

Organic Solar Cells

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Organic solar cell is recognized as a future 3rd generation solar cell. In 2009, we started CREST Project; “Bandgap Science for Organic Solar Cells.” Target of this project is 15% efficiency of organic solar cells by establishing bandgap science for organic semiconductors, which is equivalent to that for silicon semiconductor.

Conductivity (σ) is related both carrier concentration (n) and carrier mobility (μ) [$\sigma = en\mu$]. To achieve high efficiency, cell resistance ($\rho = 1/\sigma$) should be decreased by increasing both n and μ . Former and latter relate Topics 1, 2 and Topic 3, respectively.

1. Conduction-Type Control of C_{60} Films from n - to p -Type by MoO_3 Doping¹⁾

As in the case of inorganic solar cells, precise conduction type control, *i.e.*, pn -control is indispensable to fabricate efficient organic solar cells consisting of pn and pin junctions.

In this study, conduction-type control of highly purified 7N (seven nines; 99.99999%) C_{60} films from n - to p -type by doping with molybdenum oxide (MoO_3) was demonstrated. The energetic value of the Fermi level (E_F), 4.50 eV, for nondoped C_{60} films measured by the Kelvin vibrating capacitor method was positively shifted to 5.88 eV, and approached the valence band by the coevaporated doping of MoO_3 at a

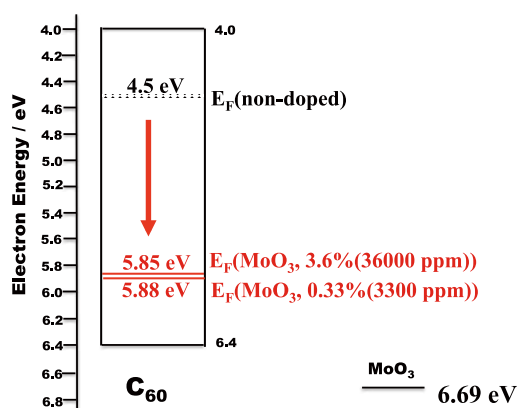


Figure 1. Positive shift of Fermi level (E_F) for C_{60} films by MoO_3 doping.

concentration of 3300 ppm (Figure 1).

Due to the observation of charge transfer (CT) absorption between C_{60} and MoO_3 , and ability of electron extraction of MoO_3 from the valence band of C_{60} (Figure 1), we concluded that the formation of CT complex [$C_{60}^+-MoO_3^-$]. Positive charge on C_{60}^+ can be liberated from the negative charge of the MoO_3^- by the heat energy of room temperature (Figure 2). Increase of the free hole concentration causes the large positive shift of E_F . Formation of p -type C_{60} was also confirmed based on the photovoltaic properties.

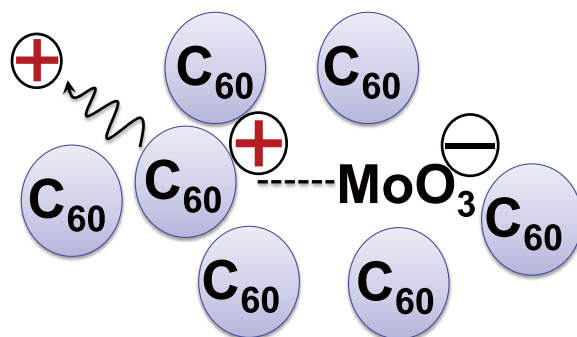


Figure 2. Mechanism of MoO_3 -doping.

2. Doping-Based Control of the Energetic Structure of Photovoltaic Co-Deposited Films²⁾

Doping based pn -control technique for co-deposited films should be developed to enhance cell efficiency since recent organic solar cells incorporate co-deposited films to generate significant photocurrent densities based on the dissociation of excitons by the photoinduced electron transfer process.

In this study, energetic structures of C_{60} :6T (α -sexithiophene) co-deposited films were intentionally tuned from n -type Schottky junctions through metal/intrinsic/metal junctions to p -type Schottky junctions by ppm-level doping with MoO_3 .

‘Three component co-evaporation’ technique was developed for the doping of MoO_3 into the C_{60} :6T co-deposited films. Precise monitoring of the deposition rate of the MoO_3

using a computer monitoring system allowed us to dope with MoO_3 to as low as 70 ppm in volume concentration. Light was irradiated on ITO electrode for the cells, ITO/ MoO_3 -doped C_{60} :6T/ MoO_3 /Ag (Figure 3).

For non-doped (0 ppm) and 400 ppm MoO_3 -doped cells, photocurrent appeared in the region from 500 to 700 nm, where there is weak absorption from the cells (masking effect). This means that an *n*-type Schottky junction was formed at the C_{60} :6T/ MoO_3 interface (Figure 4(a)). For 600 ppm-doped cell (Figure 3), the photocurrent was distributed equally throughout the wavelength region from 300 to 700 nm, *i.e.*, the generation of photocurrent occurs in the whole of the bulk of the cell. This means that the co-deposited film behaves as 'intrinsic' material (Figure 4(b)). For 1100 and 4300 ppm-doped cells (Figure 3), photocurrent appeared in the strong absorption region (300–500 nm). This means that a *p*-type Schottky junction was formed at the ITO/ C_{60} :6T interface (Figure 4(c)).

