1. Introduction

Solar cells with perovskite materials as light-absorbers have rapidly become to attract keen interests of many researchers because of their significant performances such as high power conversion efficiency (PCE), low cost, and easy attitude for production. Perovskite solar cell (PSC) was developed by replacing Ru-complexing dyes in dye-sensitized solar cell (DSC) by perovskite materials such as CH$_3$NH$_3$PbI$_3$. Since perovskite materials tend to decompose when they are in contact with solvents, an electrolyte solution used for a hole-transporting layer (HTL) in DSC was then replaced by a solid-state hole-transporting material (HTM) such as 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine) 9,9'-spirobifluorene (spiro-MeOTAD) and CuSCN. While CuSCN acting as a p-type semiconductor is available for HTM by itself, it has been reported that spiro-MeOTAD is electrically resistive and becomes to be available for HTL on doping. However, studies on the interaction between spiro-MeOTAD and dopants have not yet provided sufficient knowledge to make clear the mechanism of the doping.

One of the authors (TT) made an overview of PSC from the viewpoint of dye sensitization of silver halide (AgX) photographic systems with cyanine dyes and AgX grains as sensitizers and substrates, respectively, since the former has been derived from the latter via photo-catalyst with TiO$_2$ as a substrate. DSC with Ru-complexing dyes and TiO$_2$ as sensitizers and substrate, respectively. While the overlapping of electronic clouds among cyanine dyes in AgX photographic systems and Ru-complexing dyes in DSC is small, the electronic energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied one (HOMO) of a sensitizing dye molecule with respect to the conduction band minimum (CBM) and the valence band maximum (VBM) of a substrate are essentially important for the study of the light-induced electron transfer from the dye molecule to the substrate.

In this paper, we have studied the electronic structure and behavior of an HTL in a PSC with CH$_3$NH$_3$PbI$_3$ as a light absorber according to the above-stated consideration in order to enhance our understanding of the mechanisms of the doping of spiro-MeOTAD layers and the transport property of positive holes in HTLs of PSC.
2. Materials and Experiments

2.1 Preparation of PSC

The structure of the PSCs, which were prepared in this study, was a mesoporous type as shown in Fig. 1. A compact TiO2 layer and then mesoporous TiO2 layer were formed on an FTO glass, which are composed of pyramid-shaped particles of transparent conductive metal oxide (TCO) on a glass plate to enhance the scattering of incident light, and are used as a transparent electrode for solar cells (AGC Fabric Type-VU). A compact TiO2 layer was formed on a hot plate at 400°C by means of a spray thermal decomposition method with a solution of 0.6 ml of titanium (IV) disopropoxide bis (acetylacetonate) (Tokyo Chemical Industry Co., Ltd.) and PbI2 (Sigma-Aldrich) (mole ratio of 1:1) in DMF and volatilize DMF. An HTL layer and an anode were then formed by spin-coating a suspension of 2g of TiO2 paste containing 17wt% of TiO2 particles with diameter of 18 nm in size in water (JGC Catalysts & Chemicals Ltd., PST-18NR) in 7g of ethanol with 5000 rpm at 25°C and annealing it at 500°C for 20 min. Then, a layer of CH3NH3PbI3 was formed on the above-stated layers by the one step method. Namely, a solution of CH3NH3I (Wako Pure Chemical Corp.) and PbI2 (Sigma-Aldrich) (mole ratio of 1:1) in DMF was dehydrated (Wako Pure Chemical Corp.) (45 wt%) was coated on the above-stated layers by a spin-coater with 2000 rpm for 30 sec and heated on a hot plate at 70°C for 30 min to volatilize DMF. An HTL layer and an anode were then formed on the above-stated perovskite layer. In this paper, spiro-OMeTAD and Au were used as HTL and anode, respectively. A layer of spiro-OMeTAD (LT-S922, Luminescence Technology Corp.) and PbI2 (Sigma-Aldrich) (mole ratio of 1:1) in DMF was dehydrated (Wako Pure Chemical Corp.) (45 wt%) was coated on the above-stated layers by a spin-coater with 2000 rpm for 30 sec and heated on a hot plate at 70°C for 20 min. Then, a layer of CH3NH3PbI3 was formed on the above-stated layers by the one step method. Namely, a solution of CH3NH3I and PbI2 (Sigma-Aldrich) (mole ratio of 1:1) in DMF was dehydrated (Wako Pure Chemical Corp.) (45 wt%) was coated on the above-stated layers by a spin-coater with 2000 rpm for 30 sec and heated on a hot plate at 70°C for 30 min to volatilize DMF. An HTL layer and an anode were then formed on the above-stated perovskite layer. In this paper, spiro-OMeTAD and Au were used as HTL and anode, respectively. A layer of spiro-OMeTAD (LT-S922, Luminescence Technology Corp.) was formed by spin-coating its chlorobenzene solution (12 wt%) with 3000 rpm for 30s. In this study, Li-TFSI and tBP25-28 were used as dopants for an HTL layer of spiro-OMeTAD. The former was added to a final concentration of 0.064M, while the latter was added to a final concentration of 0.193M. The chemical structures of these compounds are shown in Fig. 1. An anode was prepared by depositing Au in vacuum on the surface of the HTL.

