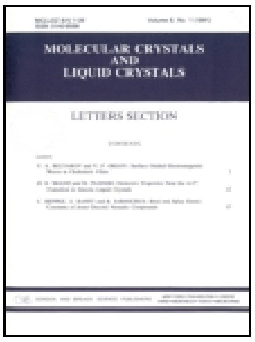
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Effects of pn Doping in Thiophene/Phenylene Co-oligomers Thin Films

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Doping effects in thiophene/phenylene co-oligomers (TPCOs) have been studied by means of extreme-UV (EUV) excited photoelectron spectroscopy (EUPS) and electro-luminescence experiments. Doped poly-crystalline films were fabricated by p-type doping with MoO_3 to inherent p-type TPCO, BP1T (2,5-bis(4-biphenylyl)thiophene), and by n-type doping with Cs_2CO_3 to n-type AC5-CF_3 (1,4-bis{5-[4-(trifluoromethyl)phenyl]thiophen-2-yl}benzene), respectively. Doping concentrations were 2% in both cases. The work function of BP1T was shifted from 4.0 to 4.3 eV and that of AC5-CF_3 was shifted from 4.8 to 3.9 eV. The energy shifts are reasonable directions for p- and n-type doping. We also confirmed higher current injection with the doping films.

Keywords Thiophene/phenylene co-oligomers; organic laser; pn doping; EUPS; organic EL

Introduction

Thiophene/phenylene co-oligomers (TPCO) are attracting organic semiconductor materials for photonic devices, because of their good performances of optical and transport properties [1]. Recently, the precursor phenomena of current-injected lasing have been observed in TPCO single crystals [2–4]. In order to achieve current injected lasing, we need to realize high current density over 1 $\mathrm{kAcm^{-2}}$. Such high current density was realized in field effect transistor (FET) devices by using Ca electrode to reduce an energy barrier for electron

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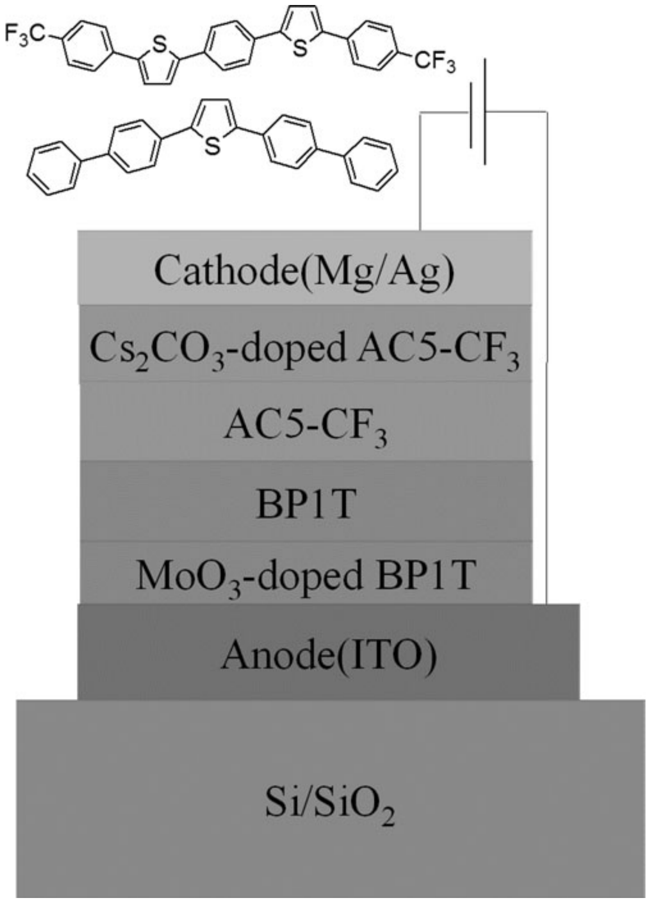

