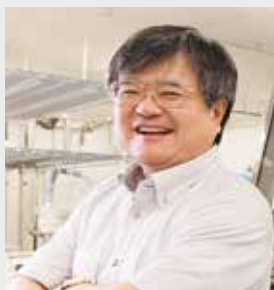


Organic Solar Cells

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Education

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Professional Employment

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Awards

2017 11th JSAP Fellow Awards
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Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

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.

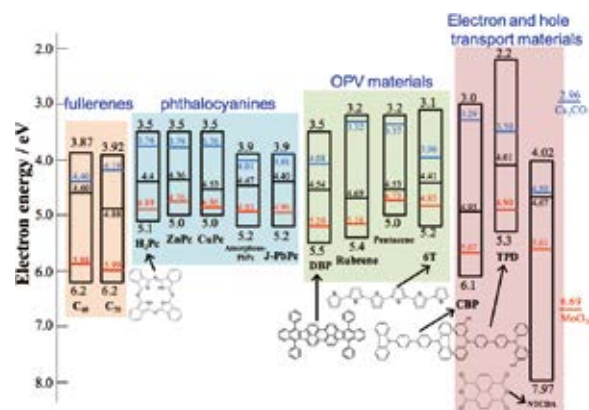


Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100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

Selected Publications

- C. Ohashi, S. Izawa, Y. Shinmura, M. Kikuchi, S. Watase, M. Izaki, H. Naito and M. Hiramoto, “Hall Effect in Bulk-Doped Organic Single Crystal,” *Adv. Mater.* **29**, 1605619 (6 pages) (2017).
- C. Ohashi, Y. Shinmura, M. Kubo and M. Hiramoto, “ppm-Doping Effects in the Simplest n^+p -Homojunction Organic Photovoltaic Cells,” *Org. Electron.* **27**, 151–154 (2015).
- 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).

1. Hall Effect in Doped Organic Single Crystals

Control of *p*-type and *n*-type that holes and electrons are responsible for electric conduction, respectively, by the addition of a trace amount of impurity (doping) is the central technology in 20 century's inorganic single crystal electronics as represented by the silicon chips, the solar cells, and the light emitting diodes. The number of carriers created by doping and their moving speed (mobility) can be freely evaluated by Hall effect measurement using a magnetic field. However, in the field of organic electronics emerging in 21 century, no one has attempted not only to dope impurities into the organic single crystal itself but also the Hall effect measurement.

We combined the rubrene organic single crystal growth technique with the our original ultra-slow deposition technique of one billionth of a nanometer (10^{-9} nm) per second, which includes a rotating shutter having aperture, and have succeeded in producing the 1 ppm doped organic single crystal and in detecting the Hall effect signal for the first time (Figures 2 and 3). As an acceptor dopant, iron chloride (Fe_2Cl_6) was used.

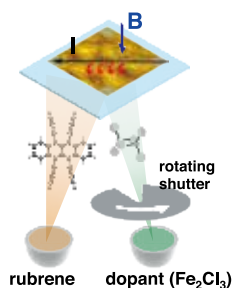


Figure 2. Ultra-slow co-deposition technique to produce the doped rubrene single crystal. Magnetic field (B) and excitation current (I) for Hall effect measurements are also shown.

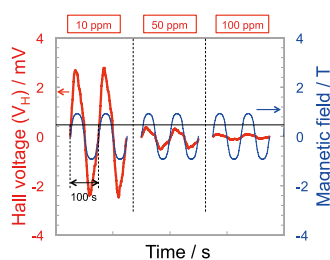


Figure 3. Hall voltage signals (red) observed under the application of AC magnetic field (blue) for the 50-, 100-, 500-, and 1000-ppm doped devices.

Hall voltage (V_H) signals were detected when applying a magnetic field to the FeCl_3 -bulk-doped homoepitaxial layer (Figure 3). V_H showed a systematic decrease for the 50-, 100-, 500-, and 1000-ppm doped devices, respectively. This is due to the increase in the hole concentration (N) (Figure 4(a), red).

Two unique observations were observed for the doped

single crystals.

- (i) High ionization rate of dopant molecules: The doping efficiencies of a single crystal and amorphous films of rubrene were compared. The rubrene single crystal reached a maximum value of 24% at 100 ppm (Figure 4(b), red), which was significantly larger than the value of 1.2% for the amorphous film that formed from vacuum deposition (Figure 4(b), blue). We presume that the ionization rate was dominated by the density of hole traps.
- (ii) Scattering effects from lattice disturbances: The Hall mobility (μ_H) decreased above 10 ppm (Figure 4(c)). We think that this could be attributed to hole scattering by doping-induced lattice disturbances, such as lattice distortion from the substitution of rubrene molecules with ionized and neutral dopant molecules, and the formation of various types of defects, such as dopants that were inserted at interstitial positions, the formation of doping-induced vacancies, *etc.*

The present results have the meaning of dawn of organic single crystal electronics similar to the silicon single crystal electronics. In future, organic single crystal devices such as high performance organic single crystal solar cells would be developed.

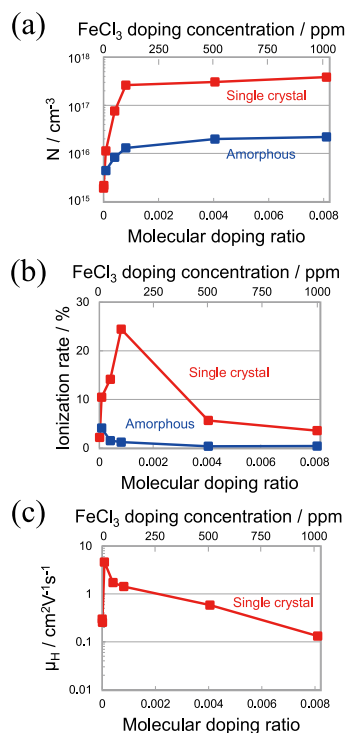


Figure 4. Dependences of (a) the hole concentration per unit volume (N), (b) the ionization rate, and (c) the Hall mobility (μ_H) on the molecular doping ratio (MR) and the FeCl_3 doping concentration by volume for doped single crystal (red curves). For comparison, the results for N and the ionization rate for vacuum deposited amorphous films are also shown (blue curves).

Award

HIRAMOTO, Masahiro; 11th JSAP Fellow Awards (2017).