2.2 Analyses of HTL in PSC

The performances of the above-stated cells such as current-voltage (I-V) characteristics, open-circuit voltage (Voc), short-circuit current (Jsc), fill factor (FF), and power conversion efficiency (PCE) were evaluated by means of a solar simulator (HAL-320, Asahi Spectra), an apparatus for the measurement of I-V characteristics (Pecell IV Analyzer 2.2 and Keithley 2400) with 1SUN (100 mW/cm²) and AM (Air Mass) 1.5G. The light intensity was calibrated by the ISUN checker, which was attached to HAL-320. The performances of the above-stated cells were traced for 20 days in room air without any barrier film to get the information of their stability.

The work function, i.e., the energy difference between the highest occupied level (Fermi level for Au, VBM for CH3NH3PbI3, and HOMO for spiro-OMeTAD) and the vacuum level, was measured by means of photoelectron yield spectroscopy in air (PYSAX; Riken Keiki AC-2) and compared with the performances of the cells in this study. Every PYSAX measurement was carried out in room air at room temperature in the range from 3.80 to 6.20 eV with energy step of 0.05 eV by use of a light source (10 nW). Photoelectrons are captured by oxygen molecules in air to form superoxide radicals (O2•−). Then, superoxide radicals are collected and dissociated for the measurement of the yield of photoelectrons in an open counter. The distribution of the measured values for a sample with different experimental condition was small. The standard deviation for the measurement of the work function of an Au layer was ±0.02 eV. The work function of a thin layer of Au used as an anode in the cell was traced for 20 days in room air. The electronic structures of CH3NH3PbI3/HTM/Au were constructed with respect to the vacuum level on the basis of the results of the above-stated measurements by taking into account the Fermi levels of CH3NH3PbI3, which should be equalized to those of spiro-OMeTAD and Au to transfer positive holes.

3. Results and Discussions

3.1 Change in condition of HTL

It is demonstrated in this study that the performance of PSC was markedly influenced by the following three kinds of changes in the positive hole transport in the cells: the time-dependent change in the work function of an Au anode,
the doping of a spiro-OMeTAD layer with Li-TFSI and tBP, and the irradiation of the cells to light.

Fig. 2 shows the time-dependent change in the work function of a thin Au layer in room air, indicating that the work function is increasing with time after its preparation. It is known that the work function of pure Au in vacuum is 5.1 eV\textsuperscript{26}, while that of a thin Au layer in room air becomes to be about 4.8 eV owing to the pinning of its Fermi level to that of an organic layer deposited from air on its surface\textsuperscript{27}. According to a jellium model, the outermost surface region inside a metal is positively charged, and the same amount of the negative charge with electrons is spilled out to several Å in vacuum, forming an electric double layer\textsuperscript{26}). Then, the work function of a metal layer is decreased by the push-back effect, according to which the electric double layers thus formed are depressed by a phenomenon where spilled electrons are pushed back to the inside of the metal when the metal is in contact with an organic layer\textsuperscript{26, 27}. It is considered that the work function of a thin Au layer first decreased owing to the push-back effect when it was in contact with a thin organic layer coming from air, and then increased owing to the pinning of its Fermi level to that of the organic layer coming from air\textsuperscript{27}).

