Effects of Doping at the ppm level in Simple n^+p -Homojunction Organic Photovoltaic Cells

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Abstract

The effects of doping at concentrations at the ppm level in organic photovoltaic cells were clarified using simple n^+p -homojunctions. With doping from 0 to 10 ppm, the fill factor increased due to the appearance of majority carriers. From 10 to 100 ppm, the photocurrent density increased due to an increase in the built-in potential, i.e., the formation of an n^+p -homojunction. The photocurrent was increased by a factor of 1.3 by directly doping the photoactive co-deposited layer with acceptor molecules at a concentration of 100 ppm.

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For small molecule type organic photovoltaic cells,¹⁻⁸⁾ controlling the energy band structure by doping^{7, 9-12)} in order to create a built-in potential is a significant challenge, as it is for inorganic ones.¹³⁾ We think that co-deposited films should be doped since blended films consisting of organic semiconductor acting as a donor and that acting as an acceptor are used for efficient photocarrier generation in the present organic solar cells. We have previously reported on the complete *pn*-control of C₆₀:6T (α -sexithiophene)¹⁴⁾ and C₆₀:H₂Pc (metal-free phthalocyanine)^{15,16)} co-deposited films. Recently, we reported on the fabrication of *p*⁺*in*⁺-homojunction cells in C₆₀:6T co-deposited films by the use of doping only.¹⁷⁾ In those cells, the photocurrent is generated in the undoped co-deposited layer, i.e., the *i*-layer. However, we believe that direct doping of the photoactive co-deposited layer where the generation and transport of photocarriers occurs provides us with the potential to enhance the efficiency of these organic solar cells. Based on this consideration, we attempted to introduce a *pn*-homojunction into a C₆₀:6T co-deposited film. For the simplest cell, we adopted a *n*⁺*p*-homojunction that has a one-sided abrupt junction (Fig. 1(a)).¹⁸⁾ The acceptor doping concentration in the *p*-layer was varied from the extremely low concentration of 1 ppm up to 1,000 ppm.

In this letter, we report on the effects of doping at these levels in organic photovoltaic cells. An increase in photocurrent by a factor of 1.3 by directly doping the photoactive organic co-deposited layer with acceptor molecules at a concentration of 100 ppm was demonstrated.

6T (Tokyo Chemical Industry) and C₆₀ (Frontier Carbon, nanom purple TL) were purified by single-crystal sublimation.^{7,19)} FeCl₃ (Sigma-Aldrich, 99.99%)^{20,21)} and Cs₂CO₃ (Sigma-Aldrich, 99.995%)^{7,15-17)} were used for the acceptor and donor dopants, respectively. Fig. 1(a) shows the structure of the *n*⁺*p*-homojunction cell. The cells were fabricated on indium tin oxide (ITO) substrates at 10⁻⁵ Pa in an oil-free

vacuum evaporator (EpiTech Inc., ETVP-VG 100-SP) housed in a glove box (EpiTech Inc., 12ET12007). The evaporation rates of C₆₀ and 6T were 0.1 and 0.01 nm s⁻¹, respectively. We chose the ratio of 10:1 (C₆₀:6T) because the optimum value of V_{oc} (0.8 V) was achieved with this ratio, larger than the value (0.4 V) achieved with the usual ratio of 1:1.²²⁾ The thicknesses of the *n*⁺- and *p*-layers were 10 and 100 nm, respectively. A ‘Three component co-evaporation’ technique was employed to dope the co-deposited films. The Cs₂CO₃ doping concentration for the *n*⁺-layer was kept constant at 10,000 ppm. The FeCl₃ doping concentration for the *p*-layer was varied, i.e., 0, 1, 10, 100, and 1,000 ppm. Precise monitoring of the deposition rate using a quartz crystal microbalance equipped with a computer monitoring system (ULVAC, CRTM-9000G/Depoview) allowed us to introduce dopants down to the very low concentration of 100 ppm by volume, which corresponds to a FeCl₃ deposition rate of 1.1 x 10⁻⁵ nm s⁻¹. Doping concentrations of 10 and 1 ppm were realized by reducing the dopant evaporation rate using rotating disks with slits with aperture ratios of 1:10 and 1:100, respectively. The doping concentration of 1 ppm corresponds to a molecular ratio (MR) of 3.7 x 10⁻⁶.

