Double Co-deposited Organic Solar Cells with Sensitivity Through Visible to Near-Infrared

Kazuya Yokoyama^{1,2}, Toshihiko Kaji^{1,2} and Masahiro Hiramoto^{1,2}

 ¹ Institute for Molecular Science, ² CREST/JST.
5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Aichi, Japan Phone: +81-564-59-5537 E-mail: yokokazu@ims.ac.jp

1. Introduction

Organic solar cells consisting of vacuum-deposited small-molecular thin films have been intensively studied. In 1991, we proposed *p-i-n* organic solar cells in which the *i*-interlayer was a codeposited film comprising of *p*-type (donor) and *n*-type (acceptor) organic semiconductors.^{1,2)} We have observed a short-circuit photocurrent density and an efficiency of 20 mA cm⁻² and 5.3%, respectively, for a single 1-µm-thick *p-i-n* solar cell under irradiation with visible light.^{3,4)}

From the standpoint of conversion efficiency, utilization of near infrared (NIR) light containing a vast number of photons, which allows the photocurrent density to reach 30 mA cm⁻², similar to single crystal Si cells, is an important issue.

J-aggregates with a low stacking angle, which are peculiarly formed of shuttle cock-type phthalocyanines, have strong NIR absorption, and we reported on an organic *p-i-n* solar cell consisting of lead phthalocyanine (PbPc), which is one of the typical shuttle cock-type phthalocyanine, and fullerene (C_{60}). This solar cell was operated by NIR light extending to 1050 nm and the external quantum efficiency and conversion efficiency reached 43% and 2.3%, respectively.⁵



Fig. 1 Cell structure. Front cell has visible sensitivity and back cell has NIR sensitivity.

In this work, we report on organic solar cells having sensitivity in visible and NIR region. Fig. 1 shows the cell structure. Cells have double co-deposited layers, namely, visible sensitive layer and NIR sensitive layer. The front cell with visible sensitivity consists of H₂Pc and C₆₀ co-deposited layer. The back cell with NIR sensitivity consists of PbPc and C₆₀ co-deposited layer. Absorption specta of these solar cells have peaks through visible to NIR re-

gions (500-1000 nm) due to H_2Pc and *J*-PbPc, and the internal quantum efficiency (IQE) of visible and NIR regions reached 48% and 43%, respectively, for the best cell.

2. Experiment

All of the films were deposited by vacuum evaporation onto indium tin oxide (ITO) pretreated in an air plasma under 10⁻⁵ Pa pressure using an oil-free vacuum evaporator (ULVAC, VTS-350M/ERH). The cell structure was ITO / H_2Pc (20 nm) / $H_2Pc:C_{60}$ (100 nm) / PbPc:C60 (100 nm) / C_{60} (50 nm) / BCP (15 nm) / Ag. H₂Pc:C₆₀ and PbPc:C₆₀ co-deposited layers were prepared at the substrate temperature of 70°C in the presence of co-evaporant molecules; polydimethylsiloxane (PDMS41).⁶⁾ The evaporation rates were 0.05 nm s⁻¹ for H_2Pc , C_{60} and PbPc. Co-evaporant rates were kept at 0.002 nm/s for the front cell, and the co-evaporant rates were changed from 0 to 0.02 nm/s for the back cell. The current density-voltage (J-V) characteristics were measured under the irradiation of simulated solar light (Ushio Inc., MS-110AAA). The cell area was precisely defined by using a metal mask with an aperture of 2×2 mm². To measure the action spectra, a Xe-lamp equipped with a monochromator for the visible (Shimadzu, SPG-3ST, Kyoto, Japan) and a W-lamp equipped with a monocjromator for the infrared region (Shimadzu, SPG-120IR) were used. All the measurements were performed at room temperature under vacuum (10^{-3} Pa) .



Fig. 2 Absorption spectra of PbPc: C_{60} co-deposited films with illustrations of molecular stacking of the *H*- and *J*-aggregate and amorphous state. Co-evaporant rate; 0 (A), 0.001 (B), 0.005 (C) and 0.01 (D) nm/s.

3. Results and discussion

Fig. 2 shows the absorption spectra of PbPc: C_{60} co-deposited films. In the absence of co-evaporant, PbPc in the co-deposited layer mainly get to amorphous state (Fig. 2(A)). By contrast, in the presence of co-evaporant molecules, absorption peaks of amorphous state decrease and *H*- and *J*-PbPc peaks increase with the increase of the co-evaporant rate. This observation suggests that the presence of co-evaporant encourage PbPc in the co-deposited layer to form *H*- and *J*-aggregate.

Fig. 3 shows *J-V* curves of cells. With increasing co-evaporant rate on the back cell, short-circuit photocurrent density (J_{sc}) had increased and reached 8.3 mA cm⁻² for the best cell (Fig. 3(C)).



Fig. 3 J-V curves of double co-deposited organic solar cells. Solid and broken curves show photocurrent density and darkcurrent density, respectively. Co-evaporant rate of the back cell; 0 (A), 0.001 (B) and 0.02 (C) nm/s.

Fig. 4 shows the spectral dependence of the IQE of cells. The sensitivity extends through visible to NIR rigions. With increasing co-evaporant rate for the back cell, NIR sensitivity had increased because of formation of *J*-PbPc and IQE in visible and NIR region respectively reached 48 and 43% for the best cell (Fig. 4(C)).



Fig. 4 Spectral dependence of the IQE of cells. Co-evaporant rate of the back cell; 0 (A), 0.001 (B) and 0.02 (C) nm/s.

3. Conclusions

We succeeded in fabricating double co-deposited organic solar cells with sensitivity through visible to NIR region. In the presence of co-evaporant, PbPc in the co-deposited layer mainly form *H*- and *J*-aggregate. In the present cell, visible light is absorbed at the front cell and NIR light is absorbed at the back cell. With increase of the co-evaporant rate for the back cell, cell performance improved due to formation of J-PbPc. As a result, J_{sc} and conversion efficiency of the best performance cell reached 8.3 mA cm^{-2} and 1.5%, respectively.

Fig. 5 shows the performance mechanism of present cell. In the front cell, visible light is absorbed by H_2Pc , and then, photogenerated holes and electrons are transported through H_2Pc and C_{60} , respectively. In the back cell, NIR light is absorbed by *J*-PbPc, and then, photogenerated holes and electrons are transported through *H*-PbPc and C_{60} , respectively. Namely, each component (C_{60} , H_2Pc , *H*-PbPc and *J*-PbPc) has a different function in this cell.



Fig. 5 Model of the function-separated mechanism of the present cell. Visible and NIR light are absorbed by H_2Pc and *J*-PbPc, respectively. Photogenerated holes are transported through H_2Pc and *H*-PbPc. Photogenerated electrons are transported through C_{60} .

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