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COMMUNICATION

The Effect of Electric-field on Phase Separation of Semiconductor/Insulator Composite Film

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Shiwei Wang^{a,b,*}; Zhuo Chen^a

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Electric-field induced technique has been successfully utilized to control the phase separation and the interfaces of semiconductor/insulator composite film, which provided a new research approach and objects for scientists working in related fields.

Semiconductor/Insulator (S/I) composite system has been extensively studied and widely applied in thin-film transistors (TFTs).¹ The greatest challenges of the TFTs with layered structures is the interface optimization, because charge transport in TFTs occurs in the first few molecular layers near the gate dielectric layer, a well-defined interface between the organic semiconductor and the gate insulator is crucial for device performance.² In practice, it is desirable to prepare all components of TFTs via solution-processing methods, including the semiconductor, dielectric, and electrodes. However, the underlying polymer is always swelled and dissolved during the deposition of the upper layers, the challenge of which is difficult to avoid for the layered structures of TFTs.³

Insoluble underlying polymer by robust cross-linking and/or orthogonal solvents have been used to resolve these problems mentioned above.⁴ Although significant progress has been achieved over the past few years using these approaches, it is difficult to prepare all kinds of polymer TFT devices comprising insulating and semiconducting polymer pairs using compatible solvents.⁵ Fortunately, phase separation in polymer blends provided new opportunities to overcome this limitation.⁶

Semiconducting polymer blends (SPB) have been considered to be the promising materials for TFTs, which combine the advantageous properties of each component, so the even performance of SPB exceeds those of any individual component.⁷ Separated phase domains would tend to be formed when the intrinsic immiscibility of the components in a polymer blend during solvent-casting process.⁸ A complex morphology with varieties of microstructures will be created typically by phase separation. Under specific and well-

controlled conditions, self-stratified structures will be formed via vertical phase separation of the components in the polymer blend thin films,^{9, 2a} which significantly promotes the development of TFT devices because the semiconductor and insulator layers can be deposited simultaneously from a blend solution in a one-step process. As report, scientists have ever successfully fabricated top-gate, low-voltage TFT devices using self-organized S/I bilayers. However, a rather high temperature was required for the cross-linking of the overlayer, which has prohibited the application of this technique to all-polymer TFTs seriously, because plastic substrates usually cannot tolerate such a high temperature.¹⁰

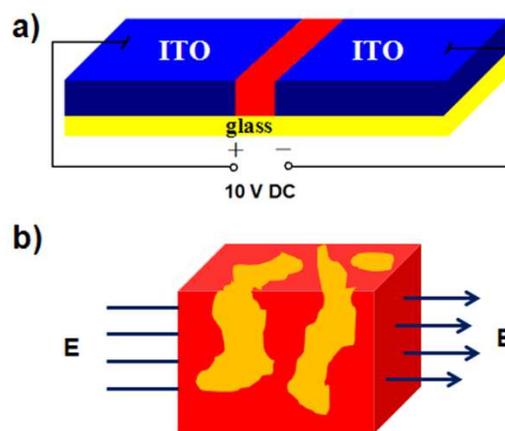
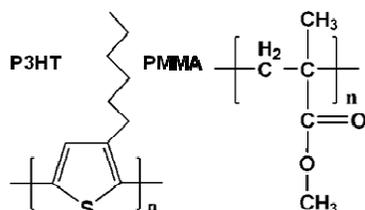


Figure 1. The device (a) and the partial enlarged drawing (b) of the processing of S/I composite film under DC electric-field.

As reported recently, surface-directed vertical phase separation of P3HT/PMMA blend film has been successfully obtained by spin-coating in a one-step on a hydrophilic substrate.¹¹ However, the scale of the phase separation was quite limited because of the relatively weak driving force. Herein, the phase interfaces and separation of S/I composite film has been successfully controlled by electric-field (EF)

inducing technique, the phase separation scale and contact of which was superior to any other solution-processing methods mentioned before. The optimized morphology of SPB film formed under EF was quite conducive to the electronic transmission and efficiency improvement.¹² More meaningful, it has presented a new research approach and objects about interface and phase morphology for scientists working in related fields.