We are now trying to fabricate *pn*- and *pin*-homojunctions to create built-in potentials directly in the co-deposited films to realize high efficient organic solar cells.

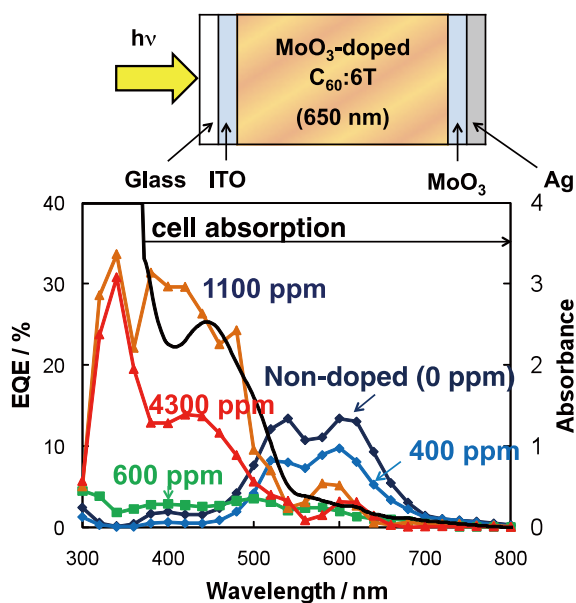


Figure 3. Action spectra of the external quantum efficiency (EQE) of the short-circuit photocurrent. Black curve shows cell absorption.

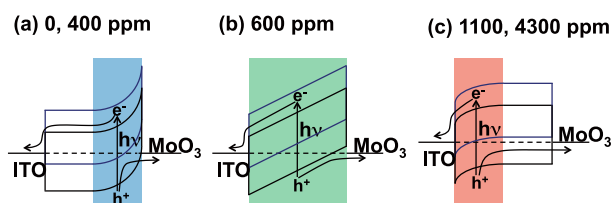


Figure 4. Energetic structures of the ITO/ C_{60} :6T/ MoO_3 cells for various MoO_3 -doping concentrations.

3. Co-Evaporant Induced Crystalline Co-Deposited Films in Organic Solar Cells³⁾

Nano-structure control of co-deposited films, *i.e.*, route formation for electrons and holes photogenerated in the co-deposited films is indispensable to fabricate efficient organic solar cells.

In this study, a novel method for crystallizing co-deposited films is developed. This method utilizes a liquid as a non-sticking co-evaporant during vacuum deposition (Figure 5).

Photocurrent enhancement was observed particularly for relatively thick (~400 nm) co-deposited films having greater light absorption (Figure 5). Co-deposited films based on H_2Pc and C_{60} with much improved crystallinity have been produced by introducing co-evaporant and confirmed by analysis using UV-Vis, XRD and FESEM (Figure 5). Striking enhancement in photocurrent generation is achieved in organic solar cells without exception, based on a variety of co-deposited films such as $\text{PbPc}:\text{C}_{60}$, $\text{AlClPc}:\text{C}_{60}$, and $\text{rubrene}:\text{C}_{60}$. We believe that this method is generally applicable for growing high-quality crystalline films by vacuum deposition and opens the possibility of producing high-performance organic solar cells.

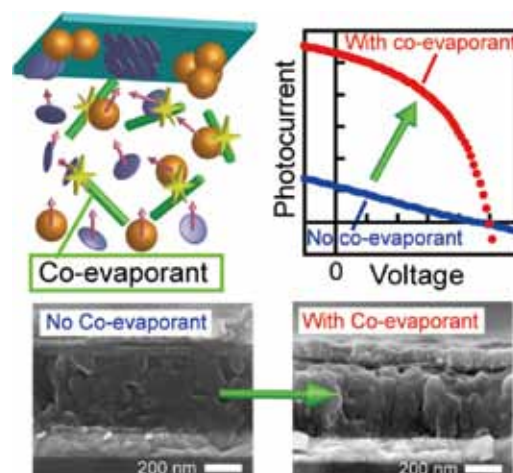


Figure 5. (Upper-left) Model of co-evaporant induced crystallization. Additional co-evaporant molecules hit C_{60} and phthalocyanines (Pc) at or near the substrate and promoting crystallization in the co-deposited film. (Upper-right) Photocurrent-voltage characteristics of $\text{H}_2\text{Pc}:\text{C}_{60}$ co-deposited cells with/without co-evaporants, showing dramatic improvements of cell performances. (Lower) Enhanced crystallization is clearly observed in the co-deposited film with a co-evaporant, including a transformation of the grain from a random structure without the co-evaporant to a column structure with the co-evaporants.

References

- 1) M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, *Appl. Phys. Lett.* **98**, 073311 (2011).
- 2) N. Ishiyama, M. Kubo, T. Kaji and M. Hiramoto, *Appl. Phys. Lett.* **99**, 133301 (2011).
- 3) T. Kaji, M. Zhang, S. Nakao, K. Iketaki, K. Yokoyama, C. W. Tang and M. Hiramoto, *Adv. Mater.* **23**, 3320 (2011).