Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp1313-1314

Improved Photovoltaic Characteristics by MoO_3-doping to Thick Hole Transporting Films

Yusuke Shinmura[1,2], Masayuki Kubo[1,2], Toshihiko Kaji[1,2] and Masahiro Hiramoto[1,2]

[1] Institute for Molecular Science
5-1 Higashiyama Myodaiji, Okazaki, Aichi 444-8787, Japan
Phone: +81-564-59-5537 E-mail: shinmura@ims.ac.jp
[2] JST, CREST
5, Sanbancho, Chiyoda, Tokyo 102-0075, Japan

1. Introduction

Recently, the conversion efficiency in organic solar cells have increased. For high conversion efficiency, high open-circuit voltage (V_{oc}) is indispensable. V_{oc} depends on the gap between the highest occupied molecular orbital (HOMO) level of the donor and the lowest unoccupied molecular orbital (LUMO) level of the acceptor. Therefore, the donors having deep-lying HOMO level are promising materials for the solar cells with high V_{oc} because of a wide HOMO (D)-LUMO (A) gap. Thus, we focus on hole transporting materials (HTMs) with triphenylamine moieties having deep-lying HOMO.

On the other hand, using thick-films (ca. 1 μm) in photovoltaic cells is effective way to absorb entire irradiated solar light efficiently. Decreasing cell resistance is essential to use thick-film consisting of high-resistance organic materials for photovoltaic cells. Previously, we reported the control of the conduction type of C_{60} from *n*- to *p*-type by doping of molybdenum oxide (MoO_3).[1] MoO_3-doping to donor materials is expected to reduce cell resistance due to increase a hole concentration.

In this study, we report improving photovoltaic characteristics in the solar cells having thick HTMs by MoO_3-doping.

2. Experimental Methods

N,N'-bis-(3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (TPD) (Tokyo Chemical Industry, 99.99%), α-naphthylphenylbiphenyl diamine (NPD) (Luminescence Technology, 99.99%) and N,N'-diphenylcarbazole (CBP) (Luminescence Technology, 99.99%) were used as HTMs. HTMs were used without further purification.

All of the films were deposited by vacuum evaporation onto indium tin oxide (ITO) glass substrates under 10^{-5} Pa pressure using an oil-free vacuum evaporator (ULVAC, VTS-350M/ERH). MoO_3 doping was performed by co-evaporation with the HTMs. The Fermi levels (E_F) of HTMs films of 100 nm in thickness were measured by using a Kelvin vibrating capacitor apparatus (Riken-Keiki, FAC-1), in which a capacitor apparatus between a vibrating Au plate and the HTMs films on the ITO glass substrate. Both the evaporation chamber and the Kelvin probe was built into a glove-box (Miwa, DBO-1.5) purged by N_2 gas. The concentrations of H_2O and O_2 were kept below 0.5 and 0.2 ppm, respectively. Thus, during the film deposition and E_F measurements, the HTMs films were not exposed to air at any time. Specific resistances of 1 μm-thick HTMs films were measured by van der Pauw method using hall effect/specific resistance measurement system (TOYO Corporation, ResiTest8300) without exposure to air by setting the sample films into a sample container inside the glove-box. The current voltage (*J*-*V*) characteristics and action spectra were measured by irradiating with simulated solar light (AM1.5, 100 mW cm^{-2}) and with monochromatic light from a Xe-lamp through a monochromator, respectively.

3. Results and Discussion

Fig. 1 shows the energy diagrams of HTMs, C_{60}, MoO_3 and Ag films. The MoO_3 showed a remarkably positive value of E_F at 6.69 eV, which is more positive than the upper edge of the valence bands of all of three HTMs. The values of E_F for non-doped HTMs are located nearly center of the energy gap. By doping MoO_3 at a concentration of 4000 ppm (0.4 %), the values of all HTMs films are shifted toward the positive direction and close to the upper edge of the valence bands.

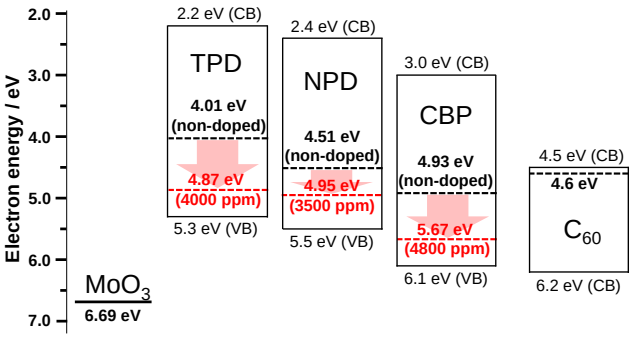

Fig. 1 Energy diagram of hole transporting materials, C_{60}, MoO_3. By MoO_3-doping , E_F values were positively shifted to 4.87, 4.95 and 5.67 eV for TPD, NPD and CBP respectively.