The current-voltage (J-V) characteristics were obtained under simulated solar light (AM 1.5G, 100 mWcm⁻²). The position of the Fermi level (E_F) was determined using a Kelvin probe (Riken-Keiki, FAC-1). Level bending in doped organic semiconductors can be measured by using photoelectron spectroscopy²³⁾ or by using Kelvin probes. We chose Kelvin probes to map the level bending profiles in the cells.²⁴⁾ The films and cells were prevented from exposure to air at all times during both fabrication and measurement.

Fig. 1(b) shows the energy band diagram of the C₆₀:6T co-deposited film. The bandgap in this film is determined by the conduction band of C₆₀ (CB_{C60}) and the valence band of 6T (VB_{6T}). In order to fabricate an *n*⁺-layer, heavy doping with

Cs₂CO₃ (10,000 ppm) was performed. For the *p*-type layers formed on the *n*⁺-layer, FeCl₃ doping concentrations of 10, 100, and 1,000 ppm caused E_F to shift towards VB_{6T} (5.50 eV) with more positive values of 5.01, 5.15, and 5.21 eV, respectively.²⁵⁾ These observations suggest that an *n*⁺*p*-homojunction is expected to form as the FeCl₃ concentration is gradually increased.

Fig. 2 shows the current-voltage characteristics for *n*⁺*p*-homojunction cells with *p*-layer doping concentrations of 0, 1, 10, 100, and 1,000 ppm (Fig. 1(a)). The magnitude of the short-circuit photocurrent density (J_{sc}) increases progressively with the FeCl₃ doping of the photoactive C₆₀:6T layer as follows; 3.51 for 0 ppm (black solid curve), 4.02 for 10 ppm (orange solid curve), and 4.48 mAcm⁻² for 100 ppm (red solid curve). Simultaneously, there is a progressive increase in the magnitude of the forward current density (black, green, and red broken curves). That is, the cell resistance (R_s) decreases systematically with FeCl₃ doping and the minimum R_s of 2.35 Ωcm² is obtained at 100 ppm (see Fig. 4(b)). J_{sc} increases by a factor of 1.3 and the maximum efficiency of 1.51% is at 100 ppm. However J_{sc} decreases and R_s increases with a further increase in doping concentration to 1,000 ppm (blue curves). This confirms that the photocurrent can be increased significantly by directly doping the photoactive co-deposited layer with extremely low concentrations at the ppm level.

Level bending occurs only on the *p*-side of the *n*⁺*p*-homojunction since the *n*⁺-layer is heavily doped (10,000 ppm). Therefore, the width of the depletion layer (W_{dep}) formed in the *p*-type layer depends on the FeCl₃ doping concentration in the layer. Level bending in the *p*-type layer is accompanied by bending of the vacuum level since the Fermi levels (E_F) are aligned. Thus, we can measure the value of the work function, which is defined as the difference between the vacuum level and E_F, using a Kelvin probe, and we can measure the variation of this with the thickness of the film. Fig. 3(a) shows the dependence of the work function on the *p*-type layer

thickness for various doping concentrations. In the cases of 0 (black dots) and 1 ppm (green dots), the observed work function has a constant value of 4.20 eV, which is the same as the Fermi level in the n^+ -layer, i.e., no **level bending** was observed. This shows that layers with these doping levels act as intrinsic layers. **The absence of any change in work function at the extremely low doping concentration of 1 ppm (Fig. 3(a), green dots)** may be attributed to trap filling, i.e., **doping induced carriers are captured by traps.**²⁶⁾ In the cases of 10 (orange dots), 100 (red dots), and 1,000 ppm (blue dots), **level bending** was observed. This clearly shows that layers doped at these levels act as p -type layers. The width of the depletion layer (W_{dep}) and the built-in potential (V_{bi}) can be determined from the points (shown by arrows) at which the **level bending** ends. For example, $W_{\text{dep}} = 50$ nm and $V_{\text{bi}} = 1.0$ V at a doping concentration of 100 ppm. Moreover, the hole concentration (N_{h}) can be calculated **using** equation (1).