Scheme 1. Molecular structure of P3HT and PMMA

Regular poly(3-hexylthiophene) (P3HT) and poly(methyl methacrylate) (PMMA) were used as model systems, acting as the semiconductor and insulator, respectively, the molecular structures of which are shown in Scheme 1. A channel of 200 μm width was etched on indium tin oxide (ITO) glass by laser (wavelength is 1064 nm), the depth of the channel was about 170 nm, which was just the thickness of the ITO layer, because the glass under ITO was hard enough to endure the etching from the laser. The longitudinal sections on both sides of the channel could be acted as electrodes during the electric voltage was added (Fig. 1a). During the process of solvent volatilization of the film, 10V DC voltage was added on both sides of the channel, which was filled with the mixture solution of P3HT and PMMA. Thus the S/I composite film with special morphology was formed under the evaporation of the solvent and EF (ESI[†]), the process of which is outlined as in Fig. 1b.

It was worth mentioning that 10V DC voltage was the most appropriate for the system from the verification of numerous comparative tests. The extent of the phase separation scale was quite small when the voltage was lower than 10V, which was so insignificant that cannot be observed easily. However, if the voltage was more than 10V, it was difficult to control and easy to be power shortage between the electrodes, resulting in the destruction of the film.

Polarizing microscope was used to characterize the morphology of the composite film (Fig. 2). It can be seen that P3HT molecules were agglomerated into pellets and distributed in the PMMA film evenly without the EF, (Fig 2A). Under the effect of DC EF and the same other conditions with the comparing samples, the P3HT pellets have been turned into regular rods rapidly and gathered in the negative pole ultimately, the two phases separated rather thoroughly and completely (Fig 2B). The distinct interfaces between S/I phases have been obtained, which could not be achieved by conventional approaches. It can be inferred that π -electrons of the conjugated polymer chain moved freely in a certain range, and the electron cloud distribution of semiconductor is often homogeneous in normal. When EF is applied on the surface of the conjugated polymer film, the electron clouds in which will be distributed unevenly due to electrostatic attraction, conversely, the driving force of electron clouds under EF will lead the directional movement of the whole

molecules. The mechanism inferred above is universal for conjugated polymers and rather meaningful for the research on morphology, molecular dynamics, interface science and the electric-optical device.

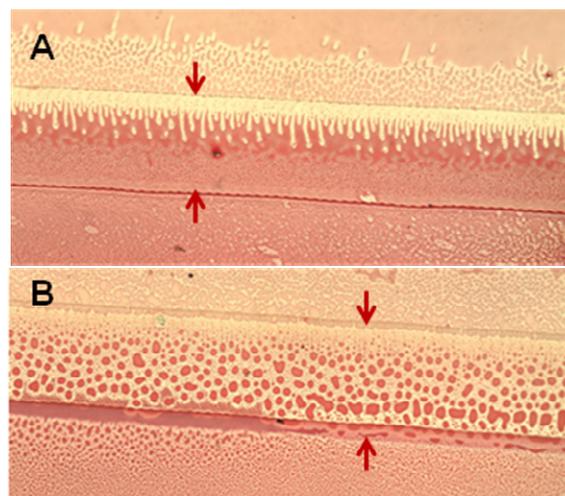


Figure 2. Polarizing microscope photos of P3HT/PMMA (mole ratio was 1:1) film after (A) and before (B) electric-field induced treatment at room temperature (The magnification was 10 \times 10).

Atomic force microscopy (AFM) was carried out to confirm the morphology of the composite film under EF in detail. The phase diagrams of the P3HT/PMMA film are shown in Fig.3, which is coincident with the polarizing microscope photograph. It can be conjectured that the composition of the rodlike structure is P3HT, and it is more important that obvious phase separation and phase interface has been successfully obtained. The root mean square (rms) roughness of the P3HT and PMMA part is calculated to be about 5.9 nm and 7.0 nm (for 5 μm \times 5 μm areas) respectively, illustrating the high quality of the composite films.

