

## Charge Transfer at the Interfaces between Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) and Pentacene as Investigated by ESR

Masaaki Ito<sup>1</sup> and Kazuhiro Marumoto<sup>\*1,2</sup>

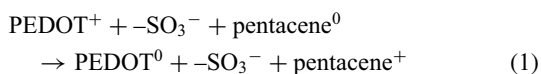
<sup>1</sup>*Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573*

<sup>2</sup>*Japan Science and Technology Agency (JST), PRESTO, Kawaguchi, Saitama 322-0012*

(Received March 5, 2012; CL-120190; E-mail: marumoto@ims.tsukuba.ac.jp)

Electron spin resonance (ESR) study was performed on organic layered films of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/pentacene that were fabricated with different deposition speed of pentacene on PEDOT:PSS in order to investigate charge formation at the PEDOT:PSS/pentacene interfaces. Clear increases in ESR signals of not only pentacene but also PEDOT were observed, which are caused by the charge transfer at the interfaces. The charge transfer is prominent at high deposition speed of pentacene, which means that slow deposition speed is suitable for solar-cell fabrication without charge formation.

Organic thin-film solar cells utilizing organic semiconductors have attracted considerable attention as next-generation solar cells because of their nanoscale structure, flexibility, light weight, and low fabrication costs.<sup>1–6</sup> The improvement of the device performance and understanding of the degradation mechanisms are important problems. The formation of charge trappings in the devices is known to worsen and deteriorate device characteristics, because trapped charges affect the electric field distribution in devices.<sup>7</sup> Thus, the analysis of the charge formation is essential to improve device characteristics. For charge formation in organic layered films that is used for solar-cell structure, electron transfer from pentacene to poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) at the PEDOT:PSS/pentacene interfaces has been proposed by ultraviolet photoelectron spectroscopy (UPS) study.<sup>8</sup> Here, PEDOT:PSS is widely used as a typical hole buffer layer for bulk-heterojunction organic thin-film solar cells to improve device performance.<sup>1,4,5</sup> The above electron transfer has been described by the following reaction:<sup>8</sup>



where  $-\text{SO}_3^-$  is the sulfonate in PSS.

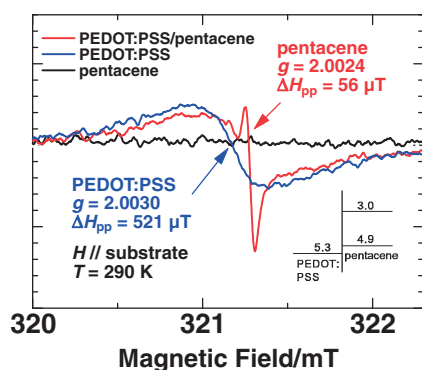
Electron spin resonance (ESR) is an effective method to study charges with spins in organic materials from microscopic viewpoints, since ESR is a highly sensitive and powerful method that is capable of studying organic materials at the molecular level.<sup>9,10</sup> We have applied the ESR method to organic field-effect devices to investigate the charge carriers in such devices.<sup>9,10</sup> We have also successfully observed the above electron transfer from pentacene to PEDOT with ESR, where the ESR intensity due to hole formation in pentacene increases whereas the ESR intensity due to holes in PEDOT decreases by filling holes with electrons from pentacene.<sup>11</sup> However, a detailed study of the charge transfer for the deposition speed of pentacene molecules on

PEDOT:PSS has not yet been performed. This study is an interesting problem because previous study shows that the device performance clearly depends on the deposition speed of pentacene on PEDOT:PSS,<sup>12</sup> which is considered to relate with charge formation at the PEDOT:PSS/pentacene interfaces.

