# **Degradation mechanism for Planar Heterojunction Perovskite Solar Cells**

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# Abstract

Perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>:MAPbI<sub>3</sub>) have been recently emerged as a promising cost- and energy efficient light absorber material for photovoltaic applications. Unfortunately, perovskite solar cells (PSCs) have a problem with decreacement of power conversion efficiencies (PCE) due to degradation in the air. To detect the reason of degradation on PSCs, we exposed deposited films to the  $O_2$  or  $(H_2O+N_2)$  atmosphere condition. Analysis of the film revealed that the large energy band gap was shown due to influence of H<sub>2</sub>O molecule in MAPbI<sub>3</sub>. In (H<sub>2</sub>O+N<sub>2</sub>) atmosphere conditions, the existence of MAI molecule has found to affect the morphology, absorption and as well as crystalline diffraction peak. The resultant MAPbI<sub>3</sub> crystalline structure was degraded by H<sub>2</sub>O molecules in the air exposure condition.

### 1. Introduction

Organometallic halide PSCs have recently emerged as promising cost-effective and highly efficient nanostructured solar cells<sup>1,2)</sup>. The first PSC with a PCE of 3.81% was reported in 2009 by Kojima et al<sup>3)</sup>. Currently, typical PCE values of perovskite solar cells are over  $20\%^{11}$  far higher than that of organic thin-film solar cells. Unfortunately, perovskite solar cells have a problem with decreacement of PCE due to degradation in the air<sup>4)</sup>. To avoid this problem, we introduce our system with no air exposure from fabrication to measurement. In this paper, we try to detect degradation mechanism due to the effect of air exposure among fabrication steps.

#### 2. Experiment

Device structure of our PSCs is ITO / compact-TiOx / MAPbI<sub>3</sub> / spiro-OMeTAD / Au. Bare ITO was treated with oxygen plasma for 20 min before use. The compact-TiOx layer was prepared by chemical bath deposition (CBD) method of low temperature process which is around 150 °C<sup>5)</sup>. The perovskite layer was formed by sequential deposition and evaporation of lead iodide (PbI<sub>2</sub>) and methylamine iodide (CH<sub>3</sub>NH<sub>3</sub>I:MAI). To remove MAI remains on MAPbI<sub>3</sub>, this films of deposited films by sequential vacuum deposition of PbI<sub>2</sub> and MAI were rinsed with 2-propanol. Finally, we obtained 200 nm-thick MAPbI<sub>3</sub> film. Then, hole transport layer (spiro-OMeTAD) and Au electrode were deposited in glove box and evaporation chamber without air expose, respectively. Measurement of

solar cell characteristics was done in encapsulated container filled in nitrogen gas.

#### 3. Results

To clarify the influence of air exposure on PSCs, we exposed deposited films in the air for 30 min among various fabrication steps. The deposited film after MAI deposition and deposited film washed 2-propanol solvent after MAI deposition were exposure for 30 min in air. The current density-voltage (J-V) characteristics at scan speeds of 0.01 V/s are presented in Fig. 1. The parameters of forward scan measurements from the negative bias side to the opposing positive bias side under AM 1.5G simulated solar light are listed in Table I. The PCE of reference without air exposure was 4.1%. The PCE of PSC exposed after 2-propanol washed is 3.6%. The PCE of PSC exposed after MAI deposition is dramatically reduced to 0.45%, which is 90% reduction compared that of reference without air exposure. These results indicate that the MAI remains on perovskite surface are trigger of degradation.



Fig. 1 J-V characteristics of PSC without exposure, PSC exposed after MAI deposition and PSC exposed after 2-propanol washed for 30 min in air.

Table I Solar cell parameters calculated from J-V curves.

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condition of air exposure	Jsc (mA/cm <sup>2</sup> )	Voc (V)	FF	PCE (%)
Reference without air exposure	8.03	0.94	0.54	4.09
After MAI deposition	2.51	0.73	0.25	0.45
After 2-propanol washed	10.2	0.87	0.41	3.62

The degradation mechanism for  $MAPbI_3$  film in air exposure has never reported. To clarify the influence of air exposure on  $MAPbI_3$  films, we introduced the  $O_2$  or

 $(H_2O+N_2)$  gases in cylindrical holder in which deposited film after MAI deposition is placed. The UV-vis spectra of various conditions are shown in Fig. 2. The UV-vis spectrum of O<sub>2</sub> atmosphere condition was almost same as that of reference without air exposure. On the other hand, The UV-vis spectrum of  $(H_2O+N_2)$  atmosphere condition was significantly decreased at light absorption region from 400 to 700 nm. This spectral change is comparable to changing the band gap to being wide of MAPbI<sub>3</sub> films.



