Lead iodide as a buffer layer in UV- induced degradation of CH3NH3PbI3 films

Ambrose A. Melvina, Vasil Dimitrov Stoichkovb, Jeff Kettleb, Dmitri Mogilyanskyc,

Eugene A. Katza,c\*, Iris Visoly-Fishera,c\*

aDepartment of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Midreshet Ben-Gurion 8499000, Israel.

bSchool of Electronic Engineering, Bangor University, Dean Street, Bangor, Gwynedd, Wales LL57 1UT, UK

cIlse Katz Institute for Nanoscale Science & Technology, Ben Gurion University of the Negev, Beer Sheva 8410501, Israel

E-mail: keugene@bgu.ac.il, irisvf@bgu.ac.il

**Abstract**. Encapsulated CH3NH3PbI3 films, the 'work horse' of the organic–inorganic perovskite-based photovoltaics, grown by one step- and two step- deposition methods, were used to study the effect of the film preparation method on their photostability. Time dependent light absorption decay under exposure to concentrated sunlight was used to estimate the degradation of the films. Films deposited by one step showed a significant decrease in the CH3NH3PbI3 absorbance when illuminated through the substrate, while films obtained through two step deposition exhibited almost no photodegradation under similar sunlight exposure. On the other hand, both types of films degraded significantly when irradiated through the top encapsulation. Unreacted PbI2 present near the substrate is suggested to be responsible for enhancing the photostability of the films obtained by two step deposition. Here, remnant PbI2 works as a UV filter and reduces UV light-induced degradation. The results demonstrate the significance of the preparation method in determining photochemical stability of the perovskite films, due to favorable property of remnant PbI2 in the absorber as a UV- protective layer.

**Keywords**: Perovskites, solar cell, stability, photodegradation, UV light

1. Introduction

Organic–inorganic perovskites are of interest for photovoltaics due to their ease of processing and high photo-conversion efficiency (PCE) of over 20 % (Kojima et al., 2009; Saliba et al., 2016). A significant enhancement in efficiency over the last 8 years was driven by optimization of the thin film formation and structural design of the device (Burschka et al., 2013; Liang et al., 2014). It is well understood that the films' morphological and structural properties play a crucial role in the device performance. Compact, uniform, highly crystalline perovskite films with good coverage are beneficial for attaining a high PCE (Burschka et al., 2013; Gujar and Thelakkat, 2016). Three methods are commonly used for the formation of perovskite films, including one-step deposition from a single precursor solution, two-step sequential solution deposition and vapor-assisted deposition (Burschka et al., 2013; Gujar and Thelakkat, 2016; Im et al., 2014). In the two step method for the deposition of CH3NH3PbI3 a PbI2 layer is deposited from solution on the substrate, followed by its exposure to CH3NH3I solution resulting in spontaneous perovskite formation. The two step sequential deposition was found to prevent uncontrolled precipitation (Burschka et al., 2013), and result in dense morphology with good integration/coverage of the substrate, towards high performance and reproducibility of the device (Schlipf et al., 2015).

Along with the hybrid perovskites' advantages for efficient and low-cost photovoltaics, the material instability under exposure to light, heat, oxygen and moisture is also known. Light- induced degradation of CH3NH3PbI3 typically results in the formation of PbI2 and organic species, which is accelerated by elevated temperatures (Frolova et al., 2015; Frost et al., 2014; Misra et al., 2015; Niu et al., 2014). The perovskite film and device lifetimes were found to depend on its composition and morphology (Jacobsson et al., 2016; Merdasa et al., 2016; Misra et al., 2016; Noh et al., 2013). Accordingly, the deposition method is expected to affect the stability via determining the film morphology. The two-step deposition method frequently results in unreacted PbI2 layer under the formed CH3NH3PbI3 due to diffusion limitations imposed by the growth of the perovskite film at the PbI2 interface (Cao et al., 2016). Remnant PbI2 can also be found throughout the perovskite film due to initial degradation during inadequate fabrication process or local stoichiometric deviation even at one-step deposition.(Jacobsson et al., 2016) PbI2 presence was found to have a positive effect on the efficiency of the device due to passivation of grain boundaries and/ or the TiO2 surface (Bi et al., 2016; Cao et al., 2014; Chen et al., 2014; Haruyama et al., 2014; Jacobsson et al., 2016; Liu et al., 2016; Nakayashiki et al., 2015; Wang et al., 2014; Wang et al., 2016). Increase in PbI2 concentration in the precursor solutions was demonstrated to result in the formation of remnant PbI2 crystallites distributed over the depth of the perovskite film, probably in the vicinity of grain boundaries (Kim et al., 2016, Du et al., 2017). PbI2 role as a charge selective layer was also suggested (Calloni et al., 2015; Chen et al., 2014), while if too thick it may block the desirable charge transfer (Du et al., 2016).

