



Thickness-dependent electrical properties of soluble acene–polymer blend semiconductors



Seung Goo Lee^{a,1}, Hwa Sung Lee^{b,1}, Shichoon Lee^c, Chang Wan Kim^d, Wi Hyung Lee^{e,*}

^a Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

^b Department of Chemical & Biological Engineering, Hanbat National University, Daejeon 305-719, Republic of Korea

^c Department of Materials Science and Engineering, Jungwon University, Goesan 367-805, Republic of Korea

^d School of Mechanical Engineering, Konkuk University, Seoul 143-701, Republic of Korea

^e Department of Organic and Nano System Engineering, Konkuk University, Seoul 143-701, Republic of Korea

ARTICLE INFO

Article history:

Received 4 March 2015

Received in revised form 8 May 2015

Accepted 22 May 2015

Available online 23 May 2015

Keywords:

Organic transistor

Organic semiconductor

Soluble acene

diF-TES-ADT

Polymer blend

ABSTRACT

This study examined the electrical properties of 2,8-difluoro-5,11-bis(triethylsilylethynyl)anthradithiophene (diF-TES-ADT)/poly(methyl methacrylate) (PMMA) blend semiconductors for fabricating high-performance organic field-effect transistors (OFETs). The phase-separation characteristics were investigated over a range of blend solution concentrations. Regardless of the concentration, diF-TES-ADT crystal-top/PMMA-bottom bilayer structures were formed onto SiO₂/Si substrates owing to the surface energy difference between diF-TES-ADT and PMMA. The phase-separated interfaces between diF-TES-ADT and PMMA provided efficient pathways for charge transport. Consequently, a high field-effect mobility of 0.1 cm²/V s and a current on/off ratio of 10⁷ were achieved at the optimum concentration of 20 mg/ml where thickness of phase-separated diF-TES-ADT crystal is 20 nm. When the concentration was too low (e.g., 10 mg/ml) or too high (e.g., 30, 40, and 50 mg/ml), field-effect mobility was reduced significantly. It can be concluded that this is due to the homogeneity and thickness of the phase-separated diF-TES-ADT crystals.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Organic semiconductor/insulating polymer blends have proven to be ideal materials for optimizing the electrical properties of organic electronic devices such as organic field-effect transistors (OFETs) [1–4]. Because charge transport occurs at the dielectric/semiconductor interface laterally, the conducting pathway from the source to drain electrode should be well-defined. Therefore, inducing vertical phase separation is an effective method for obtaining high mobility in OFETs [5–21]. For example, it has been demonstrated that a phase-separated structure comprising an insulating polymer top layer and an organic semiconductor bottom layer—poly(methyl methacrylate) (PMMA)-top/poly(3-hexylthiophene) (P3HT)-bottom—increases environmental stability in bottom-gate/bottom-contact OFETs [6]. Conversely, a P3HT-top/PMMA-bottom phase-separated structure provides low-voltage OFETs with minimal use of an organic semiconductor [22]. In this study, it was found that phase-separated

PMMA can also be used as a gate-dielectric in OFETs with a bottom-gate/top-contact structure.

Solution-processed organic semiconductors (soluble acenes) can be also used in OFETs based on polymer blends [23–26]. Here, vertical phase separation is also effective for providing a lateral pathway for charge transport. Blends composed of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS pentacene) and various insulating polymers were tested for fabricating OFETs [7,19,27,28]. Depending on the interaction and/or surface energy between the two components, phase-separation characteristics and device performances differed. 5,11-Bis(triethylsilylethynyl)anthradithiophene (TES-ADT) is another soluble acene, which has a smaller π - π stacking distance than TIPS-pentacene [23]. Interestingly, TES-ADT crystallizes easily under minimal solvent vapor exposure and therefore field-effect mobility is significantly increased [29,30]. Utilizing this characteristic, a TES-ADT-top/PMMA-bottom vertically phase-separated structure was fabricated by spin-casting the TES-ADT/PMMA blend solution, followed by solvent-vapor annealing [8]. Phase-separated PMMA was used as a gate-dielectric for fabricating high-performance OFETs. Although the surface energy of TES-ADT is lower than that of PMMA, spin-cast TES-ADT/PMMA blend films exhibited a high

* Corresponding author.

