Confirmation of permeation of iodide and iodine into hole-transport layer in lead halide perovskite solar cell using hard X-ray photoelectron spectroscopy

Recently, the initial power conversion efficiency (PCE) of organic-inorganic lead halide perovskite solar cells has reached 26.4% [1], a notable increase since the first PCE of 3.8% was demonstrated by Kojima *et al.* back in 2009 [2]. However, the long-term reliability of light and thermal stresses poses a challenge for practical use. In the light-induced degradation (LID) pathway, formation of PbI_2, metallic lead (Pb^0), CH_3NH_2, CH_3I, NH_3, I_2, and others has been reported. Based on these previous results and on our data, we acquired using hard X-ray photoelectron spectroscopy (HAXPES), impedance spectroscopy, and microwave photoconductivity decay, we suggested the following pair reaction model for the LID of perovskite solar cells [3]:

$$\text{Cathode reaction: } Pb^{2+} + 2e^- \rightarrow Pb^0 \qquad (1)$$

$$\text{Anode reaction: } 2I^- + 2h^+ \rightarrow I_2\uparrow, \qquad (2)$$

where the cathode and anode reactions mainly occur near the electron transport layer (ETL)/perovskite and perovskite/hole transport layer (HTL) interfaces, respectively. Moreover, the light stability of cells is strongly affected by experimental conditions, such as the ambient atmosphere and temperature. We investigated the influence of oxygen on the LID of perovskite using HAXPES and suggested that the presence of O_2 around a cell enhances anode reaction (2) according to the following reaction [4]:

$$\text{Additional cathode reaction: } O_2 + e^- \rightarrow O_2^-, \qquad (3)$$

where the oxygen captures photoinduced electrons at the adsorbed sites and superoxide (O_2^-) is produced; O_2^- contributes to the production of H_2O and CH_3NH_2 gas via oxidation process, resulting in PbI_2 formation and photodecomposition.

Effective interfacial layers between the ETL and perovskite layer, self-assembled monolayers (SAMs) such as 4-(1',5'-Dihydro-1'-methyl-2'*H*-[5,6]fullereno-C_{60}-I_h-[1,9-*c*]pyrrol-2'-yl)-benzoic acid (C_{60}SAM), and other approaches have been proposed to improve the light stability of perovskite cells [5]. Surface passivation of the ETL using SAMs, such as C_{60}SAM, suppresses cathode reaction (1). We investigated the change in the HTL induced by illumination of a sample with a C_{60}SAM layer using HAXPES measurements [6]. We prepared a sample with a glass/indium tin oxide (ITO)/antimony-doped tin oxide (ATO)/compact titanium oxide (TiO_2)/mesoporous TiO_2/C_{60}SAM/perovskite 550 nm/n-butylammonium bromide/thick poly(triaryl amine) (PTAA) 100 nm structure (Fig. 1), where the Lewis acid tris(pentafluorophenyl)borane (TPFPB) was added to the PTAA as a dopant. The samples were encapsulated with a glass cover and absorber, and sealed under a nitrogen atmosphere (oxygen concentration <10 ppm). The substrate and glass cover were glued using a UV-cured epoxy resin. One-half of the samples were shaded using a mask; then, 1 sun light was irradiated on the glass substrate side of the sample for 3 h in dry air at ~28.8°C using a light source. The HAXPES samples before and after the light illumination test (LIT) were prepared by cutting the shaded and illuminated areas. The HAXPES samples had dimensions of 5 mm × 5 mm. A HAXPES apparatus at SPring-8 **BL16XU** was used. The incident angle of the X-ray beam was 85° and

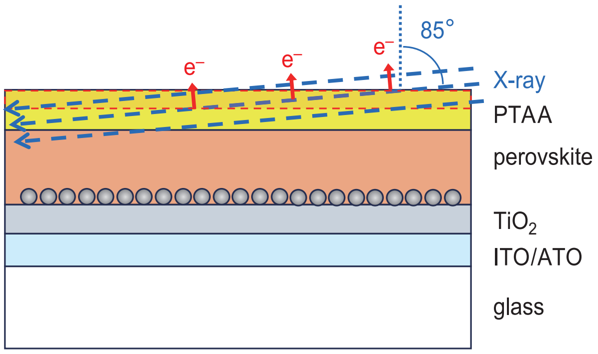

Fig. 1. Schematic of the HAXPES sample. The incident angle of the X-ray beam was 85° and the hard X-rays were incident on the side of the PTAA.

the excitation energy was 6 keV. Hard X-rays were incident on the side of the PTAA. The experimental sampling depth of the HAXPES was estimated to be approximately 50 nm. HAXPES measurements began more than 18 h after completing the LIT; thus, irreversible changes in the samples caused by long-term light illumination were mainly detected. Given that the PTAA was sufficiently thicker than the photoelectron escape depth of ~50 nm, Pb 4*f* signals originating from the perovskite layer were not observed. However, I 3*d* signals of I^- (~619.5 eV) and I^0 (~620.7 eV) were detected in both cases before and after the LIT. This indicates that iodide and iodine diffused to some extent from the perovskite to the PTAA during the first deposition of the PTAA. After LIT, the fractions of I^- and I^0 increased with respect to the amount of F 2*s* and B 1*s* spectra derived from TPFPB, as shown in Fig. 2. This indicates that during illumination, the iodine species permeated the PTAA. The permeation of iodine species into the PTAA proceeded gradually, even though C_{60}SAM was used to suppress the degradation of the HTL side under illumination. However, despite the permeation of iodine species into the PTAA, the solar cell with the C_{60}SAM interlayer showed almost no LID after the light stability test. Based on the pair reaction model, the suppression of the cathode reaction near the ETL/perovskite interface by introducing C_{60}SAM should lead to the suppression of anode reaction (2) near the perovskite/HTL interface under illumination, corresponding with the decrease in the peak area ratio of I^0/I^- after the LIT, as shown in Fig. 2.

Finally, we developed a new structure for improving both the PCE and light stability in which the surface of the ETL was modified by combining C_{60}SAM with a suitable gap-filling self-assembled monolayer (GFSAM) [6]. This GFSAM was formed using an isonicotinic acid solution. We confirmed a decrease in the band offset and an improvement in electron extraction at the TiO_2/perovskite interface using HAXPES and time-resolved microwave conductivity data for the sample based on a combination of C_{60}SAM and isonicotinic acid, respectively. After six months of outdoor exposure, the PCE of solar cells with C_{60}SAM and isonicotinic acid remained almost unchanged, with a retention rate of ~100%.

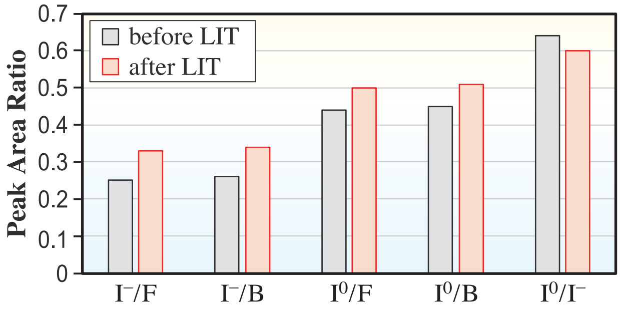

Fig. 2. Peak area ratios (peak areas of I 3*d* spectra divided by those of B 1*s* or F 2*s* spectra) for the samples with glass/ITO/ATO/c-TiO_2/mp-TiO_2/C_{60}SAM/perovskite 550 nm/BABr/PTAA 100 nm before and after LIT.

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