This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 11:09
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Junction Formation by Doping in $H_2Pc:C_{60}$ Co-Evaporated Films for Solar Cell Application

Masayuki Kubo [a b] , Yusuke Shinmura [a b] , Norihiro Ishiyama [a b] , Toshihiko Kaji [a b] & Masahiro Hiramoto [a b]
[a] Institute for Molecular Science, Myodaiji , Okazaki , Aichi , Japan
[b] JST, CREST, 5, Sanbancho , Chiyoda-ku , Tokyo , Japan

To cite this article: Masayuki Kubo , Yusuke Shinmura , Norihiro Ishiyama , Toshihiko Kaji & Masahiro Hiramoto (2013) Junction Formation by Doping in $H_2Pc:C_{60}$ Co-Evaporated Films for Solar Cell Application, Molecular Crystals and Liquid Crystals, 581:1, 13-17

To link to this article: http://dx.doi.org/10.1080/15421406.2013.808137

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 581: pp. 13–17, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.808137

Junction Formation by Doping in H_2Pc:C_{60} Co-Evaporated Films for Solar Cell Application

MASAYUKI KUBO,[1,2,*] YUSUKE SHINMURA,[1,2]
NORIHIRO ISHIYAMA,[1,2] TOSHIHIKO KAJI,[1,2]
AND MASAHIRO HIRAMOTO[1,2]

[1]Institute for Molecular Science, Myodaiji, Okazaki, Aichi, Japan
[2]JST, CREST, 5, Sanbancho, Chiyoda-ku, Tokyo, Japan

pn-*control for the co-evaporated films were successfully accomplished. By* V_2O_5*-doping or* Cs_2CO_3*-doping, Fermi levels (*E_F*) of metal-free phthalocyanine:fullerene (*H_2Pc:C_{60}*) co-evaporated films positively or negatively shifted, suggesting that whole co-evaporated film behaved as* p-*type or* n-*type, respectively. A series of junction such as Schottky junction and* pn-*homojunction were formed by doping in* H_2Pc:C_{60} *co-evaporated films (1:1).*

Keywords Co-evaporated films; doping; Fermi level; junction formation; organic solar cells

Introduction

Controlling of pn properties is one of the key issues for small-molecular-type organic photovoltaic cells [1–9] since it enables intentional design energetic structures similar to inorganic cells [10,11]. Recently, we reported the complete pn-control of fullerene (C_{60}) [12,13] and metal-free phthalocyanine (H_2Pc) [14]. However, due to the absence of photosensitization in the single organic semiconductors, little photocurrent is expectable. In order to obtain practical magnitude of photocurrent, co-evaporated films should be used. Therefore, as a next step, we tried to form the built-in potential by doping directly in co-evaporated films.

In this paper, we report the pn-control and a series of junction formation by doping in H_2Pc:C_{60} co-evaporated films.

Experimental

C_{60} (Frontier Carbon, nanom purple TL) and H_2Pc (Dainippon Ink and Chemicals, INC., Fastogen Blue EP-101) samples were purified by single-crystal formed sublimation. V_2O_5 (SIGMA-ALDRICH, 99.99%) and Cs_2CO_3 (SIGMA-ALDRICH, 99.995%) were used as dopants to act as acceptor and donor, respectively. They were doped by the three-sources co-evaporation with C_{60} and H_2Pc. Precise monitoring of the deposition rates of the V_2O_5

---

[*] Address correspondence to Masayuki Kubo, Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan. Tel./Fax: +81-564-59-5537. E-mail: kubo@ims.ac.jp

(2×10^{-4} nm s^{-1}) and Cs_2CO_3 (1×10^{-4} nm s^{-1}) were achieved by using a quartz crystal monitors (QCMs; ULVAC, CRTM-6000G) equipped with a computer monitoring system (ULVAC, Depoview), which allowed us to dope with V_2O_5 and Cs_2CO_3 to as low as 1000 and 500 ppm in volume concentrations. All of the films were deposited by vacuum evaporation onto ITO glass substrates under 10^{-5} Pa pressure using an oil–free vacuum evaporator (ULVAC, VTS-350M/ERH). The Fermi level (E_F) of 100 nm-thick H_2Pc:C_{60} co-evaporated films were measured by Kelvin vibrating capacitor apparatus (Riken-Keiki, FAC-1) [15]. Both the evaporation chamber and the Kelvin probe for E_F measurement of various co-evaporated films were built in to a glove-box (Miwa, DBO-1.5) purged by N_2 gas. Thus, the H_2Pc:C_{60} co-evaporated films were not exposed to air at any time. The photovoltaic properties were also measured without exposure to air by setting the cells into a sample container with a quartz glass window inside the glove-box. The container was then evacuated to 10^{-5} Pa, and the action spectra were measured by irradiating with monochromatic light from a Xe-lamp through a monochromator. The external quantum yield (EQE) values were calculated as the ratio of the number of carriers collected under the short-circuit condition to the number of photons irradiated to the cell, which was measured by silicon photodiode (Hamamatsu Photonics, S1337-66BQ).

