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Electrical and optical degradation study of methylammonium-based perovskite materials under ambient conditions

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ABSTRACT

Hybrid perovskites have emerged over the past five years as absorber layers for novel high-efficiency low-cost solar cells which combine the advantages of organic and inorganic semiconductors. One of the main obstacles to their commercialization is their poor stability under light, humidity, oxygen, and high temperatures. In this work, we compare the optical and the electrical light-induced degradation of $CH_3NH_3PbI_3$ ("MAPI")-based solar cells using real-time ellipsometry measurements, electrical measurements and X-Ray Diffraction (XRD) techniques. We evidence that while the electrical degradation takes place on a short time scale (2–3 days of exposure to ambient light conditions in a nitrogen atmosphere), no optical degradation is observed before 10 days when the dissociation reaction of methylammonium lead iodide starts acting. We find a very good agreement between XRD and ellipsometry measurements; both show the appearance of PbI_2 after 1 week of exposure. We also confirm that the main mechanism at play is a light-induced degradation affecting the edges of the stack and the interfaces between the perovskite and the neighbouring layers. Last, a very good match is obtained on the optical constants of MAPI between our ellipsometry measurements and density functional theory calculations we performed, and we confirm the behavior of MAPI as an inorganic semiconductor.

1. Introduction

Even though the efficiency of hybrid perovskite solar cells (PSCs) has jumped from 4% in 2009 to certified efficiencies over 20% [1] in 2015 and a record efficiency of 22.7% [2] in 2017, the mechanisms behind their fast degradation have yet to be fully understood. Long-term stability, in particular in terms of efficiency, is a crucial point for any photovoltaics technology to reach the market.

Niu et al. [3] gave a first general understanding of the possible pathways of the chemical decomposition of the perovskite layer in 2015. This fast degradation has been attributed to different factors, among them: humidity, temperature, oxygen, and light [4]. While many studies focused on the role played by H_20 molecules in air [5], the mechanism behind ambient light-induced degradation remains unclear. Ito and co-workers [6] used UV–Vis absorption and X-Ray Diffraction (XRD) to show that after 12 h of light exposure, $CH_3NH_3PbI_3$ ("MAPI" or $MAPbI_3$) transformed into PbI_2, evidenced by the decreased UV–Vis absorption and XRD patterns. A possible mechanism to explain this degradation process is [6]:

$$2I^- = I_2 + 2e^- \tag{1a}$$

$$3CH_3NH_3^+ = 3CH_3NH_2 \uparrow + 3\,H^+ \tag{1b}$$

$$I^- + I_2 + 3\,H^+ + 2e^- = 3HI\uparrow \tag{1c}$$

The evolution of the optical properties of hybrid perovskite thin films with time can be followed using real-time spectroscopic ellipsometry techniques [7]. Shirayama et al. [8] used this method, together with Density Functional Theory (DFT) calculations, to investigate the degradation of $CH_3NH_3PbI_3$ upon exposure to humid air.

In this paper, we compare the optical and the electrical light-induced degradation of $CH_3NH_3PbI_3$-based solar cells using real-time ellipsometry measurements, electrical measurements and X-Ray Diffraction (XRD) techniques. Electrical characterization is performed on devices with a full solar cell structure using PEDOT-PSS as a hole transporting layer, and PCBM (Phenyl-C61-Butyric acid Methyl ester) as an electron transporting layer (see Section 2.1 for details). Ellipsometry

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and XRD are performed on a stack consisting of all the layers up to the perovskite layer. We followed the degradation with ellipsometry for 17 days and 2–3 measurements per day.

In order to focus on light-induced degradation, the first measurements were made while keeping the cells in a nitrogen atmosphere, even during the ellipsometry characterization (see Section 2.1). We also performed complementary ellipsometry measurements both in the dark and in air, to check if the degradation measured here could result from other factors than ambient light. We found out that keeping the cell in a nitrogen atmosphere does not seem necessary in order to study the light-induced degradation. Unless otherwise specified, the degradation studies reported here are made on layers prepared by evaporation. Additional studies on solution-processed samples are shown for comparison.

We also perform Density Functional Theory (DFT) calculations to get ab-initio values for the optical constants of MAPI. In particular, we study in detail in Section 3.3 its dielectric properties. The dielectric constant in the high-frequency regime (taking into account only electronic contribution) is obtained as a second derivative of energy with respect to electric fields. The dielectric function in the visible range is computed in the Random Phase Approximation (RPA) from KS eigenvalues and eigenvectors and compared to ellipsometry measurements we performed under a nitrogen atmosphere (see Section 2.2 for computational details).

As for the static dielectric constant (low frequency regime), ionic contributions are taken into account through the coupling of phonons with the electric field. The phonons are obtained by using the linear response approach of DFT, as known as DFPT (Density-Functional Perturbation Theory), see Section 2.2. Given the structural instability and the anharmonicity behavior previously reported for halide perovskites [9–12], we made sure to properly relax the structure to avoid soft phonon modes.

The PSC community has for some time had trouble agreeing on MAPI's exciton binding energy, and on whether it behaves more like organic compounds (high exciton binding energy, low dielectric constant) or vice-versa like inorganic compounds. We use here the phonon spectrum obtained for the pseudocubic phase of $MAPbI_3$ to confirm that it behaves as an inorganic semiconductor.

