RESEARCH ACTIVITIES

Organic Solar Cells

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Organic solar cell (OSC) is recognized as a next generation solar cell. \(pn\)-control and nanostructure control of co-deposited films consisting two kinds of organic semiconductors are key issues for the development of OSC. Recently, we have established \(pn\)-control technique for single and co-deposited films of organic semiconductors.\(^1\)\(^{-3}\) Moreover, we have developed a new method for producing phase-separated co-deposited films by introducing a co-evaporant molecules, which improves the carrier transport in the co-deposited film.\(^4\)

Here, we show the recent results on co-evaporant effect (Topic-1) and combination of doping and co-evaporant (Topic-2).

1. Nano-Structure Control of Organic Thin Films by Co-Evaporant Induced Crystallization

Nano-structure control of organic thin films is important for fabricating high performance organic electronic devices, such as organic transistors and OSCs. Especially, needle growths of organic semiconductors sometimes roughen their film surface and the electronic devices composed of such films lose their robustness. Recently, we have proposed a new method of organic film growth, “co-evaporant induced crystallization,” and succeeded in crystallizing donor–acceptor blends, the key part of OSCs, based on small molecules by using a liquid as a non-sticking co-evaporant source during vacuum deposition of the blend film and showed striking enhancements of photocurrent. In this study, this new method is utilized for controlling the needle growth of metal-free phthalocyanine (H$_2$Pc) thin films. Nominally 200 nm of H$_2$Pc films were grown on indium tin oxide (ITO) coated glass substrates with substrate heating of 70 and 40 °C. The morphologies were observed by using scanning electron microscopy (SEM), and the crystallinities were confirmed by X-ray diffraction (XRD). Figure 1 shows SEM images of H$_2$Pc thin films grown at the substrate temperature of 40 °C with and without a co-evaporant, PDMS (polydimethylsiloxane). Similar lengths of H$_2$Pc needles are observed in the both films with/without co-evaporant. From grain size comparison, in contrast, the effect of the co-evaporant is clearly noticed as the grain size enlargement typically from 20 to 50 nm. This difference implies that the co-evaporant itself does not induce the needle growth, and that the needle growth is caused by the substrate heating, which is conventionally known effective for the crystallization of organic thin films. These results suggest that the co-evaporant enhances rather 2-dimensional-growth than 3-dimensional-growth of organic films.

2. \(pn\)-Homojunction Organic Solar Cells Formed in Phase-Separated Co-Deposited Films

Since the conductivity (\(\sigma\)) is the product of the mobility (\(\mu\)) and the carrier concentration (\(n\)), i.e., \(\sigma = \sigma n \mu\), the resist-
ance ($\sigma^{-1}$) can be reduced by increasing both $n$, by means of doping, and $\mu$, by means of co-evaporant introduction. Simultaneous control of the doping and phase-separation in co-deposited films was performed by using 4-sources co-evaporation consisting of H$_2$Pc, C$_{60}$, dopants, and co-evaporant (PDMS).

Figure 2 shows the energy diagram for the phase-separated H$_2$Pc:C$_{60}$ co-deposited films. For donor (Cs$_2$CO$_3$) doping, Fermi level ($E_F$) has shifted from the undoped value of 4.48 eV to 4.22 eV (green broken line, left) and is close to the C$_{60}$ conduction band (CB$_{C_{60}}$). In contrast, for acceptor (V$_2$O$_5$) doping, $E_F$ has shifted to 4.95 eV (green broken line, right) and is close to the H$_2$Pc valence band (VB$_{H_2Pc}$). Clearly, the $pn$-control in the phase-separated co-deposited films were accomplished. Moreover, the shift in $E_F$ is revealed to occur within the “bandgap of the co-deposited film.”

The doping was used to form $pn$-homojunctions in the phase-separated co-deposited films (Figure 3). In order to determine the precise extent of the photoactive layer beyond the depletion layer (Figure 4, blue shaded area), the $J_{SC}$ for various $p$-type layer thickness ($X$) was calculated with the carrier generation efficiency following Gaussian profiles (Figure 3). Clearly, the curve with $\sigma = 250$ nm (green curve) agrees well with the observed short-circuit photocurrent ($J_{SC}$) (black dots), indicating that the photoactive layer extends 250 nm from the edge of the depletion layer.

This result means that the diffusion length of the minority carrier (electrons) reached extremely large value of 0.25 μm. Thus, photogenerated electrons far from the $pn$-homojunction can reach the edge of the depletion region and be collected by the Ag electrode. Large minority carrier diffusion length is due to the large electron mobility ($\mu = 0.1$ cm$^2$V$^{-1}$s$^{-1}$). On the other hand, a high hole concentration ($n = 1 \times 10^{17}$ cm$^{-3}$) in the $p$-type C$_{60}$:H$_2$Pc film ensures hole extraction by the ITO electrode. This allows the fabrication of very thick cells up to 0.5 μm thick with large values of fill factor (FF) of around 0.56.

The present cell is the first example of organic solar cell utilizing long minority carrier diffusion length like inorganic Si solar cells.

Figure 2. Phase-separated energy structure of C$_{60}$:H$_2$Pc co-deposited film doped with Cs$_2$CO$_3$-doped (n-type) and V$_2$O$_5$-doped (p-type) films.

Figure 3. Dependence of calculated $J_{SC}$ (solid lines) and observed $J_{SC}$ (black dots) on $p$-layer thickness ($X$). Gaussian profiles of minority carriers outside the depletion layer are also shown.

Figure 4. Energy structure of the cell. The depletion and minority carrier diffusion regions are indicated by the red and blue shaded areas, respectively.

References

Award
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