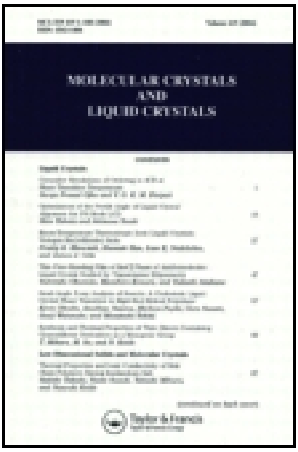

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effects of the Surface Wettability of a Polymeric Insulator in a Solution-Processed Organic Transistor

Dong-Wook Kim [a], Jin-Hyuk Bae [b], Jong Sun Choi [a] & Jaehoon Park [c]

[a] Department of Electrical, Information and Control Engineering, Hongik University, Seoul, 121-791, Korea

[b] Centre Microélectronique de Provence, Ecole Nationale Supérieure des Mines de Saint-Etienne, Gardanne, 13541, France

[c] School of Engineering and Computer Science, Durham University, Durham, DH1 3LE, United Kingdom

Version of record first published: 17 Sep 2012.

To cite this article: Dong-Wook Kim, Jin-Hyuk Bae, Jong Sun Choi & Jaehoon Park (2012): Effects of the Surface Wettability of a Polymeric Insulator in a Solution-Processed Organic Transistor, Molecular Crystals and Liquid Crystals, 567:1, 50-56

To link to this article: http://dx.doi.org/10.1080/15421406.2012.702380

Mol. Cryst. Liq. Cryst., Vol. 567: pp. 50–56, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.702380

Effects of the Surface Wettability of a Polymeric Insulator in a Solution-Processed Organic Transistor

DONG-WOOK KIM,[1] JIN-HYUK BAE,[2] JONG SUN CHOI,[1]
AND JAEHOON PARK[3,*]

[1]Department of Electrical, Information and Control Engineering, Hongik University, Seoul 121-791, Korea
[2]Centre Microélectronique de Provence, Ecole Nationale Supérieure des Mines de Saint-Etienne, Gardanne 13541, France
[3]School of Engineering and Computer Science, Durham University, Durham DH1 3LE, United Kingdom

We investigated the effects of the surface wettability of two polymeric insulators in a 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) thin-film transistor (TFT). The chemical solvent of TIPS-pentacene was more wettable on a poly(4-vinylphenol) (PVP) insulator than on a poly(vinylidenefluoride-trifluoroethylene) (PVDF-TrFE) insulator. TIPS-pentacene molecules formed large crystals on the PVDF-TrFE layer, resulting in high field-effect mobility for the TFT. In contrast, for the PVP case, the mobility largely varied with the processing temperature of a TIPS-pentacene film. These results demonstrate that the surface wettability of an insulator is important for the crystallization of a solution-processed organic semiconductor and the resulting TFT performance.

Keywords Thin-film transistor; TIPS-pentacene; Polymeric insulator; Surface wettability

Introduction

During the past decades, organic thin-film transistors (TFTs) have attracted much attention due to their potential applications such as flexible displays, various sensors, memory cards, and radio frequency identification tags [1–3]. In particular, solution processes such as spin-coating, drop-casting and various printings are very advantageous for large-area and low-cost manufacture of organic TFTs. Intensive efforts have thus been devoted to improve the performance of solution-processed organic TFTs [4–7]. For example, there has been a wide range of discussions about the effects of chemical solvents, used for dissolving organic semiconducting molecules, on the performance of these TFTs. Shin *et al*. reported that the boiling temperature of a solvent critically affects the electrical properties of a solution-processed organic TFT [4]. This is because the crystallization of organic semiconducting molecules occurs during the solvent evaporation. On the other hand, a post-annealing

---

These authors contributed equally to this work. Dr. Park is currently with Electronics and Telecommunications Research Institute in S. Korea.

[*] Address correspondence to Dr. Jaehoon Park: Durham University, Durham DH1 3LE, United Kingdom Telephone: + 44-191-334-2000 Fax: + 44-191-334-2407. E-mail: j.h.park@durham.ac.uk, jaypark@etri.re.kr

process for a solution-processed organic semiconductor was also introduced to increase the field-effect mobility of the transistor [6]. These works indicate the significant effects of processing temperatures for solution-processed organic TFTs on the crystallization of an organic semiconductor and the device performance. Nevertheless, the crystallization of a solution-processed organic semiconducting molecule has not been fully understood in terms of the surface wettability of a polymeric insulator against a chemical solvent for the organic semiconductor so far.

In this work, we fabricated the 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) TFTs using two different polymeric gate insulators, poly(4-vinylphenol) (PVP) and poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE). The crystallization of TIPS-pentacene molecules on each polymeric layer and its effect on the mobility of the TIPS-pentacene TFT are discussed on aspects of the surface wettability of a polymeric insulator against a chemical solvent for TIPS-pentacene, 1,2 dichlorobenzene (DCB). The influence of the processing temperature of the TIPS-pentacene film on the mobility variation for both TFTs is also studied. The surface morphologies of polymeric insulators were examined by atomic force microscope (AFM) (XE150, PSIA Inc.)