In the present letter, we have performed ESR study to investigate the charge formation at the PEDOT:PSS/pentacene interfaces from a viewpoint of deposition speed of pentacene on PEDOT:PSS. We found that the ESR intensity clearly depended on the deposition speed of pentacene molecules on PEDOT:PSS during organic film fabrication. Increases in the ESR intensities due to hole formation not only in pentacene but also in PEDOT were observed at high deposition speed of pentacene. Such hole formation in PEDOT by depositing pentacene on PEDOT:PSS has not yet been reported to our best knowledge. We here propose mechanisms for the charge transfer between pentacene and PEDOT:PSS. These findings are important as basic information for understanding the operation of solar cells because charge formation in organic solar cells affects the device characteristics and worsens the device performance.<sup>7</sup>

Organic materials of pentacene (purity: 99%, Aldrich) and PEDOT:PSS (Baytron P A14083) were used for fabricating layered films. PEDOT:PSS was spin-coated on a quartz substrate at 4500 rpm under argon gas atmosphere; quartz substrate was cleaned with 2-propanol and acetone. The dimension of quartz substrates was  $3 \times 30$  mm for the data in Figures 1 and 2, and  $3 \times 20$  mm for the data in Figure 3. Indium-tin-oxide (ITO) films were partially coated on the  $3 \times 20$  mm quartz substrate. Film thickness of PEDOT:PSS was approximately 30 nm. Then, the film was annealing at 160 °C for 10 min under argon gas atmosphere. Pentacene was deposited on the PEDOT:PSS film at a speed of  $0.07 \pm 0.07 \text{ \AA s}^{-1}$  up to the pentacene thickness of 1.5 nm at the initial stage of pentacene deposition, followed by pentacene deposition at averaged deposition speed with various values of  $0.07\text{--}0.7 \text{ \AA s}^{-1}$  up to the pentacene thickness of approximately 42 nm. We have inserted these fabricated PEDOT:PSS/pentacene films into ESR sample tubes under vacuum conditions ( $2.0 \times 10^{-4}$  Pa) and then performed ESR measurements at room temperature under dark conditions.<sup>13</sup>

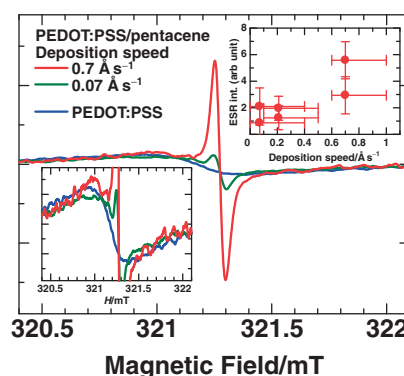
Figure 1 shows the ESR signals of organic layered films of PEDOT:PSS/pentacene (red line), PEDOT:PSS (blue line), and pentacene (black line). The data for PEDOT:PSS was taken from ref 11. In these films, the areas of each film are the same ( $3 \times 28 \text{ mm}^2$ ), and the thickness of pentacene and that of PEDOT:PSS are fixed to approximately 42 and 30 nm, respectively. Here, the averaged deposition speed of pentacene was  $0.07 \text{ \AA s}^{-1}$  up to 42 nm; the fluctuation of the speed was



**Figure 1.** ESR signals of organic thin films of PEDOT:PSS/pentacene (red line), PEDOT:PSS (blue line), and pentacene (black line) under dark conditions at 290 K. Inset: Energy diagram of PEDOT:PSS/pentacene. Energy values are approximate and given in eV with respect to the vacuum level.

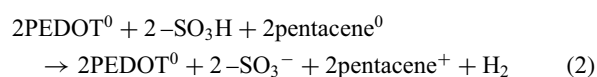
between 0 and  $0.4 \text{ Å s}^{-1}$ . A sharp ESR signal ( $g = 2.0024$ ,  $\Delta H_{pp} = 56 \mu\text{T}$ ) due to pentacene is clearly observed for the PEDOT:PSS/pentacene film. Decrease in the broad ESR signal ( $g = 2.0030$ ,  $\Delta H_{pp} = 521 \mu\text{T}$ ) due to PEDOT is also observed for the PEDOT:PSS/pentacene film compared with that for only the PEDOT:PSS film. These results demonstrate the electron transfer from pentacene to PEDOT:PSS using the deposition speed of  $0.07 \text{ Å s}^{-1}$ , as discussed in the previous study.<sup>11</sup> The present result is consistent with the previous work where pentacene film was fabricated with the averaged deposition speed of  $0.21 \text{ Å s}^{-1}$ ; the fluctuation of the speed was between 0.1 and  $0.5 \text{ Å s}^{-1}$ .<sup>11</sup> This electron transfer is reasonably explained by the energy-level difference between the highest occupied molecular orbital (HOMO) of pentacene (4.9 eV) and the work function of PEDOT:PSS (5.3 eV), as shown in the inset of Figure 1. Here, the energy values are approximate and given in eV with respect to the vacuum level.<sup>11,14</sup> The value for the lowest unoccupied molecular orbital (LUMO) of pentacene was taken from the literature.<sup>14</sup> The electrons in the HOMO of pentacene with higher energy (4.9 eV) can transfer to the Fermi level of PEDOT:PSS with lower energy (5.3 eV), resulting in the hole formation in pentacene. Such electron transfer from p-type semiconductors pentacene or copper phthalocyanine to PEDOT has been reported by UPS studies.<sup>8,15</sup> Note that the ESR signal of the PEDOT:PSS film with a broad line width ( $\Delta H_{pp} = 521 \mu\text{T}$ ) (see blue line) is ascribed to hole carriers in PEDOT doped by PSS.<sup>11</sup>