Figure 1. Molecular structures of BP1T and AC5-CF_3 and the LED structure with doping layers.

injections [4]. FET devices operated with high electric field enable high carrier density in the very thin activation layer. High current density over 1 $kAcm^{-2}$ was also achieved in organic light emitting diode (OLED) [5], and the report suggested the importance of the reduction in heat radiation. To reduce the heat radiation, the total resistance of devices should be reduced. Doping to organic semiconductor layers is effective to reduce the electric resistance as well as the carrier injection barrier by controlling their Fermi levels. In the present work, we report doping effects to TPCO organic semiconductors revealed by means of extreme-UV (EUV) excited photoelectron spectroscopy (EUPS) [6] and electroluminescence (EL) experiments of OLEDs. We have confirmed Fermi level shift of both the p- and n-type TPCOs and the increase of current density in the OLED structures.

Sample Preparation

We used 2,5-bis(4-biphenylyl)thiophene (BP1T) as p-type TPCO and 1,4-bis{5-[4-(trifluoromethyl)phenyl]thiophen-2-yl}benzene (AC5-CF_3) as n-type TPCO. Molecular structures of these co-oligomers are shown in the upper part of Fig. 1. We chose MoO_3 for

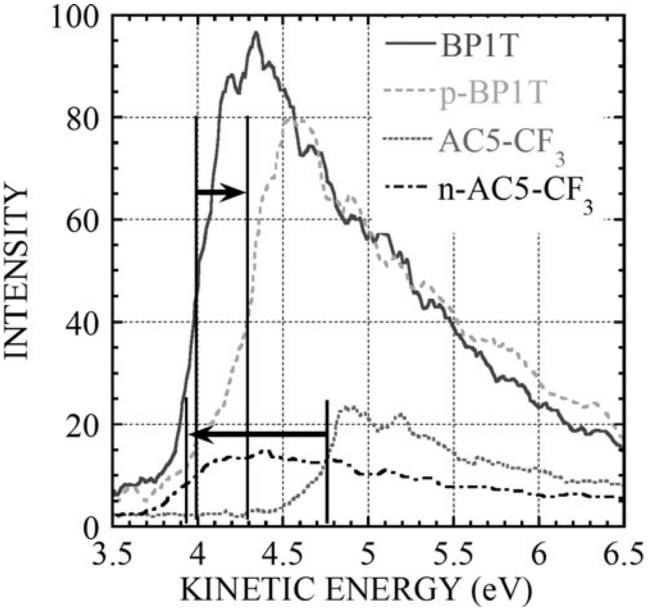

Figure 2. Secondary emission spectra of EUPS in four kinds of TPCO films. The horizontal arrows indicate the directions of the shifts in both p- and n-type doping.

a p-type dopant and Cs_2CO_3 for an n-type dopant. They worked well as dopants in organic photovoltaic cells [7]. The doping was carried out by using a co-evaporation method and doping concentration was fixed at 2% of the volume fraction in both p- and n-type cases. All the organic layers in this report were prepared by thermal deposition under high vacuum on the order of 1×10^{-5} Pa with the deposition rate of 0.05–0.15 nm/s. Substrates were kept at RT during the deposition. For the EUPS experiments, four kinds of films were formed on bare Si substrates: undoped and MoO_3 doped BP1T films, undoped and Cs_2CO_3 doped AC5-CF_3 films. The thickness of the samples was typically 100 to 400 nm. In the EL experiments, we prepared two kinds of OLED samples, with and without doping layers. The layered structure is shown in Fig. 1. Indium tin oxide (ITO) films were sputtered on Si substrates with thermally oxidized Si layers. In the LED samples with the doping layers, the thickness of p- and n-doping layers was 50 nm, and that of the undoped layers was 150nm. In the LED samples without doping layers, the thickness of BP1T and AC5-CF_3 was 200nm, namely, the total thickness of the organic semiconducting layers were the same in the both LEDs. Finally, Mg/Ag cathodes were thermally evaporated in vacuum on the order of 1×10^{-4} Pa.