$$N_{\text{h}} = 2\epsilon\epsilon_0 V_{\text{bi}} / e W_{\text{dep}}^2 \quad (1)$$

At 100 ppm, N_{h} was calculated to be $1.8 \times 10^{17} \text{ cm}^{-3}$. **The doping efficiency was determined to be around 30%.** The dependences of W_{dep} , V_{bi} , and N_{h} on doping concentration are shown in Figs. 3(b), 4(c), and 4(d), respectively. The energy band diagrams of the n^+p -homojunction cells (Fig. 3(b)) can be found by turning the curves in Fig. 3(a) upside down.²⁷⁾

Fig. 4(a) shows the dependences of J_{sc} and the fill factor (FF) on doping concentration. The doping effects can be divided into three regions. From 0 to 10 ppm, both FF and J_{sc} increase rapidly. From 10 to 100 ppm, J_{sc} still increases while FF maintains a constant value. From 100 to 1,000 ppm, both J_{sc} and FF decrease.

Fig. 4(b) shows the dependences of the fill factor (FF) and the cell resistance (R_{s}) on doping concentration from 0 to 100 ppm. Clearly, R_{s} decreases and FF increases from 0 to 10 ppm. Once acceptor doping is performed, holes and electrons inevitably act as majority and minority carriers, respectively. At 10 ppm, the number

(N_h) of majority carriers (holes) is $2.3 \times 10^{16} \text{ cm}^{-3}$. Thus, we conclude that the increase in FF at 10 ppm doping is due to the appearance of majority carriers in the p -layer.

Fig. 4(c) shows the dependences of J_{sc} and the built-in potential (V_{bi}) on doping concentration from 0 to 1,000 ppm. Clearly, there is a close relationship between J_{sc} and V_{bi} . In particular, there are simultaneous increases in J_{sc} and V_{bi} at the relatively low doping concentrations of 10 and 100 ppm. The increase in V_{bi} is also shown in the energy band diagrams for 10 and 100 ppm in Fig. 3(b) and one can see that J_{sc} increases with increasing V_{bi} . Based on these considerations, we conclude that the increase in J_{sc} is due to the increase in V_{bi} , that is, the formation of an n^+p -homojunction.

From 100 to 1,000 ppm, both FF and J_{sc} decrease (Fig. 4(a)). Simultaneously, R_s increases considerably from 2.35 to $50 \Omega \text{ cm}^2$. The mobility of the majority carriers (holes), μ_h , can be calculated from equation (2).

$$\sigma_h = eN_h\mu_h \quad (2)$$

Here, N_h and σ_h are the hole concentration, which is obtained by Kelvin band mapping (Fig. 3(a)), and the hole conductivity, which is obtained from the cell resistance ($\sigma_h = LR_s^{-1}$; L : cell thickness) determined from the forward dark current for the n^+p -homojunction cells ($n^+ \text{-C}_{60}:6\text{T}/p\text{-C}_{60}:6\text{T}/\text{MoO}_3$) (Fig. 2, broken curves), respectively. The mobility, μ_h , was calculated to be 1.5×10^{-4} and $1.1 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 100 and 1,000 ppm, respectively.²⁸⁾ Fig. 4(d) shows the dependences of the hole concentration (N_h) and the hole mobility (μ_h) on doping concentration from 10 to 1,000 ppm. μ_h decreases at concentrations from 100 to 1,000 ppm (blue solid curve). We think that this is due to the disturbance of the hopping transport of holes by negatively ionized and neutral acceptor dopants although there still remains the possibility that it may be due to a nanoscopic change in morphology. Harada et al.^{29, 30)} reported a decrease in mobility for higher doping concentrations of C_{60} films. The decrease in μ_h dominates the cell resistance (R_s) in spite of the increase in N_h , causing