Fig. 3 shows the time-dependent change in the I-V characteristics of the cell, indicating that both $V_{oc}$ and $J_{sc}$ increased during its storage for 4 days after its preparation. The increase of $V_{oc}$ with time was in accord with the increase in the work function of a thin Au layer with time after its preparation (Fig. 2). While the big change in work function taking place for such a short period as seen in Fig. 2 is quite probable and verified for metals including Au in air\textsuperscript{27}, it is not considered to be probable for organic materials available for electronic devices. It is therefore considered that the time-dependent increase in the work function of the Au anode in the cell brought about the time-dependent increase in $V_{oc}$. While the work function of a thin Au layer kept for 20 days after its preparation was larger than that of the layer kept for 4 days, $V_{oc}$ of the cell kept for 20 days in air after its preparation was smaller than that of the cell kept for 4 days. It is considered that this discrepancy arose from the fact that the degradation of a CH$_3$NH$_3$PbI$_3$ layer in the cell was in progress as observed in the previous paper\textsuperscript{28)} since the cells were kept in air without any barrier film.

Then, the HTL composed of a thin spiro-OMeTAD layer was doped with Li-TFSI and tBP\textsuperscript{23, 24} according to the procedure described in the previous section. Two cells with undoped and doped spiro-OMeTAD layers as HTLs were prepared and subjected to the measurements of their performances at different 16 positions in each cell. The results are shown in Fig. 4. The averaged values and their coefficients of variation are listed in the tables in Fig. 4. The fluctuation of the performances of the cells with an undoped spiro-OMeTAD layer was large, especially for $J_{sc}$, and could be much improved by the doping.
Fig. 5 shows the PYSA spectra of an un-doped spiro-OMeTAD layer, CH$_3$NH$_3$PbI$_3$/un-doped spiro-OMeTAD layers, and CH$_3$NH$_3$PbI$_3$/doped spiro-OMeTAD layers. While the work function of spiro-OMeTAD was hardly influenced by its contact with MAPbI$_3$, it was significantly increased by the doping. It is considered from this result that the dopants drew electrons from the spiro-OMeTAD layer to bring about the increase in its work function and to decrease the photoelectron yields from it. Fig. 6 shows the PYSA spectra of un-doped spiro-OMeTAD/Au layers, CH$_3$NH$_3$PbI$_3$/undoped spiro-OMeTAD/Au layers, and CH$_3$NH$_3$PbI$_3$/doped spiro-OMeTAD/Au layers. The doping significantly decreased the photoelectron yield from Au layer in this system, and increased the work function of the Au layer. It is considered from this result that the dopants drew electrons from the spiro-OMeTAD layer to lower its Fermi level and that of the Au anode, decreasing the photoelectron yield from the Au anode.

Fig. 7 shows the effect of irradiation on the PYSA spectra of the PSCs with undoped spiro-OMeTAD layer as an HTL. As seen in this figure, the irradiation increased the work function of the Au anode of the cell and decreased the photoelectron yield from it. It is considered from the result in this figure that positive holes created in the CH$_3$NH$_3$PbI$_3$ layer in the cell were transferred to the spiro-OMeTAD layer and captured by traps to deepen the Fermi levels of the spiro-OMeTAD layer and the Au anode of the cell, and that the above-stated condition created by the light irradiation was kept for a relatively long time (more than 5 min).

3.2 Electronic structures of HTL

Fig. 8 (a) and (b) show the electronic structures of CH$_3$NH$_3$PbI$_3$/undoped spiro-OMeTAD/Au and CH$_3$NH$_3$PbI$_3$/doped spiro-OMeTAD/Au layers. An inserted table shows their work functions.