EUPS Experiments

The details of EUPS experiments on TPCO films were reported in ref. 6. Here, we focus on the results of secondary electron spectra of the doped and undoped films obtained by EUPS. Figure 2 shows the observed spectra. The solid and dashed curves show the spectra of the undoped and p-doped BP1T films, respectively. The dotted and dashed-dotted curves show the spectra of the undoped and n-doped AC5-CF_3 films, respectively.

Secondary electron spectra enable us to determine work functions of semiconductors [8]. Cut-off positions in the spectra give work functions, as indicated by the vertical lines in the figure. We can determine the change of the work functions, namely, Fermi level shifts of doping effects in TPCOs. The Fermi level of BP1T shifts from 4.0 eV to 4.3 eV with the 2% doping of MoO_3, as shown by the long vertical lines in Fig. 2. The Fermi level of AC5-CF_3 shifts from 4.8 eV to 3.9 eV with the 2% doping of Cs_2CO_3, as shown by the short vertical lines in Fig. 2. The shifts are reasonable directions in the p- and n-type doping of semiconductors [9], because the Fermi level shifts to the highest occupied molecular orbital (HOMO) side in p-type doping, and to the lowest unoccupied molecular orbital (LUMO) side in n-type doping. The charge carrier generation by the doping of Cs_2CO_3 in AC5-CF_3 is probably larger than that by the doping of MoO_3 in BP1T, because the large shift in the Fermi level corresponds to the large carrier concentration [9]. The clustering of the MoO_3 dopants may be induced in TPCO, as shown in other organic semiconductors [10].

The intensity of secondary emissions decreases with the increase of free carrier densities, because the intensity of the secondary electron spectrum gives qualitative information on the free carrier density of the sample [6]. As shown in the figure, the intensities of doping spectra are smaller than those of undoped ones. This is quite consistent, because the large carrier density.

EL Experiments

The current density vs voltage (*J*-*V*) characteristics of the LEDs with and without doping layers were measured in the vacuum chamber on the order of 1×10^{-3} Pa at RT. The *J*-*V* characteristics and EL spectra were measured using a semiconductor parameter analyzer and a liquid N_2 cooled charge-coupled device attached to a monochromator guided with the optical fibers. Figure 3 shows the observed *J*-*V* curves of the LED devices. We can obtain approximately 20 times larger current density in the devices with the doping layers. The total thickness of the doping layers (100 nm) is thinner than that of the undoped layers (300nm), so that the increase of the current density is considered to come from the reduction of the contact resistance between the electrodes and the organics layers. The EL spectra of both LEDs with and without the doping layers are shown in Fig. 4. The peaks observed in the both spectra were coincident with those in the photoluminescence spectra of AC5-CF_3 [11]. This fact suggests that the electron injection is not enough, so that electrons act as minority carriers and dominate the EL spectra.

As shown in Fig. 4, we obtained five times enhancement of the EL intensity by introducing the doped layers. Note that when we observed the EL spectra, the operation voltage was over 20 V in both the cases. The observed EL intensity depended on each device and decreased within a few tens of minutes, so that the 5 times enhancement was not a strict value. Relatively small enhancement in the EL intensity compared to the current density may come from the insufficient carrier blocking between the BP1T layer and the AC5-CF_3 layer, because the band offsets for the electron and hole are 0.55 and 0.25 eV, respectively [6]. The band offset near or over 1 eV for hole blocking layers were reported in other OLED devices [12, 13]. The small band offset for holes also acts as hole dominated OLEDs in this BP1T/AC5-CF_3 junction. Larger band offsets of p-i-n junctions with double hetero-structures are desired for more strong EL intensity. We will prepare the devices in the future.