Fig. 2 UV-Vis spectra of MAPbI<sub>3</sub> films without exposure and with exposure in  $O_2$  and  $(H_2O+N_2)$  atmosphere condition.

Figure 3 shows AFM images of MAPbI<sub>3</sub> films without exposure and with exposure in O<sub>2</sub> condition and (H<sub>2</sub>O+N<sub>2</sub>) atmosphere condition. The 300 nm uniform particle shaped grains were observed in MAPbI<sub>3</sub> films without air exposure and with O<sub>2</sub> atmosphere conditions. On the other hand, the film exposed in (H<sub>2</sub>O+N<sub>2</sub>) atmosphere has morphology with non-uniform 1  $\mu$ m large grains. These results indicate that MAI remains on MAPbI<sub>3</sub> surface became rough by H<sub>2</sub>O molecules intercalation into MAPbI<sub>3</sub> film inside.



Fig. 3 AFM images  $(2\mu m \times 2\mu m)$  of the MAPbI<sub>3</sub> films without exposure and with exposure in O<sub>2</sub> and (H<sub>2</sub>O+N<sub>2</sub>) atmosphere condition. RMS: Root mean square

Figure 4 shows that the X-ray diffraction (XRD) spectra of MAPbI<sub>3</sub> films without exposure and with exposure in  $O_2$  and (H<sub>2</sub>O+N<sub>2</sub>) atmosphere condition. The main diffraction peak at around 14 degree assigned to the (110) plane of MAPbI<sub>3</sub>. The diffraction peak at around 10 and 12 degree assigned to the (001) planes of MAI and PbI<sub>2</sub>, respectively. The MAI diffraction peak (001) was observed in reference

without air exposure and with  $O_2$  atmosphere conditions. On the other hand, the MAI diffraction peak (001) disappeared during exposure in (H<sub>2</sub>O+N<sub>2</sub>) atmosphere condition.



Fig. 4 XRD spectra of  $MAPbI_3$  films without exposure and with exposure in O<sub>2</sub> and (H<sub>2</sub>O+N<sub>2</sub>) atmosphere condition.

Here we discuss why the band gap of MAPbI<sub>3</sub> was changed to being wide and MAI diffraction peak (001) was disappeared during exposure in (H<sub>2</sub>O+N<sub>2</sub>) atmosphere condition. It is well known that the band gap of perovskite film is easily shifted by substitution of organic molecules. When  $CH_3NH_3^+$  was substituted to NH=CHNH<sub>3</sub><sup>+</sup>, UV-vis spectrum of perovskite film is red-shifted<sup>6)</sup>. When  $CH_3NH_3^+$ was substituted to  $C_6H_5C_3H_4NH_3^+$ , was UV-vis spectrum is blue-shifted<sup>7)</sup>. We assume that the reacted MAI molecule with H<sub>2</sub>O molecule acts as a new organic molecule with another chemical and physical property. Therefore, MAI diffraction peak (001) was disappeared and band gap of film was changed.

# 4. Conclusions

We investigated the effect of air exposure on PSCs, by introducing the deposited films to the  $O_2$  or  $(H_2O+N_2)$  atmosphere condition. The PCE of PSC exposed after MAI deposition is dramatically reduced to 0.45%, which is 90% reduction compared that of reference without air exposure. In  $(H_2O+N_2)$  atmosphere conditions, the MAI remains have found to affect the morphology and absorption of MAPbI<sub>3</sub>. In addition, the MAI diffraction peak (001) disappeared during exposure in  $(H_2O+N_2)$  atmosphere condition. We assume that the reacted MAI molecule with  $H_2O$  molecule acts as a new organic molecule with another chemical and physical property. Therefore, MAI diffraction peak (001) was disappeared and band gap of film was changed.

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