However, the effect of remnant PbI2 on the material degradation is not well established. Improved thermal stability was reported for the dense perovskite films with complete surface coverage produced by an optimized two-step sequential deposition method (Kim et al., 2017). The authors attributed the improved stability mostly to the complete conversion of the precursors to perovskite and the absence of un-reacted PbI2. The presence of PbI2 was also found to accelerate CH3NH3PbI3 photo-degradation, possibly due to an autocatalytic effect (Du et al., 2016; Liu et al., 2016). Here we study the effect of remnant PbI2 on the photostability of CH3NH3PbI3 films by comparing the stability of films fabricated by the one-step and two-step solution deposition techniques, with different quantities and spatial distribution of remnant PbI2 in the perovskite films. Specifically, we study the effect of illuminating by concentrated sunlight through the remnant PbI2 layer compared to direct CH3NH3PbI3 illumination. Previously, we suggested to use concentrated natural sunlight for accelerated degradation study of perovskite thing films (Misra et al., 2015) and verified the relevance of this accelerated stressing by comparison of the results with the degradation under outdoor standard operational conditions of solar cells (Misra et al., 2016).

2. Experimental Section

*2.1 Materials*

All chemicals were used without further purification. Microscope glass slides were used both as substrates as well as encapsulating plates. The glass substrates were first washed with a detergent and rinsed with warm water. They were then subjected to sonication in solvents including deionized water (J.T Baker HPLC Grade), acetone (Bio lab CP Grade Assay 99.5%), and isopropanol (Bio lab CP Grade Assay 99.5%) for 5 mins each. The glass substrates were then dried under airflow and exposed to UV-ozone cleaning for another 15 mins. The quality of the glass surface cleaning was validated by contact angle measurements which was found to be 9.3±1o Following the perovskites film deposition (see below) the samples were encapsulated in the 'glass on glass' configuration sealed using nitrocellulose polymer. Encapsulation was performed inside the glove box under N2 atmosphere.

*2.2 CH3NH3PbI3 film preparation by one step deposition:*

PbI2 (Aldrich, 99.999%) and CH3NH3I (Dyesol, 99.99%) were dissolved at 1:1 molar ratio in DMF (AR, Frutarom) in 40 wt. %. The solution was filtered using a 0.45 µm microfilter then heated to 70 ºC for 30 minutes while being stirred. The filtered warm solution was then spin casted on glass substrates at 2000 rpm for 30sec and annealed at 40 ºC for 60sec to dry, followed by 100 °C for 5min.

*2.3 CH3NH3PbI3 thin film preparation by two step deposition:*

PbI2 (0.87 M) was dissolved in DMF, filtered using a 0.45 µm microfilter, and then spin casted at 2000 rpm for 30 sec and annealed at 90 °C for 20 minutes. CH3NH3I 0.19 M solution in isopropanol (Bio lab AR Grade Assay 99.8%) was then casted on the previously formed PbI2 layer by spin casting at 2000 rpm for 30 sec and annealed at 90°C for 20 minutes.

