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# Molecular Orientation of Poly(3-hexylthiophene)/Fullerene Composite Thin Films

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## 1. Introduction

Organic semiconductors are essential to the future of any kind of broad-based large area flexible electronics industry because of their ease of fabrication processes. In addition, the wide range in their molecular structure offers a substantial flexibility in the functionality of organic semiconductors [1]. The understanding of the unique properties that characterize these potentially high-performance materials holds great promise filling niches not occupied by inorganic electronics. An increasing amount of attention is being paid to composites of conjugated polymers and fullerenes as active materials for organic thin-film transistors (OTFTs). The performance of the OTFTs is determined by charge mobility, which in turn is greatly influenced by the molecular orientation and morphology in the solution-deposited films. In this work, we report on the elucidation of poly(3-hexylthiophene)/[6,6]-phenyl $C_{61}$-butric acid methyl ester (P3HT/PCBM) composite thin films structure by electron spin resonance (ESR) technique. We further demonstrate the transistor performance of the P3HT/PCBM thin films.

## 2. Experimental

P3HT and PCBM were used as received from Rieke Metals and Kanko Chemical, respectively. Quartz-glass substrate was used, since they exhibit no ESR background signal. The P3HT/PCBM thin films were deposited by spin coating using dichloromethane as solvent. The mixing ratio of P3HT to PCBM in dichloromethane was 5:1 and 1:1 by weight. P3HT/PCBM solutions were soaked into warm water with ultrasonic wave. The P3HT/PCBM solution was deposited using a syringe with a filter of 0.2 μm in diameter. ESR measurements were performed with an X-band ESR (JEOL) spectrometer. The microwave power was 10 mW, and the magnetic field modulation was 0.63 mT. Angle setting of a magnetic field against the P3HT/PCBM thin films was done by a homemade goniometer. Angular variation was done at every $10^{o}$ step over the range of 0-$350^{o}$. All ESR measurements were recorded at the room temperature. The top-contact configuration OTFTs was fabricated on (100)-oriented Sb-doped $n^{+}$-type Si wafers. The substrates were cleaned by standard RCA method. The gate oxide was thermally grown in dry oxygen, and the thickness was 200 nm. Au was evaporated on the P3HT/PCBM thin film through a designated shadow mask in vacuum chamber for top source and drain contact (channel width, $W$ = 5 mm and channel length, $L$ = 100 μm). All electrical measurements were performed using a computer-controlled electrical analyzer.

## 3. Result and Discussion

We present the angular variation of $g$-value to discuss the molecular orientation. Figure 1 shows angular variation of $g$-value for P3HT/PCBM composite thin films deposition and the theoretical curve (solid line), respectively. The best-fit curve is defined by an extended normal distribution function by the following equation

$$P(\theta) = \frac{1}{\sqrt{2\pi \sin^2 \theta}} \exp\left\{ -\frac{\sin^2\left(|\theta| - \Theta\right)}{2\sin^2 \sigma} \right\} \qquad (1)$$

where $\Theta$ is the statistical tilt and $\sigma$ is the deviation (or distribution) angle.

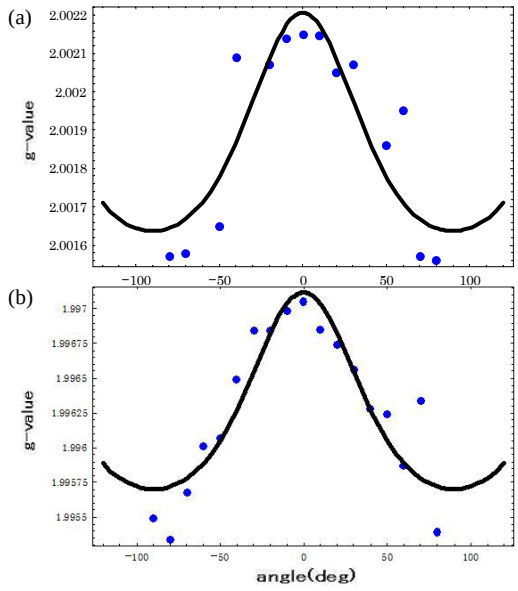


Fig. 1 Angular variation of g-value of ESR spectra of (a) P3HT/PCBM (5:1) and (b) P3HT/PCBM (1:1) composite thin films. The solid line is a best-fit curve by the normal distribution function with the tilt angle.