Next, we present the results for films that were fabricated with different deposition speeds of pentacene on PEDOT:PSS. Figure 2 shows the typical ESR signals of organic layered films of PEDOT:PSS/pentacene fabricated with the averaged deposition speed of  $0.7 \text{ Å s}^{-1}$  (red line) and  $0.07 \text{ Å s}^{-1}$  (green line); the fluctuation of the speed of  $0.7 \text{ Å s}^{-1}$  was between 0.6 and  $1.0 \text{ Å s}^{-1}$ . The result for the PEDOT:PSS film (blue line) is also plotted, which is taken from the previously study.<sup>11</sup> The data clearly shows that the ESR signal due to pentacene with a sharp  $\Delta H_{pp}$  greatly increases as the deposition speed of pentacene increases from  $0.07$  to  $0.7 \text{ Å s}^{-1}$ . The inset on the right side in Figure 2 shows the dependence of the peak-to-peak ESR intensity on the deposition speed of pentacene. The data shows some error bars, which are probably due to deviation of the

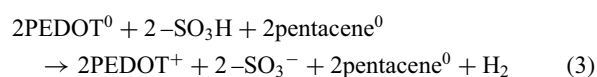


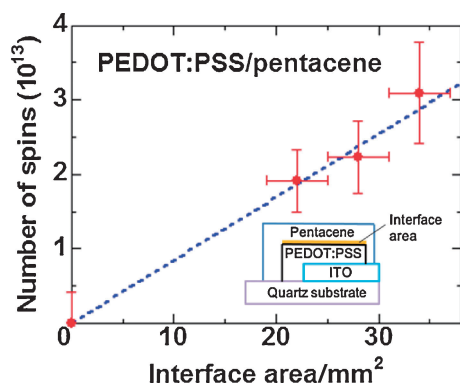
**Figure 2.** Typical ESR signals of organic thin films of PEDOT:PSS/pentacene fabricated with deposition speeds of pentacene of  $0.7 \text{ Å s}^{-1}$  (red line) and  $0.07 \text{ Å s}^{-1}$  (green line). ESR signal of PEDOT:PSS film (blue line) is also shown. Inset on the right hand side: Dependence of the peak-to-peak ESR intensity of pentacene on the deposition speed of pentacene. Two layered films were fabricated with the deposition speeds of 0.07, 0.21, and  $0.7 \text{ Å s}^{-1}$ . Inset on the left hand side: The enlargement of the ESR signals in the main panel.