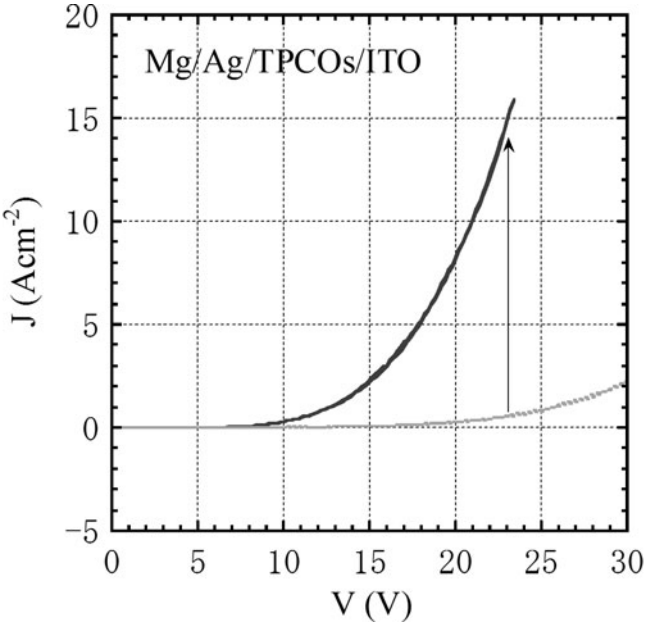

Figure 3. *J-V* characteristics of the LED devices with the doping layers (the black line) and without doping layers (the gray line).

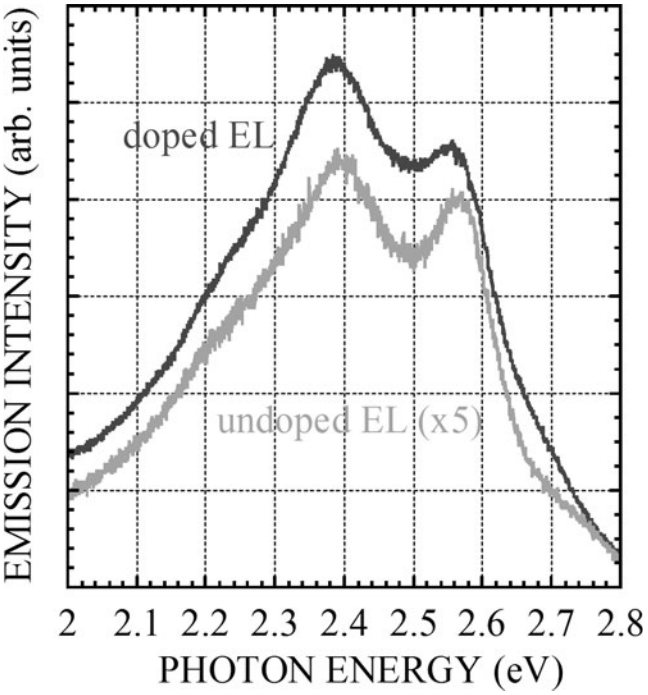

Figure 4. EL spectra with the doping layers (the black line) and without the doping layers (the gray line). The EL intensity of the undoped spectrum is multiplied by five.

Summary

We have studied doping effects in TPCO materials by means of EUPS and EL experiments. We determined the change of work functions, the Fermi level shifts induced by doping in p-type BP1T and n-type AC5-CF_3. The Fermi level of BP1T shifts from 4.0 eV to 4.3 eV with the 2% doping of MoO_3, and that of AC5-CF_3 shifts from 4.8 eV to 3.9 eV with the 2% doping of Cs_2CO_3. The charge carrier generation with the doping of Cs_2CO_3 in AC5-CF_3 is probably effective compared with that with the doping of MoO_3 in BP1T, because of the larger shift of the Fermi levels. We obtained approximately 20 times larger current density and 5 times enhancement of the EL intensity in the LED devices with the doping layers. Relative small enhancement of the EL intensity may come from the insufficient carrier blocking between the BP1T layer and the AC5-CF_3 layer.

Acknowledgments

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