Table I summarizes the best-fit values of the tilt and deviation angle. The result indicates similar degree of orientation for both composite thin films. ESR spectra only indicate the molecular orientation of the P3HT in the composite thin films. The side chains and the thiophene rings of the P3HT cast thin films have been reported to preferentially orients perpendicular to the substrate as shown in Fig. 2 [2,3].

Table I Summarize of the best-fit values of the tilt and deviation angles in P3HT/PCBM composite thin films

| Sample | Tilt angle ($^o$) | Deviation angle ($^o$) |
|---|---|---|
| P3HT/PCBM(5:1) | 0 | 35 |
| P3HT/PCBM(1:1) | 0 | 35 |

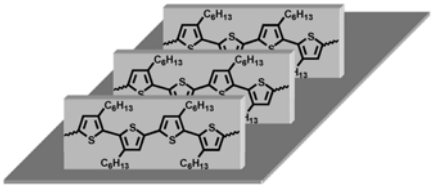

Fig. 2 Schematic diagram of molecular structure of P3HT cast thin films on a substrate.

Figure 3 shows the output characteristics of OTFTs with spin-coated P3HT/PCBM composite thin films as an active layer. It displayed an excellent saturation property in the output characteristic with the increasing of relative ratio of PCBM. Table II summarizes mobility and on/off current ratio of the devices. The mobility and on/off current ratio was improved by increasing the PCBM in the composite thin films.

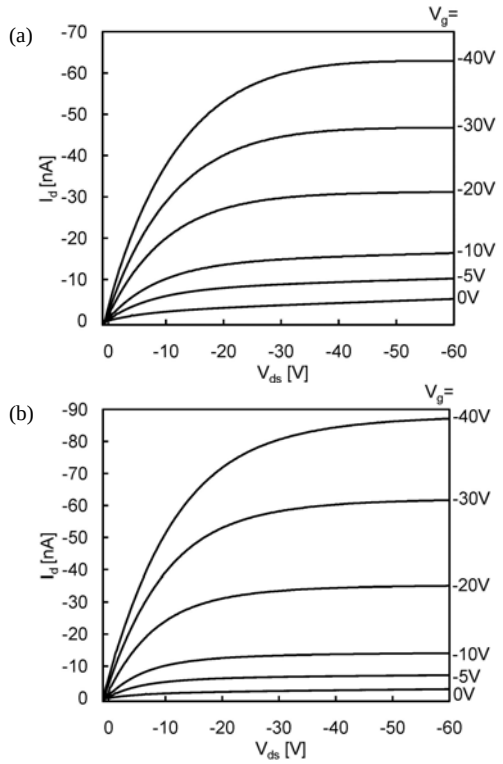


Fig. 3 Output characteristics of (a) P3HT/PCBM (5:1) and (b) P3HT/PCBM (1:1) of OTFT devices for different gate voltages.

Table II Summarize of the mobility and on/off current ratio in P3HT/PCBM composite thin films

| Sample | Mobility ($cm^2$/Vs) | $I_{on}/I_{off}$ |
|---|---|---|
| P3HT/PCBM(5:1) | $3.35\times10^{-3}$ | 11.9 |
| P3HT/PCBM(1:1) | $4.61\times10^{-3}$ | 31.1 |

## 4. Conclusions

Electron spin resonance analysis only exhibited the molecular orientation of the P3HT. In addition, PCBM molecules did not affect the orientation of P3HT chains. The performance of OTFTs with the spin-coated P3HT/PCBM composite thin films was evaluated. Even though the PCBM did not affect the molecular orientation of the composite films, PCBM did affect the performance of the OTFTs. Optimization of relative ratio of PCBM over P3HT might be contributed to the higher carrier mobility. Furthermore, the morphology aspects of the P3HT/PCBM composite thin films using X-ray diffraction technique will be discussed later.


## Acknowledgements

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## References


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