R_s to increase and, as a result, FF to decrease. Thus, we conclude that the decrease in FF is due to the decrease in hole mobility (μ_h). As shown in Fig. 3(b), the width of the depletion layer (W_{dep}) reduces from 50 to 20 nm as the doping concentration is increased from 100 to 1,000 ppm. As a result, we conclude that the decrease in J_{sc} is due to the decrease in W_{dep} , which is the width of the photoactive layer.³¹⁾

In conclusion, by directly doping a photoactive co-deposited layer at the ppm level, we were able to increase both the photocurrent and the fill factor. The increases in FF and J_{sc} from 0 to 100 ppm are due to the decrease in R_s following the introduction of majority carriers and the increase in V_{bi} , respectively. The decreases in FF and J_{sc} from 100 to 1,000 ppm doping are caused by the decrease in mobility of the majority carriers as a result of the disturbance of hopping transport by dopant molecules and by the decrease in W_{dep} , respectively. The most important technical significance of the doping is the intentional design of built-in potentials in the cells. We believe that a new design concept that includes the doping technology needs to be developed in order to realize a high-performance cell.

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- 25) Undoped (0 ppm) and the extremely low doping concentration of 1 ppm showed no level bending (Fig. 3(a)). This means that with extremely low doping concentrations of less than 1 ppm there is no possibility of the bands bending and the observed E_F s for 0 and 1 ppm were determined by the E_F of the n^+ -layer.
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- 28) R_s can be obtained from the resistance of the hole-only device configuration (p^+ -C₆₀:6T/ p -C₆₀:6T/ p^+ -C₆₀:6T). At 100 ppm, the values of R_s and μ_h were determined to be 3.2 Ωcm^2 and $1.1 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. These values almost concur with those obtained from the n^+p -homojunction cell.
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Figure Captions

Fig. 1 (a) **Structure** of n^+p -homojunction cell **with** a one-sided abrupt junction. (b) Energy band diagram of n^+ -C₆₀:6T co-deposited films doped with Cs₂CO₃ (10,000 ppm) and that of p -C₆₀:6T doped with FeCl₃ (1, 10, 100, 1,000 ppm) on an n^+ -layer. The positions of E_F are shown by the broken lines. The work functions of Cs₂CO₃ and FeCl₃ are also shown.

Fig. 2 Current-voltage characteristics for the n^+p -homojunction cells **with** p -layer doping concentrations of 0 (black curves), 1 (green curves), 10 (orange curves), 100 (red curves), and 1,000 ppm (blue curves). The photo and dark currents are shown by the solid and broken curves, respectively. The maximum efficiency was **observed** at 100 ppm [J_{sc} : 4.48 mA/cm², V_{oc} : 0.80 V, FF: 0.42, Efficiency: 1.51%].

Fig. 3 (a) The dependence of the work function on the p -layer thickness for various doping concentrations. The p -layers were formed on n^+ -layers. (b) Energy band diagrams of n^+p -homojunction cells with 10, 100 and 1,000 ppm FeCl₃-doped p -layers.

Fig. 4 (a) Dependences of J_{sc} and the fill factor (FF) on doping concentration. (b) **Dependences** of the fill factor (FF) and the cell resistance (R_s) on doping concentration. (c) Dependences of J_{sc} and the built-in **potential** (V_{bi}) on doping concentration. (d) Dependences of the hole concentration (N_h) and hole mobility (μ_h) on doping concentration.

Figure

Fig. 1

(a)

(b)

Fig. 2

Fig. 3

(a)

Fig. 3

(b)

Fig. 4

(a)

(b)

Fig. 4

(c)

(d)