Organic Solar Cells

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Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc*. We have been focused on the establishment of "bandgap science for organic solar cells." We believe that the following features are indispensable. (a) Organic semiconductors purified to sub-ppm level, at least seven nines (7N; 0.1 ppm), should be used. (b) A ppm-level doping technique should be developed. (c) Every individual organic semiconductor should be capable of displaying both *n*- and *p*-type characteristics by impurity doping alone, *i.e.*, complete *pn*-control should be developed. (d) Unintentional and uncontrollable doping by oxygen and water from air should be completely eliminated. (e) The doping technique should be applicable not only to single organic semiconductor films, but also to codeposited films consisting of two kinds of organic semiconductors since a key element for exciton dissociation in organic solar cells is having a co-deposited films.

Recently, we have showed that in principle, almost all single organic semiconductors can be controlled to both *n*-type and *p*-type by doping alone, similar to the case of inorganic semiconductors (Figure 1). This can be regarded as a foundation for the construction of high efficient organic solar cells.

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100 nm) are also shown.

Selected Publications

• M. Hiramoto, M. Kubo, Y. Shinmura, N. Ishiyama, T. Kaji, K. Sakai, T. Ohno, M. Izaki and M. Hiramoto, "Bandgap Science for Organic Solar Cells," *Electronics* **3**, 351–380 (2014).

• M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, "Conduction Type Control of Fullerene Films from *n*- to *p*-Type by Molybdenum Oxide Doping," *Appl. Phys. Lett.* **98**, 023302 (3 pages) (2011).

• M. Hiramoto, H. Fujiwara and M. Yokoyama, "Three-Layered Organic Solar Cell with a Photoactive Interlayer of Codeposited Pigments," *Appl. Phys. Lett.* **58**, 1062–1064 (1991).

1. Ionization Sensitization of Doping in Co-Deposited Organic Semiconductor Films

We have developed the *pn*-control technique by impurity doping for co-deposited films[1] such as C_{60}:H_2Pc (fullerene: metal-free phthalocyanine) since a key element for exciton dissociation in organic solar cells is having a co-deposited films. During the course of these studies, we made accurate estimates of the carrier concentrations generated by impurity doping by means of Kelvin band-mapping,[2] from which we found evidence of higher doping efficiencies for co-deposited films compared to those for the respective single films.

Figure 3 shows the dependence of the doping efficiency on the doping concentration for C_{60}:H_2Pc and their component films. The doping efficiency is defined by the ratio of the carrier concentration created to the molecular concentration of Cs_2CO_3. The doping efficiencies of single films of C_{60} and H_2Pc are around 10%. In contrast, those of the co-deposited films of C_{60}:H_2Pc are around 50%. Thus, we conclude that the doping efficiency was significantly enhanced in the co-deposited films.
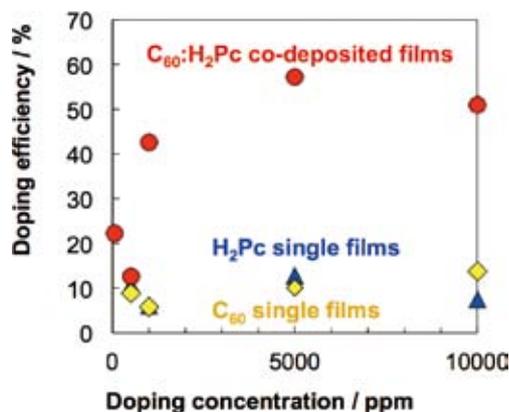
Figure 2. Dependence of doping efficiency on Cs_2CO_3 doping concentration for C_{60}:H_2Pc co-deposited films and their component films.

By making contact with C_{60}, since the electron transfer from the conduction band of H_2Pc to that of C_{60} (Figure 4(a), blue arrow) occurs accompanied with energetic relaxation (0.7 eV), the electron concentration in H_2Pc decreases. Due to the shift in equilibrium, the electrons liberated from the donor levels accelerate, *i.e.*, the ionization rate (doping efficiency) for donors increases only in the H_2Pc region. Figure 4(b) shows the cross sectional energy structures of charge separating H_2Pc/C_{60} superlattice after contact. In this model, the H_2Pc regions act as electron supplying layers to the C_{60} regions. The C_{60} regions act as electron transporting highways. Based on this model, we expected that the total ionization rate in H_2Pc:C_{60} co-deposited films would increase further by increasing the H_2Pc ratio and obtained the ionization rate of 97% at a H_2Pc:C_{60} ratio of 99:1.
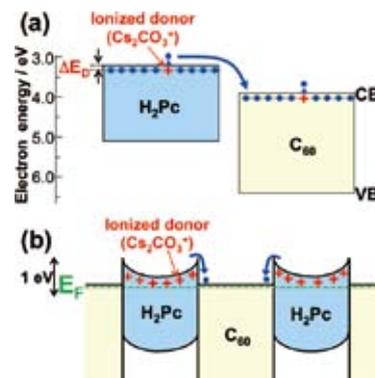
Figure 3. (a) Energy diagrams of Cs_2CO_3-doped H_2Pc and C_{60} single films before contact. CB, VB, and ΔE_D denote the conduction band, the valence band, and the activation energy of the donors, respectively. (b) Cross sectional energy structure of a Cs_2CO_3-doped H_2Pc/C_{60} superlattice model after contact.

2. Mapping of Band-Bending for Organic *pn*-Homojunctions

A precise band-mapping for organic *pn*-homojunctions, which have various balance of doping concentration between *p*- and *n*-type layers, was performed by measuring the film thickness dependence of the work function from both sides of the *pn*-homojunction interface using a Kelvin probe. Band-bending including the simultaneous development of depletion layer in underlying *n*-type layer induced by the deposition of *p*-type layer, and vice versa, should be taken into account for the precise fitting based on the Poisson equation. Validity of the conventional theory of space charge layer suggests that the dopants are spatially fixed even in the organic semiconductor films. The present result allows the precise design of the built-in potential in the organic solar cells.
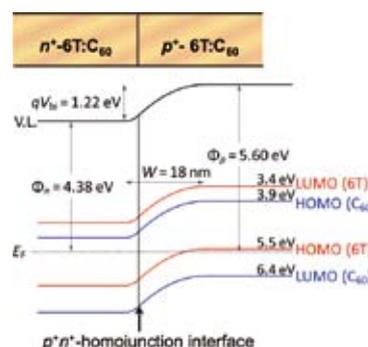
Figure 4. Energy band diagram of the p^+n^+-homojunction. VL, E_F, VB, and CB denote the vacuum level, Fermi level, the valence band and the conduction band, respectively.

References

1) M. Kubo, T. Kaji and M. Hiramoto, *Appl. Phys. Lett.* **103**, 263303 (2013).
2) Y. Shinmura, N. Ishiyama, T. Kaji and M. Hiramoto, *Appl. Phys. Express* **7**, 071601 (2014).