*2.4 Film exposure to concentrated sunlight:*

The encapsulated films were subjected to natural sunlight concentrated outdoors and transmitted indoors via an optical fiber (**Fig. S3a**) (Gordon et al., 2004; Katz et al., 2006). The transmitted sunlight is transferred to the sample through a kaleidoscope (0.5 x 0.5 cm2) placed on the sample to achieve flux uniformity over the illuminated area (**Fig. S3b**). Sunlight exposure was performed during clear-sky periods around noontime at Sede Boqer (Lat. 30.8oN, Lon. 34.8oE, Alt. 475 m), and the solar spectrum delivered to the sample was found to be very close to the standard AM1.5G solar spectrum (Berman and Faiman, 1997; Gordon et al., 2004). The incident sunlight intensity on the sample was measured using a spectrally blind pyranometer (thermopile) of 5% accuracy. Some of the exposure experiments were conducted with a UV filter (Solarnix) placed on top of the sample between the encapsulation plate and the kaleidoscope, blocking 99.5% of the incoming UV intensity (**Fig. 4b**). Exposure was performed in two directions: either through the substrate or through the encapsulation glass plates. The samples were placed on a metallic substrate whose temperature was tuned using a thermal bath. The substrate temperature was set to 25oC during sunlight exposure for stability studies. The temperature of the sample was measured using a T-type thermocouple placed inside the sample adjacent to the illuminated area, inserted before encapsulation (**Fig. S2, inset**). This was achieved by scratching the glass of the cover plate by a driller. The thermocouple was place out of the illuminated area but very close to its edge. The temperature inside the encapsulated sample was found to increase for about 6 min and then stabilized.

*2.4 Optical, crystallographic and spectroscopic characterization:*

The UV−vis absorption spectra of the films were recorded using a Cary 5000 UV−vis−NIR spectrophotometer (Agilent Technologies) in transmission mode. Rotating and grazing angle X-ray diffraction (XRD) data were collected with Panalytical Empyrean powder diffractometer equipped with position-sensitive X’Celerator detector using Cu Kα radiation (λ = 1.5405 Å) and operated at 40 kV and 30 mA. JEOL 7400F field emission gun high resolution scanning electron microscope (HRSEM), operating at 3 kV acceleration voltage, was used for morphological characterization and for elemental analysis using energy dispersive spectroscopy (EDS).

3. Results and discussion

We carried out degradation studies of encapsulated CH3NH3PbI3 films under concentrated solar irradiation as a function of the fabrication method (one and two step deposition). The morphology of the fresh, non-exposed CH3NH3PbI3 films prepared using either method is shown in **Figure 1**. Grain size of one and two step synthesized film was estimated using line analysis by “Image J” software (Rashband, 2014) and was found to be 1.15±0.31μm and 0.64±0.12μm respectively. The one step deposited film also revealed significant porosity (**Fig. 1a, c**), in contrast with the compact morphology of the films obtained through two step deposition (**Fig. 1b, d**). The thickness of both films was close to 800 nm (**Fig. 1c, d**). The absorption spectra of fresh CH3NH3PbI3 films prepared by both methods were similar to published spectra of such films (**Fig. 2**), (Lv et al., 2015; Misra et al., 2015) with an absorption edge close to the CH3NH3PbI3 band gap at 780 nm. The film prepared by two-step deposition also showed a significant absorption edge at 500 nm and very strong absorbance at shorter wavelength, indicating large amount of remnant PbI2, probably under the CH3NH3PbI3 film. Such PbI2 absorbance is missing from the spectrum of CH3NH3PbI3 prepared by one-step deposition (**Fig. 2**). The film prepared by one-step deposition showed smaller absorbance values probably due to its porous nature (Li et al., 2015; Zhang et al., 2015) and to the added PbI2 absorbance of the two-step deposited film.



**Figure 1.** SEM images of fresh CH3NH3PbI3 films obtained through one step- (a, c) and two step- (b, d) deposition methods in top and cross-section views. The films' thickness is indicated in µm on panels c and d.

The photostability was characterized by the changes in light absorption as a function of exposure time to concentrated sunlight (100 suns = 10 W/cm2). With the exposure, the absorbance of the one step-deposited film was found to decrease in the wavelength range of 500-780 nm attributed to CH3NH3PbI3 absorption, with increased absorption at wavelengths ~500 nm and shorter, attributed to PbI2 formation during degradation (Misra et al., 2015; Misra et al., 2016) (**Fig. 2a**). In contrast, the film obtained through two step deposition showed degradation in PbI2-related absorbance with almost no change in the CH3NH3PbI3 absorbance (**Fig. 2b**). These films were illuminated through their transparent substrates (**Fig. 2, right panel**), as they would be illuminated in photovoltaic device.



