MICROSCOPIC AND KELVIN PROBE STUDY OF CHARGE TRANSPORTING LAYERS ROLE IN MAPI PEROVSKITES WITH VARIED COMPOSITION

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Abstract

Perovskites are one of the most intensively studied photovoltaic materials nowadays. Microscopic studies can provide useful information about material roughness, conductivity, structure, mechanical and opto-electronic properties as well as about kinetic effects from short to long time scale for understanding and improving the photovoltaic performance. Here, time-resolved photovoltage was measured by Kelvin probe in the dark and under white light illumination. Morphology was characterized by optical and atomic force microscopy. We identify the impact of charge transporting layers (CTLs) on structural and opto-electronic properties of MAPbI₃ perovskite with different ratio of MAI and PbI₂.

Keywords: Perovskites, ionic migration, solar cells, charge transporting layers

1. INTRODUCTION

Perovskites are one of the most intensively studied photovoltaic materials nowadays due to their strong optical absorption, adjustable band gap, long carrier diffusion lengths, ambipolar charge transport, high carrier mobility, and high tolerance of defects [1]. They are applied in various opto-electronic devices, such as solar cells, light-emitting diodes, photodetectors, or lasers. The power conversion efficiencies (PCEs) of perovskite solar cells (PSC) have reached over 23 % [2]. The hysteresis, common for various perovskite-based solar cells, has been regarded as one of the main problems to be solved. The hysteresis was described first in detail by Snaith et al. [3]. Three main causes of hysteresis were proposed: (a) interfacial traps which are filled/emptied depending on bias, (b) ferroelectric polarization, and (c) screening of the built-in electric field by mobile ions in the film. The influence of ion migration [4-6], hole transporting materials (HTMs), and grain boundaries [7,8] on hysteresis was previously investigated. The research in PSC made great progress but there are still unexplained ionic defects (halides, Pb and methylammonium vacancies) in grain boundaries and interfaces crucially governing the devices performance and stability [9-11].

To elucidate these factors, we study here the impact of precursor stoichiometry (methylammonium (MAI) and PbI₂) and charge transporting layers (CTLs) on the degradation process of MAPbI₃ perovskite. The influence of CTLs (SnO₂ and Spiro-OMeTAD as electron and hole transporting materials) and different ratio of MAI and PbI₂ (MAI/PbI₂ = 0.9, 1.0) was investigated by Atomic Force Microscopy (AFM) and Kelvin probe. All samples were measured repeatedly during 28 days.

2. MATERIALS AND METHODS

Samples were made according to established protocol [12]. The Indium Tin Oxides (ITO) substrates were cleaned. SnO₂ solution were then spin-coated on substrates as the electron transport layer (ETL). The thickness was around 40 nm. Methylamine iodide and lead (II) iodide were predissolved in N, N-
dimethylformamide as precursor solution before spin-coating process. After SnO$_2$ annealing, MAPbI$_3$ precursor solution was then spin-coated on ETL as an intrinsic layer at 3000 rpm for 20 s. The thickness of perovskite film was around 300 nm. The iodine was doped into the spiro-OMeTAD solution in different concentrations. The dopant was varied from 0 mg/mL to 15 mg/mL in a gradient of 3 mg/mL. The perovskite samples with MAI/PbI$_2$ ratios 0.9 and 1.0 and CTLs with and without were investigated by AFM (AC mode, 75 kHz tip) using WITec Alpha 300 RAS system and software Control 5.1. Data acquisition and processing were done by the WITec Control and Project Five 5.1 software. The work function and photovoltage of the samples with and without CTLs were investigated by Kelvin Probe (KP Technology) in Faraday cage in the dark and under illumination with a switching on/off period of three minutes. Thereby obtained photovoltage can be related to open-circuit voltage ($V_{oc}$) of the device [13]. The Kelvin Probe measurements were repeated after 14 and 28 days.

3. RESULTS AND DISCUSSION

3.1. Optical and Atomic Force Microscopy characterization

Figure 1 shows optical and AFM topography images of the samples, where PVSK stands for perovskite. The optical images show flat surface with occasional black spots. A mechanical scratch is also noticeable in the ITO/PVSK and ITO/SnO$_2$/PVSK images.