![Fig. 5 PYSA spectra of an undoped spiro-OMeTAD layer, CH$_3$NH$_3$PbI$_3$/undoped spiro-OMeTAD layers, and CH$_3$NH$_3$PbI$_3$/doped spiro-OMeTAD layers. An inserted table shows their work functions.](image)

![Fig. 4 I-V characteristics of perovskite solar cells with undoped (a) and doped (b) spiro-OMeTAD/Au layers as measured at 16 different points on each cell. Upper and lower tables show the average values and coefficients of variation (CV) of the performances of the cells with I-V characteristics shown in (a) and (b), respectively.](image)
doped spiro-OMeTAD/Au layers, respectively, as constructed with respect to the vacuum level according to the process described in Section 2.2. In this study, the ionization energies of CH$_3$NH$_3$PbI$_3$ and spiro-OMeTAD were measured as 5.52 eV and 4.98 eV, respectively. The ionization energy of spiro-OMeTAD on CH$_3$NH$_3$PbI$_3$ was measured as 5.00 eV, indicating the vacuum level shift as -0.02 eV. The ionization energy (i.e., work function) of Au on spiro-OMeTAD/CH$_3$NH$_3$PbI$_3$ was measured as 4.52 eV, indicating that the vacuum level shift between spiro-OMeTAD and Au was 0.60 eV, and that the Fermi level of spiro-OMeTAD was by 0.48 eV higher than its HOMO level. The electronic structure in Fig.8 (b) was constructed similarly.

While the orientation of the single crystals of metals and organic semiconductors influence their work functions, they are not taken into account for the construction of the electronic structures in Fig. 8, since the samples were amorphous or polycrystalline with randomly oriented small crystallites. As seen in Fig. 8 (a), the Fermi level of the Au anode in the layer with an undoped spiro-OMeTAD, which was measured immediately after the preparation of the film, was -4.52 eV, being higher by 0.48 eV than the HOMO level of a spiro-OMeTAD layer. This result indicates that positive hole traps with ≦0.48 eV in depth were present and should hinder the transport of positive holes in an undoped spiro-OMeTAD layer by trapping them. The Fermi level of the Au anode was close to that of Au layer immediately after its preparation, which then increased by ~0.3 eV on its storage in air for 4 days as seen in Fig. 2.

The comparison between Fig. 8 (a) and (b) reveals that the dopants could lower the Fermi levels of, not only spiro-OMeTAD layer, but also Au anode and CH$_3$NH$_3$PbI$_3$ layer by drawing electrons from the spiro-OMeTAD layer. In the undoped spiro-OMeTAD layer, positive hole traps with ≦0.48 eV in depth were present and captured positive holes. On the other hand, only traps with ≦0.09 eV in depth were present and captured positive holes in the doped spiro-OMeTAD layer. This result could provide an explanation for the observed result that the values of $J_{sc}$ of the cell could be significantly improved and their coefficient of variation could be much decreased by the doping. In addition, it is considered that the big increase in the work function of the Au anode by the dopants contributed to the increase of $V_{oc}$ of the cell by the dopants.

As discussed above, the electronic structure of a spiro-OMeTAD layer in a device could be evaluated and has turned out to be useful for studying the behavior of positive holes in the layer responsible for the performance of the device. The usefulness of the knowledge of the electronic structure should be further enhanced when it would be supported by the measurements of the conductivity, mobility of positive holes, number and depth of positive hole traps in a spiro-OMeTAD layer.
4. General Discussions

In order to characterize the performance of a PSC from the viewpoint of its electronic structure, the performance of a PSC composed of FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Au was studied with variation of factors relating to the layers, through which positive holes were transferred. Then, the results were correlated with the electronic structure of CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Au layers, which were constructed from the PYSR spectra of individual and combined layers of their components, as shown in Fig. 8.

The electronic structures of the CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Au layers were constructed under the assumptions that the Fermi levels were present in individual layers of its components and brought about the electron transfer phenomena to equalize the Fermi levels among them. Since the electronic structure of CH$_3$NH$_3$PbI$_3$ is substantially an inorganic semiconductor, its Fermi level was measured and discussed in many papers. Although spiro-OMeTAD is an organic semiconductor, the Fermi level of a spiro-OMeTAD layer and its role in the electronic phenomena in the layer were discussed in the literature.