E-mail address: whlee78@konkuk.ac.kr (W.H. Lee).

¹ S.G. Lee and H.S. Lee contributed equally to this work.

percentage of intermixing regimes. When using solvent annealed TES-ADT/PMMA blend film, vertical phase separation was increased and highly crystalline TES-ADT crystals were formed on the PMMA layer.

By attaching fluorine atoms in anthradithiophene backbone of TES-ADT, F-F or F-S interaction was imposed and accordingly crystallinity of difluorinated-6,13-bis(triethylsilylethynyl) anthradithiophene (diF-TES-ADT) was enhanced much [31]. Using a one-step spin-casting process, we fabricated a highly crystalline diF-TES-ADT crystal-top/PMMA-bottom bilayer structure by blending diF-TES-ADT with PMMA [18]. Because the solvent evaporation rate is important for optimizing phase-separation characteristics, solvents with different vapor pressures were used. A vertically phase-separated structure was obtained using the solution with the maximum evaporation rate. The vertically phase-separated structure was then used for producing OFETs that possessed excellent environmental and bias stabilities.

Previous studies have not investigated how the concentration of diF-TES-ADT/PMMA blend solution affects phase-separation characteristics or how the phase-separation characteristics affect thickness-dependent electrical properties of OFETs. In this study, we examined the phase-separation characteristics of diF-TES-ADT/PMMA blend films, which were spin-cast from solutions with different concentrations while maintaining a 1:1 mixing ratio. The phase-separation characteristics were determined by morphological and structural analyses. The results were then correlated with the OFETs' thickness-dependent electrical properties.

2. Experimental section

DiF-TES-ADT, PMMA (MW = 996 kg mol⁻¹), cyclohexane, and 1,2-dichlorobenzene were purchased from Aldrich Chemical Co. Silicon wafers with a 300-nm-thick thermally grown SiO₂ layer were cleaned with piranha solution and distilled water. DiF-TES-ADT/PMMA (1:1 w/w) blend solutions with total concentrations of 10, 20, 30, 40 and 50 mg/ml in 1,2-dichlorobenzene were spin-cast onto silicon substrates (~1500 rpm) to fabricate the uniform blend films. The residual solvent was removed by drying the samples in a vacuum oven. The morphologies of diF-TES-ADT/PMMA blend films were analyzed by obtaining optical microscopy (OM, Zeiss) and atomic force microscopy (AFM, Digital Instruments) images. The inner structure of the blend films were characterized with normal mode X-ray diffraction (XRD) and two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) measurements, performed at the 9A and 3C beamlines of the Pohang Accelerator Laboratory in Korea.

The gold source and drain electrodes were prepared by evaporating gold through a shadow mask (channel length = 50 or 100 μm and channel width = 800 μm). The electrical properties of the OFETs were measured using a Keithley 4200-SCS Source Measure Unit under ambient conditions. To selectively etch the diF-TES-ADT layer, the diF-TES-ADT/PMMA blend films were immersed in cyclohexane. The film thickness values were measured using surface profilometry (Alpha-Step 500). The film morphologies were characterized by AFM.

3. Results and discussion

Fig. 1(a) shows the chemical structure of diF-TES-ADT. The diF-TES-ADT crystals were formed during spin-casting as shown in Fig. 1(b). Because the fluorine groups in diF-TES-ADT increased intermolecular interaction, crystallization was improved. However, crystal connectivity was not sufficient for facilitating lateral transport of charge carriers. Therefore, low field-effect mobility (approximately 10⁻³ cm²/V s) was obtained when the

diF-TES-ADT film on the SiO₂/Si substrate was used as a semiconductor and gold was used as source/drain electrodes in OFETs. A lateral connection of the semiconducting layer is required to ensure lateral transport of charge carriers in OFETs. An insulating polymer, such as PMMA, can provide efficient connection among the diF-TES-ADT crystals by using semiconductor/insulating polymer blends [11,18]. However, the phase-separation characteristics of the diF-TES-ADT/PMMA blends must be optimized. Because of the significant surface energy difference, spin-casting of a diF-TES-ADT/PMMA blend solution resulted in a vertically phase-separated thin-film, consisting of a diF-TES-ADT-top layer and a PMMA-bottom layer.