![Figure 1 Optical and AFM topography images for MAI/PbI$_2$ 0.9 (1st-2nd row) and MAI/PbI$_2$ 1.0 (3rd-4th row) without and with various CTLs combinations](image)
Otherwise not much differences can be identified in the optical images. On the other hand, the AFM images illustrate that both CTLs and MAI can influence the morphology of the perovskite. ITO/PVSK and ITO/ETL/PVSK with MAI/PbI$_2$ = 1.0 seems to have somewhat smoother surfaces and bigger grains (~ 57 nm height, ~ 430 nm diameter) compared to the samples with MAI/PbI$_2$ = 0.9 (~ 23 nm height, ~ 180 nm diameter). AFM images of samples with SnO$_2$ (rows 2 and 4, 2nd column) exhibit similar structure as ITO/PVSK, only there is noticeably less of fine structured grains. The deposition of SnO$_2$ on the ITO surface thus helped reduce granularity and improved PVSK uniformity. After the Spiro coating the surface roughness (Sq) of the samples reduced significantly (for MAI/PbI$_2$ = 0.9: Sq(ITO/SnO$_2$/PVSK) ≈ 988 nm, Sq(ITO/SnO$_2$/PVSK/Spiro) ≈ 81 nm; for MAI/PbI$_2$ = 1.0: Sq(ITO/SnO$_2$/PVSK) ≈ 34 nm, Sq(ITO/SnO$_2$/PVSK/Spiro) ≈ 29 nm). The Spiro is thus filling the rough surface rather than being conformal. Topography images of ITO/PVSK/Spiro samples still show some noticeable crystal structures (15 nm high with diameter 35 nm), which are less pronounced in the samples with SnO$_2$ layer deposited below the PVSK (Figure 1, 4th column, rows 2 and 4). Thus, the complete layer stack with both CTLs provides the best overall PVSK uniformity. This may be important feature for homogeneous charge collection via CTLs and reducing degradation due to ion migration.

3.2. Kelvin Probe study

The influence of CTLs and PVSK morphology on materials work function (WF), photovoltage (PV) and stability in time was studied by Kelvin probe. Figure 2 shows the results for the samples with ratio MAI/PbI$_2$ = 0.9. The sample with ITO/PVSK (Figure 2A) was stable, with WF of 4.96 ± 0.03 eV in the dark for the whole period of 28 days. The PV was negative (seen as higher work function after illumination) and remained also more or less stable (-0.19 V) during 28 days. The negative PV means that electrons were not extracted to the bottom electrode but rather diffused to the PVSK surface.

Work function of the ITO/PVSK/Spiro sample was also stable (5.28 ± 0.02 eV) without significant changes during 28 days (Figure 2B). However, the PV response was small -0.4 V after 28 days. This means that Spiro was actually able to extract some holes to the surface and thereby compensated the negative photovoltage of PVSK.

In the ITO/SnO$_2$/PVSK sample (Figure 2C) the WF was lowered (4.59 ± 0.07 eV) compared to ITO/PVSK samples. There was also some persistent charging observed during the short-term light on-off switching. The WF in dark fluctuated between 4.73 ± 0.06 eV and 4.54 ± 0.06 eV during 28 days. The PV also fluctuated between -0.38 V and -0.17 V during 28 days, even some increase in time was observed. The ITO/SnO$_2$/PVSK system is thus largely unstable. Moreover, overall photovoltage remained negative. Hence, even with ETL, electrons were not extracted but rather diffused to the PVSK surface.

Figure 2D displays work function and photovoltage for the complete ITO/SnO$_2$/PVSK/Spiro sample. The WF in dark decreases from 5.33 ± 0.07 eV to 5.09 ± 0.07 eV during 28 days. Photovoltage is positive in this case, compared to all other samples. Thus, only with the complete layer stack the PVSK operates as expected, i.e. holes are collected by Spiro HTL on the surface and electrons are transported to bottom SnO$_2$ ETL. It is surprising that the PV is negative on the sample even with Spiro in the absence of SnO$_2$ at the bottom. Thus, the Spiro-PVSK interface is not working correctly in that case, most likely because of different PVSK structure on ITO compared to ITO/SnO$_2$ as indicated by AFM data above.

Initially the photovoltage on ITO/SnO$_2$/PVSK/Spiro sample is high (0.73 V) and reproducible, but after 28 days there is again some persistent charging observed during the short-term light on/off switching. The PV also progressively decreases from 0.73 V to 0.19 V after 28 days. This decrease evidences degradation of the material (or more precisely of the layer stack) properties with large contribution from SnO$_2$. This is most likely due to ion migration as indicated by a slower kinetics during the light on/off switching.

