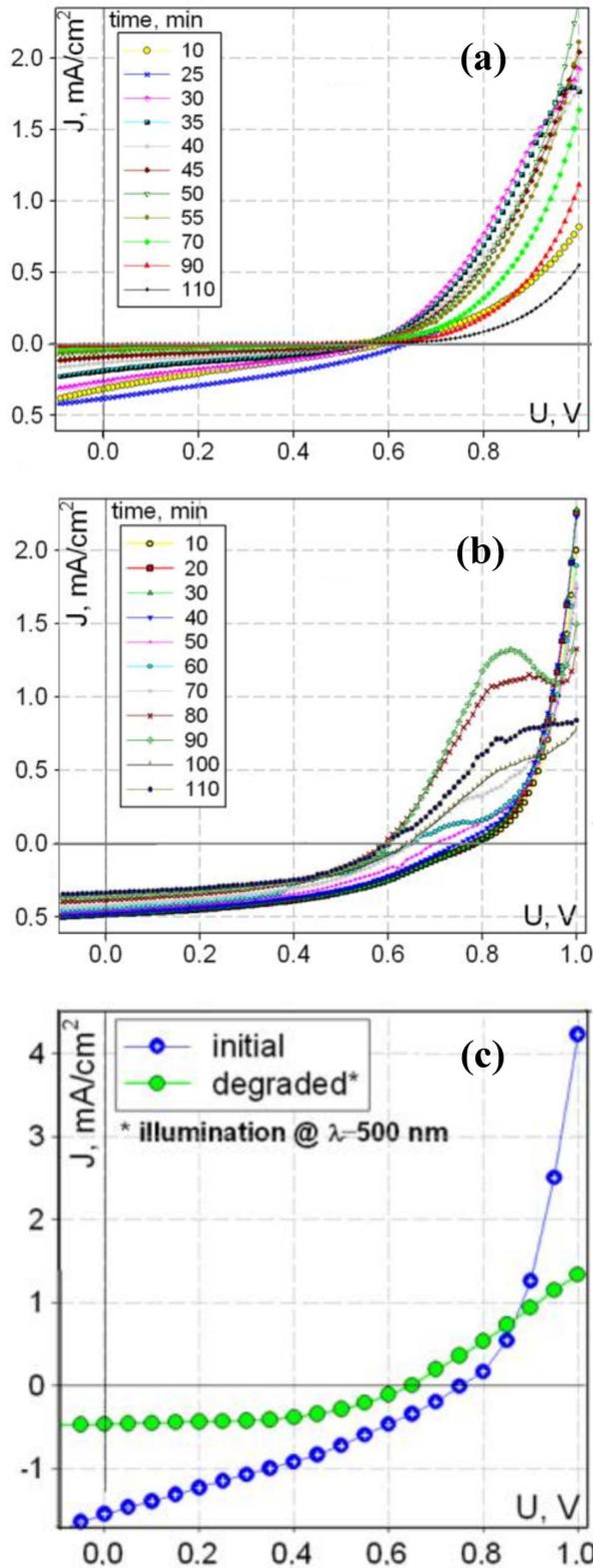


Fig. 1. $J - V$ plots for the cells glass/ITO/MoO₃/CuI/MaPbI₃/C₆₀/BCP/Ag: (a) illumination with continuous white light; (b) illumination through a filter cutting the short wavelength light; (c) illumination with a low-intensity monochromatic light of 500 nm during 20 h in the inert atmosphere.

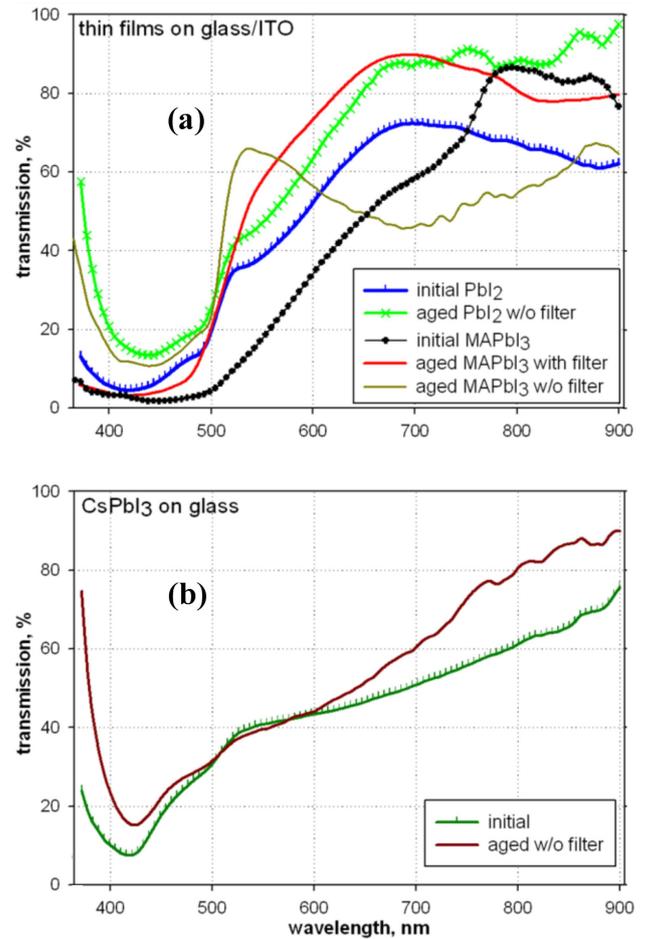


Fig. 2. Optical transmission spectra of (a) MAPbI₃, PbI₂ and (b) CsPbI₃ films.

the unfiltered (continuous) light. This suggests that the photodestruction dominates over the thermodestruction even if the perovskite material is kept under the inert conditions [5]. It should be noted that forward and reverse bias $J - V$ dependences of degraded samples (not shown) do not coincide, possibly due to the presence of ionic component in the electrical conductivity.