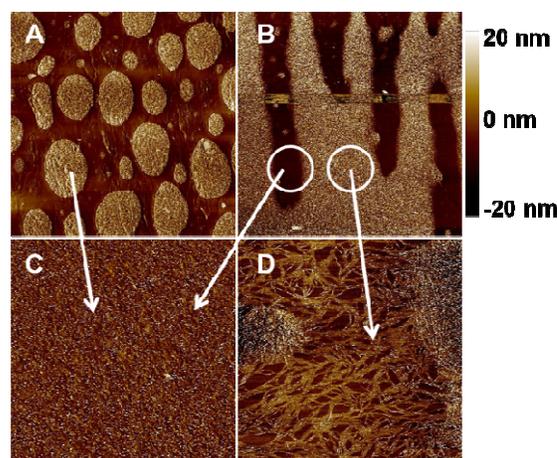


Figure 3. Phase diagrams of AFM (5 μm \times 5 μm) on P3HT/PMMA film before (A) and after (B) electric-field induced treatment and the enlargement phase of P3HT (C) and PMMA (D).

Confirming the component in the morphology of S/I film further, different ratio of P3HT/PMMA films were fabricated, the corresponding polarizing microscope images are shown in Figure 4. It can be seen that the red accumulations gradually become smaller and shallower with the increasing of PMMA, which can confirm that the pellets reunited in the composite film is P3HT.

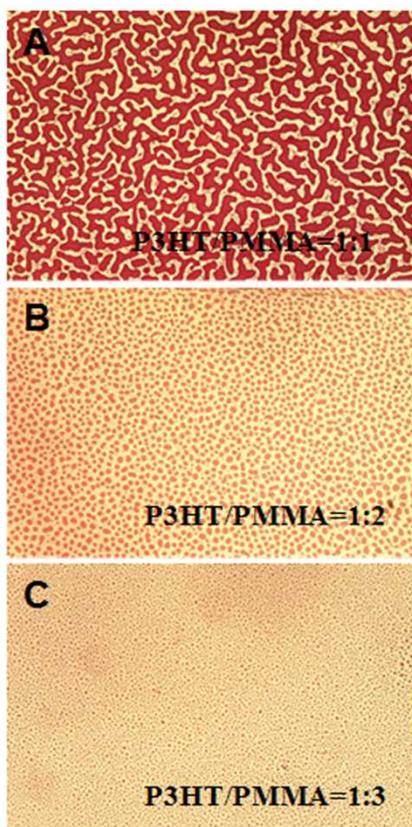


Figure 4. Polarizing microscope photos of P3HT/PMMA film in different ratios without electric-field induced treatment at room temperature (The magnification of all was 10×10).

The typical organic TFT is constructed with several layers, including substrate, insulate layer, transport layer and electrode. Adequate contact and phase separation must be able to improve the performance of TFT device. It can be asserted that EF induced technique will be widely used in fabrication of TFT by controlling the morphology of SPB film according to the relevant literature reports.^{2,13}

In summary, electric-field induced technique was successfully utilized to control the phase separation of semiconductor/insulator composite film, the interfaces between semiconductor and insulator layer were better than the ones fabricated by other film fabrication methods. More important, it provided a new research approaches and objects for scientists working in related fields.