direction of external magnetic field, fluctuation of deposition speed, and variation of the thickness of the PEDOT:PSS films when these films were independently fabricated. Actually, we confirmed that when the thickness of PEDOT:PSS films decreased the ESR intensity due to pentacene of the PEDOT:PSS/pentacene films decreased. In spite of these error bars, the ESR intensity of the films with the deposition speed of  $0.7 \text{ Å s}^{-1}$  is remarkably enhanced compared with the ESR intensity of the films with the deposition speeds below  $0.21 \text{ Å s}^{-1}$ . Here, the intensity data for the deposition speed of  $0.21 \text{ Å s}^{-1}$  is taken from the previous study,<sup>11</sup> which has a tendency to increase slightly compared with the data for the deposition speed of  $0.07 \text{ Å s}^{-1}$ .<sup>16</sup> Moreover, we also observe the increase in the ESR signal of PEDOT with a broad  $\Delta H_{pp}$ , which is more visible in the inset on the left hand side in Figure 2. That is, the ESR intensity due to PEDOT for the PEDOT:PSS/pentacene film fabricated with the pentacene deposition speed of  $0.7 \text{ Å s}^{-1}$  is increased by approximately 25% compared with that of PEDOT:PSS (blue line). This result is clearly different from that for films fabricated with slow deposition speeds of pentacene below  $0.21 \text{ Å s}^{-1}$  (see Figure 1 and Ref. 11's Figure 5), where the ESR intensity due to PEDOT (green line) is decreased by approximately 20% compared with that of PEDOT:PSS (blue line). This behavior cannot be explained by electron transfer from pentacene to PEDOT as described by the above reaction (1). To explain the above observed increases in both ESR signals of pentacene and PEDOT, we here propose phenomenological mechanisms for the charge transfer during pentacene deposition by using following reactions,



and





**Figure 3.** The dependence of the number of spins due to pentacene on the area of the PEDOT:PSS/pentacene interface. All films of pentacene were simultaneously fabricated with the deposition speed of pentacene of  $0.21\text{--}0.35\text{ \AA s}^{-1}$ . Dotted line is a guide to eyes. Inset: Schematic structure for PEDOT:PSS/pentacene layered film used in this study.

where  $\text{--SO}_3^-$  and  $\text{--SO}_3\text{H}$  are ESR silent as in the case of the PEDOT:PSS films. By these reactions, the results in Figure 2 are reasonably explained. That is, both ESR signals of pentacene and PEDOT are increased by  $\text{--SO}_3^-$  doping during pentacene deposition. The reason that these reactions only occur at high deposition speed of pentacene is not clear at present. One possibility is that high deposition speed with high kinetic energy of pentacene molecules may facilitate these reactions. We here comment on a study by atomic force microscopy, which reported the complete coverage of pentacene films with 40 nm thickness on the PEDOT:PSS layer.<sup>12</sup> Further investigation for the above electron transfer is an interesting problem, which will clarify the detailed interactions between organic molecules under vacuum deposition conditions.

Finally, in order to confirm the origin of the charge formation at the PEDOT:PSS/pentacene interfaces, we studied the organic layered films of ITO/PEDOT:PSS/pentacene with varying the interface areas. Figure 3 shows the numbers of spins due to pentacene in the films with different interface areas ( $0\text{--}34\text{ mm}^2$ ) of PEDOT:PSS/pentacene on ITO substrates, where all films of pentacene were simultaneously fabricated with the deposition speed of  $0.21\text{--}0.35\text{ \AA s}^{-1}$  and its thickness is approximately 42 nm. Here, the interface area was varied by changing the area of PEDOT:PSS (see the inset of Figure 3). The number of spins due to pentacene almost linearly increases with the increasing the area of the PEDOT:PSS/pentacene interface considering the error bars mentioned above. This further supports that charge transfer occurs at the PEDOT:PSS/pentacene interface as described above. At the area of  $0\text{ mm}^2$ , the pentacene film directly contacts with ITO surface, which shows no ESR signal due to pentacene and no charge transfer at the ITO/pentacene interface. This is consistent with the previous result that organic solar cells with ITO/pentacene interface shows no ESR signal.<sup>11</sup>

In conclusion, we have fabricated PEDOT:PSS/pentacene layered films and performed the ESR measurements at the room temperature under dark conditions. We have successfully

observed that the charge transfer clearly depends on the deposition speed of pentacene molecules on PEDOT:PSS. The ESR signals due to hole formation not only in pentacene but also in PEDOT increase as the deposition speed of pentacene increases during pentacene deposition on PEDOT:PSS films. The hole formation in PEDOT:PSS by depositing pentacene on PEDOT:PSS is observed for the first time. These charge formations are thought to worsen actual device performance.<sup>12</sup> Therefore, low deposition speed of pentacene molecules is appropriate for improving actual device performance of organic solar cells with PEDOT:PSS/pentacene interfaces by decreasing the charge formation at the interfaces.

This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 21560008 and 22340080) from the Japan Society for the Promotion of Science (JSPS) and by JST, PRESTO.

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