XRD, optical transmission and microscopic studies were performed to interpret the trend observed in the $J - V$ plots. Tang *et al.* [5] reported that MAPbI₃ is always stable under illumination if kept under the inert atmosphere. However, even if we “aged” a MAPbI₃ film on glass/ITO (blank sample) in the inert atmosphere by exposure to the white light for hundreds minutes, relative intensity of the MAPbI₃ peaks in the XRD spectra decreases, whereas intensity of peaks related to the PbI₂ phase increases.

Transparency of the strongly degraded PbI₂ films tends to increase in the near infrared, but the overall shape of the optical spectrum unaltered with aging – Fig. 2a. Absorption of photons by the hybrid perovskite MAPbI₃ suffers from aging even with a cut-off filter: the films become significantly more transparent at wavelengths

longer than 500 nm and up to 800 nm. Aging without filter leads to the further degradation of the spectral shape in this range – Fig. 2a. Similarity of spectra of the slightly degraded MAPbI₃ film and the initial PbI₂ film points to the increasing content of inorganic component in the perovskite structure.

Next, MAPbI₃ was aged as a part of the multilayer photovoltaic cell (see, Fig. 1) over 2 h with and without a KC-10 optical filter with a stepwise monitoring of XRD pattern. When the sample was aged without filter, the XRD peaks related to MAPbI₃ decrease, while the peaks of the PbI₂ (001) phase grow up. When aging was carried out using the cut-off optical filter, no significant changes in the crystalline structure are detected. Therefore, degradation processes in the bulk of the hybrid perovskite are essentially due to the absorbed photons in the range below 520 nm. Comparison of the optical and XRD studies indicates that the perovskite structure deteriorates starting from the re-texturization of the layer and the partial photodestruction of PbI₂ (decomposition to metallic Pb and I₂ [6]), but dominating process is the rapid accumulation (segregation) of PbI₂ phase.

In contrast to the hybrid perovskite, fully inorganic CsPbI₃ films (on glass) do not degrade under illumination, whatever the atmosphere (*cf.* – [3]). It is confirmed by the minor changes in the optical transmission spectra of aged samples (Fig. 2b) and by the absence of alterations in the surface morphology of CsPbI₃. So, the r.m.s surface roughness of the fresh made MAPbI₃ film measured by WLI on the scanning area of 0.9 × 0.9 mm² is 2.2 nm. Aging without filter increases this value to 3.4 nm, whereas after aging with filter roughness increases only to 2.5 nm. At the same time, the surface roughness of the CsPbI₃ film remains equal to 2.4 nm after any kind/time of aging.

ToF-SIMS analysis with an accurate depth profiling was carried out for both negative and positive secondary ions characteristic of each component of the structure, including the bulk substrate. For the intact samples, the chemical interface is less abrupt when MAPbI₃ is deposited on the ITO/glass compared to MAPbI₃ on the bare glass (from which ITO coating was etched off before depositing the perovskite). Other evidences of intermixing of the perovskite components, *e.g.*, iodine species, with the topmost ITO layers were also found. On the other hand, ITO prevents from the upward diffusion of admixtures, mainly alkali metals, from the bulk glass into the perovskite film.

ToF-SIMS confirms accumulation of PbI₂ detected earlier by XRD and reveals intensive ablation of the organic component of perovskite from the film in the aged samples. The latter process is somewhat inhibited by ITO coating. On any substrate, early stages of degradation can explicitly be seen as blurring of the chemical interface between MAPbI₃ and substrate. In case of the ITO/glass substrate, the indium species were detected throughout the degraded perovskite film, while the iodine species penetrate deeply into ITO. An interesting issue is the

oxidation of perovskite layer [7], which was traced from the concentration of a large number of different oxygen-containing species. Except for the surface concentration jump, the oxidation front develops from the substrate side in all cases, so that non-oxidized intact perovskite, or its degraded residue after aging, remains close to the surface of the film, but not in the film bulk (*cf.* – [7]).

4. Conclusion

Efficiency of the archetypal cells with a hybrid CuI/C₆₀ heterojunction was improved by insertion of the hybrid perovskite MAPbI₃. This is however not the case for the vacuum-deposited inorganic CsPbI₃, which is not compatible with the adjacent components CuI and C₆₀. In the inert atmosphere, the incident light in the range of ~ 500 nm is responsible for the degradation of hybrid perovskite MAPbI₃, removal of this factor extends the lifetime of this material. Degradation of MAPbI₃ occurs not solely through segregation of PbI₂ but also through transformation of PbI₂ that has already existed in the intact perovskite structure. The latter transformation is probably incomplete and consists in the texturizing of PbI₂ and in release of the metallic lead. Inorganic perovskite CsPbI₃ is itself much more stable than its hybrid congener MAPbI₃. However, its introduction into the multilayer cells with a given scheme/method is difficult, and the resulting devices show a very poor photovoltaic performance. Further optimization of the scheme and processing of the vacuum-only deposited photovoltaic cells incorporating inorganic perovskite is therefore a challenging issue.

Acknowledgments

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