Results

(1) **Pn**-*control of Co-evaporated Films*

Figure 1 shows the energy diagrams for V_2O_5- or Cs_2CO_3-doped C_{60}, H_2Pc single films and H_2Pc:C_{60} co-evaporated film. In the case of C_{60} film, the E_F shifted to 4.40 eV and located near the conductance band by Cs_2CO_3-doping acting as donor, and it shifted to 5.87 eV and located near the valence band by V_2O_5-doping acting as acceptor. In the case of H_2Pc film, the E_F negatively shifted to 3.76 eV by Cs_2CO_3-doping and positively shifted to 4.80 eV by V_2O_5-doping. Obviously, they act as effective acceptor and donor dopants in both C_{60} and H_2Pc single films.

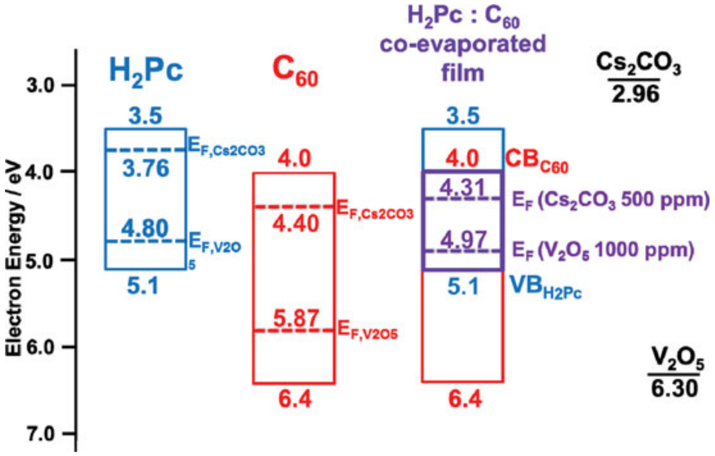

Figure 1. Energy diagrams for H_2Pc, C_{60} single films and H_2Pc:C_{60} co-evaporated film. 1000 ppm V_2O_5 and 500 ppm Cs_2CO_3 were doped. Values of the work functions of V_2O_5 and Cs_2CO_3 are also shown.

In the case of H_2Pc:C_{60} co-evaporated films, the E_F negatively shifted to 4.19 eV and reached near the conductance band of C_{60} by Cs_2CO_3-doping, and the E_F positively shifted to 4.91 eV and reached near the valence band of H_2Pc by V_2O_5-doping. This result suggests that whole co-evaporated film changed to *n*-type and *p*-type, respectively. It should be noted that the shift of Fermi levels of co-evaporated films occurs within the overlap of band gap of H_2Pc and C_{60} (Fig. 1, purple area), i.e., "band gap of co-evaporated film."

(2) Junction Formation in Co-evaporated Films

We fabricated *p*-type and *n*-type Schottky junctions and, *pn*-homojunction in H_2Pc:C_{60} co-evaporated films. The cell structures ((a), (b), (c)) and their action spectra ((d), (e), (f)) were shown in Fig. 2.

For the V_2O_5-doped cell, under the irradiation onto the ITO, the action spectrum showed a peak around the edge of the absorption spectrum (Fig. 2(b), hν(a)). This is the so-called "masking effect" and proves that the photoactive junction is located at the co-evaporated layer/Ag interface. Conversely, under irradiation onto the Ag, the action spectrum appeared in the same region as the absorption of H_2Pc:C_{60} co-evaporated film (Fig. 2(b), hν(b)). Judging from the negative photovoltage of the Ag electrode and the photoactive junction at the co-evaporated layer/Ag interface, the H_2Pc:C_{60} co-evaporated film behaves as *p*-type and an upwardly-bent Schottky junction is formed at the *p*-type