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Notes and references

a Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, Beihang University, Beijing 100191, P R China, School of Chemistry and Environment, E-mail: wswjldx2004@163.com; Fax: +086-10-82317801 Tel: +086-10-82317801

b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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- C. Liu, M. Takeo, X. B. Lu, K. Akichika, T. Kazuo, T. Kazuhito, *Adv. Mater.* 2011, **23**, 523.
- (a) X. H. Wang, W. H. Lee, G. B. Zhang, X. H. Wang, B. Kang, H. B. Lu, L. Z. Qiu, K. Cho, *J. Mater. Chem.* 2013, **1**, 3989; (b) R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.*, 2006, **5**, 222.
- (a) J. Park, S. Y. Park, S. O. Shim, H. Kang, H. H. Lee, *Appl. Phys. Lett.* 2004, **85**, 3283; (b) J. Park, S. O. Shim, H. H. Lee, *Appl. Phys. Lett.* 2005, **86**, 073505; (c) H. H. Gao, M. Vadlamudi, R. G. Alamo, W. B. Hu, *Macromolecules*, 2013, **46**, 6498.
- (a) E. J. D. Klem, H. Shukla, S. Hinds, D. D. MacNeil, L. Levina, E. H. Sargent, *Appl. Phys. Lett.* 2008, **92**, 212105; (b) M. Baghgar, E. Pentzer, A. J. Wise, J. A. Labastide, T. Emrick, M. D. Barnes, *Acc Nano.* 2013, **7**, 8917; (c) K. J. Baeg, A. Facchetti, Y. Y. Noh, *J. Mater. Chem.* 2012, **22**, 21138;
- (a) Y. Jiang, T. Okamoto, H. A. Becerril, S. Hong, M. L. Tang, A. C. Mayer, J. E. Parmer, M. D. McGehee, Z. Bao, *Macromolecules*, 2010, **43**, 6361; (b) M. H. Yoon, H. Yan, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* 2005, **127**, 10388.
- (a) W. H. Lee, Y. D. Park, *Polymer*, 2014, **6**, 1057; (b) Y. Liu and R. W. Anthony, *J. Am. Ceram. Soc.* 2013, **96**, 218; (c) Z. H. Liu, G. I. Ng, S. Arulkumaran, Y. K. T. Maung, K. L. Teo, S. C. Foo and V. Sahnuganathan, *Appl. Phys. Lett.* 2009, **95**, 223501.
- (a) Z. R. He, D. W. Li, D. K. Hensley, A. J. Rondinone, J. H. Chen, *Appl. Phys. Lett.* 2013, **103**, 113301; (b) R. B. K. Siram, Stephen, M.; F. Ali.; S. Patil, *J. Phys. Chem. C*, 2013, **117**, 9129; (c) Z. Szendrei, D. Jarzab, Z. H. Chen, A. Facchetti, M. A. Loi, *J. Mater. Chem.* 2010, **20**, 1317.
- (a) F. Liu, C. Wang, J. K. Baral, L. Zhang, J. J. Watkins, A. L. Briseno, T. P. Russell, *J. Am. Chem. Soc.* 2013, **135**, 19248; (b) E. L. Williams, S. Gorelik, I. Phang, M. Bosman, C. Vijila, G. S. Subramanian, P. Sonar, J. Hobley, S. P. Singh, H. Matsuzaki, A. Furube, R. Katoh, *RSC Adv.* 2013, **3**, 20113.
- P. Mokarian-Tabari, M. Geoghegan, J. R. Howse, S. Y. Heriot, R. L. Thompson, R. A. L. Jones, *Eur. Phys. J. E*, 2010, **33**, 283.
- (a) T. W. Lee, J. H. Shin, I. N. Kang, S. Y. Lee, *Adv. Mater.* 2007, **19**, 2702; (b) C. Wang, W. Y. Lee, R. Nakajima, J. G. Mei, D. H. Kim, Z. N. Bao, *Chem. Mater.* 2013, **25**, 4806; (c) W. T. Xu, C. Guo, S. W. Rhee, *J. Mater. Chem. C*, 2013, **1**, 3955.
- L. Z. Qiu, J. A. Lim, X. H. Wang, W. H. Lee, M. Hwang, K. Cho, *Adv. Mater.* 2008, **20**, 1141.
- I. Torres, D. M. Taylor, E. Itoh, *Appl. Phys. Lett.* 2004, **85**, 314.
- W. H. Lee, Y. D. Park, *Polymers*. 2014, **6**, 1057.