**Figure 2.** UV-vis absorbance spectra of encapsulated CH3NH3PbI3 films synthesized by (a) one step- and (b) two step-deposition techniques for different exposure times to 100 suns when illuminated through the substrate. Middle: schematic description of the illumination scheme in this experiment.

We postulate that in the case of CH3NH3PbI3 film synthesized by two step deposition the remnant PbI2 underlayer acts as irradiation filter enhancing the CH3NH3PbI3 stability. To test this hypothesis, the CH3NH3PbI3 films synthesized by one step- and two step- deposition were exposed to 100 suns through the encapsulation glass plate (**Fig. 3**). The absorption of CH3NH3PbI3 produced by the two step deposition method degraded significantly (Figure 3b) and the film changed its color to yellow indicative of PbI2 as the degradation product, in striking contrast to similar exposure conditions applied through the substrate (**Fig. 2b**). CH3NH3PbI3 made by one step deposition degraded similarly at both illumination directions (**Fig. 2a, 3a**). The formation of PbI2 following exposure to 100 suns was further confirmed by SEM/ EDS and XRD studies. EDS showed a transition of the I/Pb ratio from 2.5 before exposure to 1.8 after exposure, and SEM imaging showed sharp smaller crystals typical of PbI2 (**Fig. S1a, b**) after exposure of CH3NH3PbI3 prepared by two-step deposition. In accordance with our previous results,(Misra et al., 2015; Misra et al., 2016) XRD revealed decreased peak intensities of CH3NH3PbI3 compared to PbI2 peak intensities after the exposure (**Fig. S1c, d**). Qualitatively similar differences were noted in exposed *vs* non-exposed films of both synthesis methods.



**Figure 3.** UV-vis absorbance spectra of encapsulated CH3NH3PbI3 films synthesized by (a) one step- and (b) two step-deposition techniques for different exposure times to 100 suns when illuminated through the encapsulation plate. Middle: schematic description of the illumination scheme in this experiment.

We suggest that remnant PbI2 on the substrate acts as a protecting layer from solar UV irradiation and it is responsible for the superior stability of CH3NH3PbI3 fabricated in the two step method when illuminated through the substrate (**Fig. 2**). The light filtering properties of PbI2 are demonstrated by its transmission spectrum (**Fig. 4a**), showing negligible transmission of wavelengths shorter than ~500 nm. To test this hypothesis, exposure to concentrated sunlight was carried out in the presence of UV filter, whose transmission is negligible at UV wavelengths shorter than 370 nm (**Fig. 4b**). As expected, the presence of the UV filter eliminated almost entirely the absorption degradation of CH3NH3PbI3 fabricated in both deposition methods when illuminated from either the side of the sample (substrate or encapsulation, **Fig. 5**). The color of the films also remained unchanged in all cases. Our results suggest the role of remnant PbI2 as a protective/ stability enhancing layer in CH3NH3PbI3 absorbers. In our opinion, the fact that remnant PbI2 in the form of an underlying layer may serve as a UV filter may not contradict to the previous findings of PbI2 enhancing CH3NH3PbI3 degradation,(Du et al., 2016; Kim et al., 2017; Liu et al., 2016) possibly related to homogeneously distributed PbI2 in the CH3NH3PbI3 film. Furthermore, this suggests that the CH3NH3PbI3 degradation is primarily induced by UV irradiation, even in the absence of TiO2 as a UV-absorbing material (Leijtens et al., 2013; Niu et al., 2015). While this mechanism is significantly enhanced under concentrated sunlight, as used in our study, it is expected to be active also under conventional one sun illumination at a slower pace.



**Figure 4.** Transmission spectra of (a) PbI2 film of ~200 nm thickness, and (b) the UV filter used in this study.

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**Figure 5.** UV-vis absorbance spectra of encapsulated CH3NH3PbI3 films synthesized by (a, b) one step- and (c, d) two step-deposition techniques after illumination by 100 suns in the presence of a UV filter placed between the sample and the illuminating kaleidoscope. The samples were illuminated through the substrate (a, c) and through the encapsulation plate (b, d).