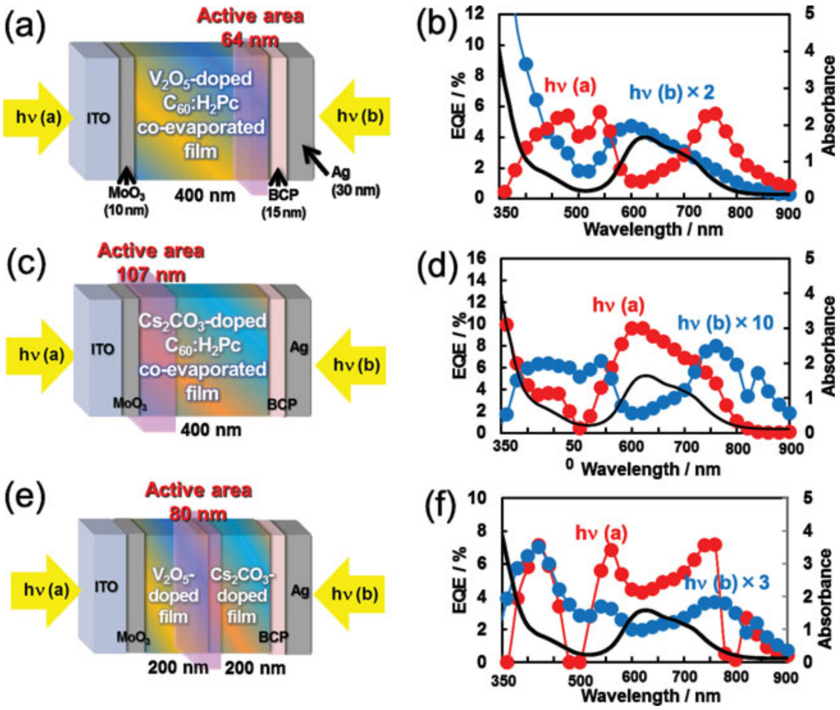

Figure 2. Cell structures ((a)(c)(e)) incorporating doped H_2Pc:C_{60} co-evaporated films and their action spectra ((b)(d)(f)). The black curves show the absorption of co-evaporated film. The volume concentrations for V_2O_5 and Cs_2CO_3 are 1000 and 500 ppm, respectively. Photoactive areas (red shaded parts) are indicated in the cell structures.

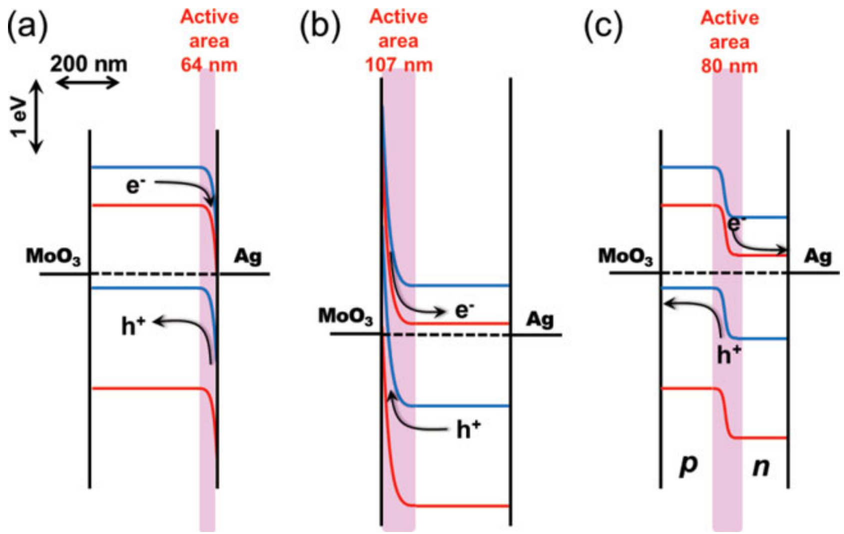

Figure 3. The energetic structures of cells in Fig. 2. Scales of energy and length are indicated by double-head arrows. (a) *p*-type Schottky junction. (b) *n*-type Schottky junction. (c) *pn*-homojunction.

H_2Pc:C_{60}/Ag interface (Fig. 3(a)). Thus, the formation of *p*-type H_2Pc:C_{60} co-evaporated film by V_2O_5 doping was confirmed by photovoltaic observation.

On the other hand, in the case of the Cs_2CO_3-doped cell, the action spectra measured by the illuminations from both sides show completely inverse characteristics to the V_2O_5-doped cell (Fig. 2(d), hν(a), (b)). Thus, we concluded that the opposite mechanism takes place for V_2O_5-doped cell, i.e., the Cs_2CO_3-doped film behaves as *n*-type and a downwardly-bent Schottky junction is formed at the MoO_3/*n*-type co-evaporated layer interface (Fig. 3(b)). Thus, the formation of *n*-type H_2Pc:C_{60} co-evaporated film by Cs_2CO_3 doping was confirmed by photovoltaic observation.