Fig. 2(a) shows the optical microscopy (OM) image of the diF-TES-ADT/PMMA blend film spin-cast from a diF-TES-ADT/PMMA blend solution (10 mg/ml, 1:1 w/w) in 1,2-dichlorobenzene. A clean and uniform thin-film (approximately 33 nm thick) was fabricated. When the thin-film was investigated with a cross-polarizer, large crystals, which were a few tens of micrometers in size, were detected (Fig. 2(b)). The noticeable transition from needle-like crystals in Fig. 1(b) to plate-like crystals in Fig. 2(b) is due to the PMMA, which acts as a binder for the growth of diF-TES-ADT crystals. Because grain size of plate-like crystals is larger than that of needle-like crystals, the formers are advantageous for facilitating charge transport. Therefore, the use of diF-TES-ADT/PMMA blend films in the OFET semiconducting layer is recommended.

To examine the variations of phase separation and crystal growth of diF-TES-ADT, the concentration of the blend solution was increased while keeping the mixing ratio fixed at 1:1 w/w. Fig. 2(c–f) show polarized OM images of diF-TES-ADT/PMMA blend films spin-cast from 20 mg/ml, 30 mg/ml, 40 mg/ml, and 50 mg/ml blend solutions, respectively. The crystal size increased when the solution concentration was changed from 10 mg/ml (Fig. 2(b)) to 20 mg/ml (Fig. 2(c)). The time needed for the formation of thin-film increased because the higher concentration solution is more viscous. The increased time resulted in diF-TES-ADT crystals with larger grain size. This is in accordance with the work of Qiu et al., which reports similar concentration effects in P3HT/PMMA blends [9]. When the solution concentration was increased further (30 mg/ml), spherulites with a Maltese cross pattern were observed, as shown in Fig. 2(d). The spherulites are typically formed in solvent-vapor annealed TES-ADT thin film and indicate that the crystals grow radially from the nucleation center. It can be suggested that diF-TES-ADT aggregates are formed spontaneously during solvent evaporation of the viscous diF-TES-ADT/PMMA solution. The aggregates provide sites for the growth of spherulites under the thinning transient wetting layer. When the solution concentration was further increased (40 mg/ml, 50 mg/ml), diF-TES-ADT crystals showed similar images of spherulites. The thickness of the diF-TES-ADT crystals increased as the solution concentration increased. For this reason, different wavelengths of birefringence are expected for diF-TES-ADT crystals with different crystal sizes. As shown in Fig. 2(d)–(f), diF-TES-ADT crystals from different solution concentrations exhibit different colors in polarized OM.

To verify the highly crystalline nature of diF-TES-ADT crystals, molecular ordering within the crystals was examined by X-ray diffraction. Fig. S1(a) in Supporting information shows the representative normal mode X-ray diffraction (XRD) profiles of diF-TES-ADT/PMMA blend films at a 20 mg/ml concentration. The XRD profile shows that the most intense reflection occurs at (001). This suggests that the triethylsilyl groups are oriented with the surface normal to the substrate because of the surface energy difference in the diF-TES-ADT molecule. The inner structure of diF-TES-ADT was confirmed by measuring two-dimensional XRD patterns, shown in Fig. S1(b) of Supporting information. In

Download English Version:

<https://daneshyari.com/en/article/1263684>

Download Persian Version:

<https://daneshyari.com/article/1263684>

[Daneshyari.com](https://daneshyari.com)