The absorption spectra of codeposited HTMs and MoO_3 films (1:1 in volume) showed charge-transfer (CT) absorption in the visible-near infrared region (not shown).

The above results suggest that HTMs are converted from insulator into *p*-type semiconductor by MoO_3-doping.

Next, we investigated the effects of changing conduction type in photovoltaic characteristics by MoO_3-doping for thick-film heterojunction cells; ITO/MoO_3 (10 nm)/HTMs (300 nm)/C_{60} (300 nm)/ Bathocuproine (BCP: 15 nm)/Ag (30nm).

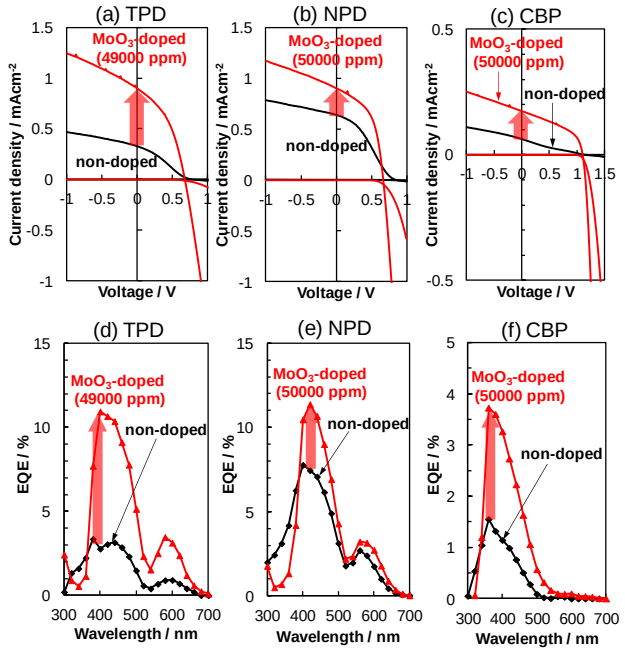

Fig. 2 Current density-voltage (*J-V*) curves and action spectra for ITO/MoO_3(10 nm)/HTMs(300 nm)/ C_{60}(300 nm)/BCP(15 nm)/ Ag(30nm) hetero junction cells. HTMs; TPD ((a) and(d)), NPD ((b) and (e)), CBP ((c) and (f)).

As shown in Fig. 2(a)-(c), fill factor and short-circuit photocurrent densities (J_{sc}) were increased by MoO_3-doping. Moreover, clear rectification characteristics were obtained.

As a doping concentration of MoO_3 increased, specific resistance of measured by van der Pauw method decreased up to four orders of magnitude. 300 nm-thickness TPD, NPD and CBP films showed sufficiently low resistance, 0.06, 0.05 and 0.002 kΩ respectively. Due to decrease of specific resistance, the fill factor of the heterojunction cells increased.

By MoO_3-doping, the external quantum efficiency (EQE) under light irradiation onto the ITO electrode were also increased (Fig. 2 (d)-(f)). Increase of EQE indicated increase of photocarrier generation efficiency. Fig. 3 shows the energy structure of TPD/C_{60} interface in case of non-doped and MoO_3-doped TPD after contact based on the energy relationships. In case of non-doped TPD, built-in potential was not formed at interface between TPD and C_{60} since the value of E_F of TPD located above that of C_{60}. On the other hand, in case of MoO_3-doped TPD, built-in potential was formed since the value of E_F of TPD located below that of C_{60}. Therefore, photocarrier generation efficiency is improved.

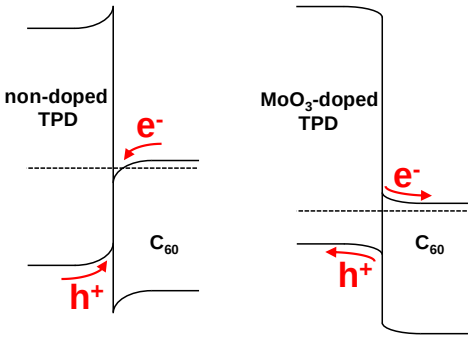

Fig. 3 The energy structure of TPD/C_{60} interface with non-doped (left) and MoO_3 doped (right) TPD, after contact.

4. Conclusions

In conclusion, photovoltaic characteristics of the solar cells using thick hole transporting films was improved by MoO_3-doping to HTMs because of decrease of cell resistance and the formation of built-in potential. This doping would be effective technique to make photovoltaic cells incorporating thick codeposited film of HTMs and C_{60} which can absorb light more efficiently.

Acknowledgements

Financial support from Core Research for Evolutional Science and Technology (CREST) from Japan Science and Technology Agency (JST) is gratefully acknowledged.

References

[1] M. Kubo, K. Iketaki, T. Kaji, and M. Hiramoto, *Appl. Phys. Lett.*, **98**, 073311 (2011).