To verify the presence of remnant PbI2 at the substrate we compared XRD diffractions patterns obtained by two different X-rays optics: usual /2 and grazing-incidence optic. In the last case the incident angle is enough small (1-2o) and the contribution of the surface layers in formation of the diffraction pattern is rather more than in the case of /2 geometry. The diffractions patterns of CH3NH3PbI3 films prepared by the one-step and by two-step deposition are shown on the **Figure 6 (a, b)** and **Figure 6 (c, d)** respectively. As expected, the diffraction peaks related to PbI2 phase are more intensive in the two step method than in the one step method (compare for example (001) peaks of PbI2 at 2θ=12.6o). Comparing two diffraction patterns from sample prepared by two step method (**Fig. 6 c, d**) it can be note that intensities of strong peaks of PbI2 (001 reflection at 2θ=12.6o) and CH3NH3PbI3 (110 reflection at 2θ=14.1o) are almost equal in the case of grazing-incidence geometry (**Fig. 6d**) whereas the peak of PbI2 approximately two times bigger than peak of CH3NH3PbI3 in the case of /2 geometry (**Fig. 6c**). This difference to our mind points to larger content of PbI2 buried away from the front surface, *i.e.*, remnant PbI2 layer on the substrate. At the same time the diffractions patterns of the sample prepared by one step deposition method show the negligible differences between intensities ratio of PbI2 and CH3NH3PbI3 peaks for two different geometries (**Fig. 6 a, b**). That indicates the smaller PbI2 content, which is homogeneously distributed as a function of distance from the film surface.



**Figure 6.** (a, c) θ/2θ and (b, d) grazing-incidence XRD diffractograms of CH3NH3PbI3 films obtained by (a, b) one step- and (c, d) two step- deposition.

We measured the temperature of the CH3NH3PbI3 films under exposure to various sunlight intensities to account for the effect of light filtering by the remnant PbI2 layer and to rule out temperature differences as degradation factors. In general, since heating of the absorbing layer under sunlight exposure is induced mostly by thermalization of photons with energies larger than the absorber's band gap, significantly larger dose of the absorbed photons is expected to increase the sample temperature. However, no significant difference was found between the temperatures of the illuminated CH3NH3PbI3 films prepared by the one step- and two step-deposition methods (**Fig. S2**). The elevated temperatures probably enhance the UV-induced degradation similarly in CH3NH3PbI3 fabricated in both methods, and are un-harmful when it is filtered by the remnant PbI2.

4. Conclusion

Degradation studies of encapsulated CH3NH3PbI3 films were carried out under concentrated solar irradiation as a function of the fabrication method - one and two step deposition. The degradation was followed by the changes in light absorption as a function of exposure time to 100 suns. The result demonstrated the significance of the preparation method in determining the photochemical stability of the CH3NH3PbI3, films. CH3NH3PbI3 films deposited by one step showed a significant decrease in the CH3NH3PbI3 absorbance with exposure time when illuminated through the substrate, while films obtained through two step deposition showed almost no change in the CH3NH3PbI3 absorbance under similar sunlight exposure. On the other hand, both types of films degraded significantly when irradiated through the top encapsulation. We suggest that a remnant PbI2 layer on the substrate acts as a filtering layer of solar UV irradiation and is responsible for the superior stability of CH3NH3PbI3 fabricated in the two step method when illuminated through the substrate. This hypothesis was supported by various control experiments. Furthermore, our results suggest a degradation mechanism in which CH3NH3PbI3 degradation is induced by UV irradiation, accelerated under concentrated sunlight and elevated temperatures, even in the absence of TiO2 as a UV-absorbing layer interfaced with CH3NH3PbI3. In the further step of research, experimental optimization of the thickness of PbI2 layer should be performed in order to achieve improvement of solar cell stability and not to aggravate collection of photo-generated charge carriers and the cell efficiency.

**Supporting Information**

Supplementary data associated with this article can be found in the online version

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