Figure 3 shows Kelvin probe measurement results of the samples with MAI/PbI$_2$ = 1.0 with and without CTLs. For ITO/PVSK samples, the WF measured in the dark (5.1 ± 0.1 eV) decreased in time (4.6 ± 0.1 eV and 4.7 ± 0.1 eV after 14 and 28 days, respectively). The PV fluctuated between -0.18 V and -0.78 V during 28 days.
Figure 2 Kelvin probe study of degradation for MAI/PbI$_2$ = 0.9 in the dark and under illumination with a switching on/off period of 180 s and degradation period for 28 days: A ITO/PVSK, B ITO/PVSK/Spiro, C ITO/SnO$_2$/PVSK, D ITO/SnO$_2$/PVSK/Spiro.

The WF in ITO/PVSK/Spiro sample (Figure 3B) was stable (5.19 ± 0.06 eV) for 14 days after 28 days decreased (5.03 ± 0.06 eV). The PV response was higher and clearly positive (0.26 V) compared to the sample with MAI/PbI$_2$ = 0.9. The positive PV means that holes were extracted by Spiro. Also, a kinetics in ITO/PVSK/Spiro was slower during the light on/off switching compared to the sample with MAI/PbI$_2$ = 0.9.

The WF in ITO/SnO$_2$/PVSK (Figure 3C) fluctuated between 4.71 ± 0.03 eV and 4.97 ± 0.03 eV during 28 days. The photovoltage fluctuation between -0.20 V and -0.05 V was observed during 28 days as well. The kinetics process during switching on/off in ITO/SnO$_2$/PVSK was slower compared to the same sample with MAI/PbI$_2$ = 0.9.

For the complete ITO/SnO$_2$/PVSK/Spiro layer stack (Figure 3D) the WF in dark decreased from 5.26 ± 0.06 to 5.02 ± 0.06 eV during 28 days. The PV is positive in this case, also as in the ITO/SnO$_2$/PVSK/Spiro with MAI/PbI$_2$ = 0.9. The function of CTLs is thus the same as described above for the sample with MAI/PbI$_2$ = 0.9. However, photovoltage is smaller and more unstable. Initially the PV on ITO/SnO$_2$/PVSK/Spiro sample is 0.32 V, after 14 days it increases to 0.51 V, and then decrease to 0.16 V after 28 days.

The observed effects are generally similar as for the samples with MAI/PbI$_2$ = 0.9. Yet there are some differences. Even for the same CTLs layers there was slower kinetics during the light on/off switching and photovoltages were much more fluctuating. These effects of the excess MAI are most likely due to more pronounced ion migration effects. This is correlated with difference in PVSK structure as hinted by AFM morphology.
Figure 3 Kelvin probe study of degradation for MAI/PbI$_2$ = 1.0 in the dark and under illumination with a switching on/off period of 180 s and degradation period for 28 days: A ITO/PVSK, B ITO/PVSK/Spiro, C ITO/SnO$_2$/PVSK, D ITO/SnO$_2$/PVSK/Spiro.

4. CONCLUSION

In this work the impact of precursor stoichiometry (methylammonium (MAI) and PbI$_2$), granularity, and charge transporting layers (CTLs) on the properties and degradation of MAPbI$_3$ perovskite was observed. The influence of CTLs (SnO$_2$ and Spiro-OMeTAD) and different ratio of MAI and PbI$_2$ (MAI/Pb$_2$ = 0.9,1.0) on morphology, ion migration and degradation were analysed by AFM and Kelvin Probe. The optical and AFM images overall illustrate how both CTLs and MAI can in certain degree influence the morphology of the perovskite. The optical images do not show much structural differences. On the other hand, the AFM morphology images showed effect of CTLs and MAI on surface properties as size of grains and roughness. Kelvin probe study revealed that also the surface work function, photovoltage including kinetics and direction of charge extraction as well as overall stability depend on CTLs and content of MAI. Thereby the Kelvin Probe results also indicated that the excess PbI$_2$ has influence on ion migration. The changes of the photovoltage kinetics on samples coated with Spiro indicated also possible structural differences in PVSK layer that could not be observed directly by AFM on surface.

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