We fabricated the cell by connecting *p*-type and *n*-type H_2Pc:C_{60} co-evaporated films (Fig. 2(e)). Irrespective of the irradiation sides, the action spectrum showed a peak around the edge of the absorption spectrum, i.e., a strong masking effect was observed (Fig. 2(f), hν(a), hν(b)). This means that the carrier generated neither at the MoO_3/H_2Pc:C_{60} interface nor at the H_2Pc:C_{60}/Ag interface. Namely, the photoactive junction is formed at the center of cell bulk. Thus, the formation of *pn*-homojunction in H_2Pc:C_{60} co-evaporated film by doping was confirmed (Fig. 3(c)).

The band bending in energy diagrams in Figs. 3(a)–3(c) can be mapped in real scale based on the Kelvin probe measurements [10,16,17] and the widths of depletion regions for *p*-type (Fig. 3(a)), *n*-type (Fig. 3(b)) Schottky junctions, and *pn*-homojunction (Fig. 3(c)) to 64 nm, 107 nm, and 80 nm, respectively. Since these widths of depletion regions acting as photoactive areas were significantly thinner compared to the total cell thickness (400 nm), EQE spectra in Figs. 2(a)–2(c) were observed.

Conclusion

We succeeded in *pn*-control and junction formations by doping in H_2Pc:C_{60} co-evaporated films. Thus, the built-in potential in co-evaporated films can be intentionally formed by using doping technique. In this work, since we used only molecular level mixtures H_2Pc and C_{60}, the magnitude of photocurrent was not large. However, we have reported the increase of photocurrent due to the phase separation by using the co-evaporant molecules [18]. We are now trying to combine the present doping technique forming built-in potential and phase separation technique by co-evaporant molecules.

Acknowledgment

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

References

[1] Spanggaard, H., & Krebs, F. C. (2004). *Sol. Energy Mater. Sol. Cells*, *83*, 125.

[2] Tang, C. W. (1986). *Appl. Phys. Lett., 48*, 183.

[3] Hiramoto, M., Fujiwara, H., & Yokoyama, M. (1991). *Appl. Phys. Lett.*, *58*, 1062.

[4] Hiramoto, M., & Sakai, K. (2008). *Mol. Cryst. Liq. Cryst.*, *491*, 284.

[5] Kaji, T., Zhang, M., Nakao, S., Iketaki, K., Yokoyama, K., Tang, C. W., & Hiramoto, M. (2011). *Adv. Mater.*, *23*, 3320.

[6] Tokito, S., Noda, K., & Taga, Y. (1996). *J. Phys. D: Appl. Phys.*, *29*, 2750.

[7] Chan, C. K., Zhao, W., Barlow, S., Marder, S., & Kahn, A. (2008). *Organic Electronics*, *9*, 575.

[8] Hasegawa, T., Miura, S., Moriyama, T., Kimura, T., Takaya, I., Osato, Y., & Mizutani, H. (2004). *SID Int. Symp. Digest Tech. Papers*, *35*, 154.

[9] Liao, H.-H., Chen, L.-M., Xu, Z., Li, G., & Yang, Y. (2008). *Appl. Phys. Lett.*, *92*, 173303.

[10] Hiramoto, M., Ihara, K., & Yokoyama, M. (1995). *Jpn. J. Appl. Phys.*, *34*, 3803.

[11] Walzer, K., Maennig, B., Pfeiffer, M., & Leo, K. (2007). *Chem. Rev.*, *107*, 1233.

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

[13] Kubo, M., Kaji, T., & Hiramoto, M. (2011). *AIP Advances*, *1*, 032177.

[14] Shinmura, Y., Kubo, M., Ishiyama, N., Kaji, T., & Hiramoto, M. (2012). *AIP Advances*, *2*, 032145.

[15] As a standard, we measured the E_Fs of several kinds of metals by Kelvin probe and adjusted these values to the values of work function measured by the atmospheric photoelectron spectroscopy apparatus (Riken-Keiki, AC-3).

[16] Ishiyama, N., Kubo, M., Kaji, T., & Hiramoto, M. (2011). *Appl. Phys. Lett.*, *99*, 073311.

[17] Kubo, M., Shinmura, Y., Ishiyama, N., Kaji, T., & Hiramoto, M. (2012). *Appl. Phys. Express*, *5*, 092302.

[18] Kaji, T., Zhang, M., Nakao, S., Iketaki, K., Yokoyama, K., Tang, C. W., & Hiramoto, M. (2011). *Adv. Mater.*, *23*, 3320.