2. Experimental and computational methods

2.1. Experimental

For solution process, the analyzed samples consist of layers of (from bottom to top) glass, ITO, PEDOT: PSS and $MAPbI_xCl_{1-x}$, the latter two made under a nitrogen atmosphere. The ITO coated glass is patterned using a wet etching process with zinc powder and HCl, cleaned with deionized H_2O (DI water), acetone and isopropanol. A PEDOT: PSS (40 nm thick) hole transport layer is deposited on the ITO substrate using a spin-coating process and heated at 120 °C for 20 min in N_2 conditions. A perovskite solution (in DMF) composed of PbI_2, $PbCl_2$ and MAI with a 1:1:4 molar ratio is spun at 6000 r.p.m onto the PEDOT: PSS layer and heated at 80 °C for 2 h in N_2 conditions. The thickness of the obtained perovskite film is estimated to be 350–400 nm. We then deposited a filtered PCBM solution by spin coating (1-step process: 3000 rpm for 35 s) in the glove box (N_2 condition), and, without annealing, we deposited the Ag cathode using thermal evaporation.

For evaporation process, the analyzed samples also consist of layers of (from bottom to top) glass, ITO, PEDOT: PSS and $MAPbI_3$, the latter two made under a nitrogen atmosphere. ITO and PEDOT: PSS are prepared in the same way as for solution-processed cells. Then, the perovskite layer (around 250 nm) is deposited by thermal co-evaporation of MAI and PbI_2 with a 3:1 ratio on the PEDOT: PSS films. The evaporation rate is controlled by temperature through different parameters (current, voltage). In order to avoid a penetration of MAI inside the PEDOT: PSS layer, a thin layer (around 10–30 nm) of pure PbI_2 is deposited prior to co-evaporation. After breaking the vacuum and cooling, we annealed the perovskite thin films at 80 °C for 1 h under a nitrogen atmosphere. PCBM and Ag were deposited the same way as in the solution process.

The samples are scanned by a UVISEL, a phase-modulated spectroscopic ellipsometer (HORIBA) with an incidence angle of 60 °C and a wavelength range of 0.6–4.6 eV (270–2100 nm). As MAPI is a direct transition semiconductor (in the first order approximation), the Tauc-Lorentz [13] formula is used to extract the optical constants of the perovskite layer, after having extracted PEDOT: PSS and ITO optical constants with Glass/ITO/PEDOT: PSS samples beforehand. The ellipsometry fitting parameter χ^2 is kept under 15, as it is usually the case in order to have a good match between our model and the actual optical parameters [13]. The study of the bottom layers allows to concentrate our efforts only on the perovskite. Thanks to a sealed box, the samples are kept in a N_2 atmosphere during the first ellipsometry measurements, but this seemed to be unnecessary as it did not influence the optical light-induced degradation.

For t < 6 days, the perovskite film is modeled using three layers to take into account the variation of index in the depth and a surface roughness layer (see Fig. 1). These 3 layers are described using the Bruggeman Effective Medium Approximation, which consists of a mix of $MAPbI_3$ and void, whose volume fraction varies for the bulk perovskite and the bottom layer. The surface roughness is described with 50% of $MAPbI_3$ and 50% of void as introduced by Aspnes et al. [14]. The volume fraction of $MAPbI_3$ decreases day by day for both layers and more importantly for the bottom layer.

For t > 6 days, the perovskite film is still modeled using 3 layers with variation of the different volume fractions for each layer from the bottom to the top. In addition, we included a fraction of PbI_2 in these layers (see Fig. 2).

The optical transitions of the perovskite thin film are reported in the Supporting Information file and are coherent with the literature [7].

The absorbance is measured using a UV–Vis spectrophotometer. Given the wavelength range where the signal is not saturated (500–800 nm), the only optical transition which can be followed day after day is the band gap one around 1.57 eV.

The XRD measurements were carried out on samples exposed to ambient light and done at regular times from right after fabrication to after 6 weeks of exposure. The incident angle was increased from 5° to 75° by steps of 0.03°.

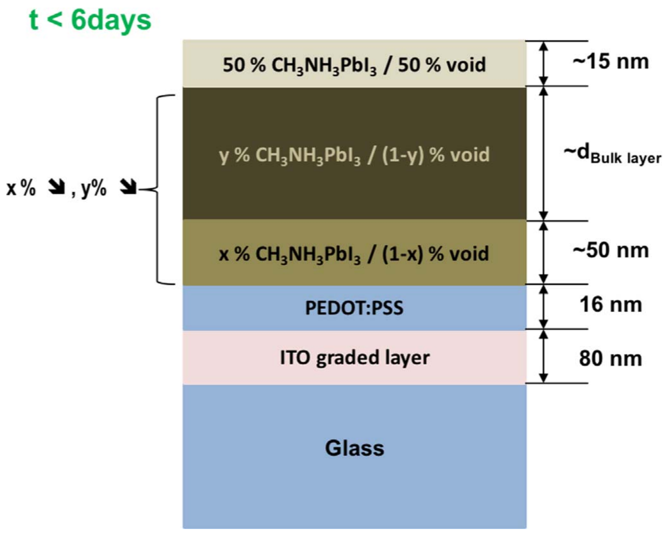

Fig. 1. Model used to fit the optical constants during the first 6 days of ageing. Layers are numbered starting from glass (L1) to the top (L6).