It is therefore considered that the equalization of Fermi level took place at the interface between the spiro-OMeTAD/CH$_3$NH$_3$PbI$_3$ layers as well as the interface between the spiro-OMeTAD/Au layers.

The Fermi level equalization should bring about the shift of the vacuum levels of the layers involved. The shift takes place at the interface between them without band-bending in the layers when the transferred electrons are mostly located at the interface. On the other hand, the shift takes place between the bulks with band-bending in the layers involved when the transferred electrons located not at their interface, but in the bulks of the layers involved.

Kahn and others did not observe any band-bending in a CH$_3$NH$_3$PbI$_3$ layer when the Fermi level equalization took place on its contact with a TiO$_2$ layer. It is therefore considered that the Fermi level equalization between CH$_3$NH$_3$PbI$_3$ and spiro-OMeTAD did not bring about any band-bending in the former. Seki and Ishii observed the vacuum level shift at the interface between many organic semiconductors and substrates when they were in contact with each other. In this paper, it is therefore considered that the Fermi level equalization of a spiro-OMeTAD layer with a CH$_3$NH$_3$PbI$_3$ layer and an Au layer took place to cause the vacuum level shifts at the interfaces, as shown in Fig. 8. Fig. 8 shows the vacuum level shifts at the interfaces between spiro-OMeTAD and CH$_3$NH$_3$PbI$_3$ layers and those between spiro-OMeTAD and Au layers without and with Li-TFSI, which have been observed for the first time to our best knowledge, and reflected the electron transfer across the interfaces. The observed vacuum level shift at the interface between undoped spiro-OMeTAD and CH$_3$NH$_3$PbI$_3$ was not however large enough to indicate the presence of any substantial electron transfer between them.

The short-circuit current of the PSCs prepared in this study was increased by the doping of a spiro-OMeTAD layer with Li-TFSI and tBP. Being in accord with the electronic structures of the systems studied in this paper, the change in the condition of HTL by the doping is considered to make the Fermi level of the spiro-OMeTAD layer closer to its HOMO level, and therefore to make the positive hole traps shallower. This result indicates that positive hole traps in a spiro-OMeTAD layer disturb the transport of positive holes in it, and could be almost eliminated by the dopants employed in this study.

These results are in good accord with the observation that the traps in a spiro-OMeTAD are filled by such a p-type dopant as Li-TFSI and light-created positive holes to exhibit ESR spectra attributable to long-lived positive holes in it. It is therefore considered that positive hole traps in spiro-OMeTAD layers are situated at the HOMO levels of their molecules with wide distribution owing to their disordered condition.

As seen in Fig. 7, the change caused in a PSC by irradiation was kept for a relatively long time. A PSC usually exhibits severe hysteresis in I-V measurement and is being studied in relation to some slow processes responsible for it. However, it seems that such slow processes are derived, not from the accumulated positive hole traps in HTL as analyzed in this study, but from ion migration or re-orientation of dipoles of methyl ammonium cations in the bulk of CH$_3$NH$_3$PbI$_3$, resulting in the appearance of hysteresis and slow recovery of light-induced changes as seen in Fig. 7.

The Fermi level of thin metal layers including an Au layer however tends to be pinned to the Fermi level of an organic layer deposited from air (estimated to be about 4.8 eV in the previous paper), as observed in Fig. 2. The work function of the Au anode on the doped spiro-OMeTAD layer was 5.25 eV and larger than that of an organic layers deposited from air. It is probable that the Fermi level of the Au anode in the cells tends to be pinned to that of an organic layer deposited from air when the cell will be kept in air. This phenomenon should bring about the electron transfer from the organic layer to the Au anode, and then the electron transfer from the Au anode to the doped spiro-OMeTAD layer. It is concerned that this change with time deteriorate the positive hole transport in the doped spiro-OMeTAD layer by increasing the depth and density of positive hole traps in it, indicating the necessity to keep the cell apart from air for the stabilization of its performance.

References

1) Akihiro Kojima, Kenjiro Teshima, Yasuo Shirai, and Tsutomu