Experimental

Figure 1 illustrates the bottom-gate and bottom-contact TIPS-pentacene TFT fabricated on a glass substrate in this study. A stripe-patterned indium-tin-oxide gate electrode was deposited onto a glass substrate [8]. PVP and PVDF-TrFE were used as a polymeric gate insulator. The PVP solution (Sigma Aldrich, 10 wt% in propylene grlycol methyl ether acetate) was mixed with a thermal cross-linking agent, poly(melamine-co-formaldehyde), of 5 wt%, following the previous work [6]. A PVP film was formed by spin-coating from solution and curing at 100°C for 10 min and at 200°C for 1 h in a drying oven; the resulting thickness of the cross-linked PVP film was approximately 670 nm. On the other hand, a PVDF-TrFE film was produced by spin-coating from solution (Sigma Aldrich, 10 wt% in cyclopentanone) and curing at 140°C for 2 h in a drying oven; the resulting film was approximately 650 nm [9]. Then, 80-nm-thick Au source and drain electrodes were thermally deposited at the rate of 0.1 nm/s through a shadow mask. The channel length (L) and width (W) were 80 and 1000 μm, respectively. Next, the TIPS-pentacene (Sigma Aldrich, 1.0 wt% in DCB) film was drop-casted between source and drain electrodes and was subsequently baked at different temperatures (room temperature (RT), 60°C, and

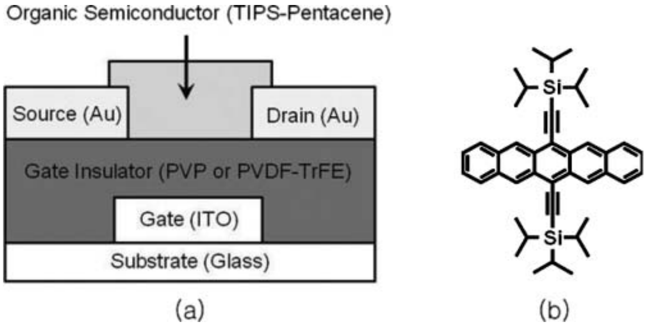

Figure 1. (a) Schematic diagram of our bottom gate, bottom contact TIPS-pentacene TFT with two different polymeric gate insulators and (b) the molecular structure of TIPS-pentacene.

120°C) to evaporate the DCB solvent in the film. Note that the fabricated PVP and PVDF-TrFE films are chemically inert against the DCB solvent. The electrical characterizations of our TIPS-pentacene TFTs were carried out using a semiconductor parameter analyzer (HP 4155A). The surface wettability of each polymeric insulator was evaluated from the contact angle of a DCB drop measured using a contact angle meter (GSA10, Co., Ltd). The X-ray diffraction (XRD) measurement was performed using a diffractometer (D8 DISCOVER, Bruker Co., Ltd.) with Cu Kα radiation.

Results And Discussion

We first examine the surface wettabilities of the two polymeric insulators against the solvent for TIPS-pentacene, DCB. Figures 2(a) and 2(b) show the contact angles of a DCB drop on the PVP and PVDF-TrFE films. It is observed that a DCB drop spreads widely over the PVP film in comparison with the PVDF-TrFE case. The measured contact angle on the PVP film was as low as 7°, whereas a relatively large value of 35° was obtained for that on the PVDF-TrFE film. Interestingly, there is a notable difference in the surface

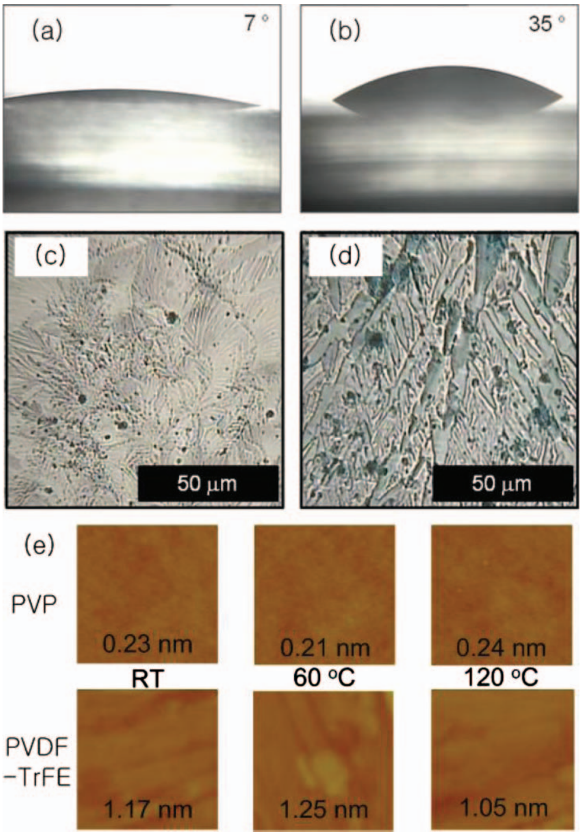

Figure 2. Contact angles of the DCB solvent on (a) the PVP layer and (b) the PVDF-TrFE layer. Optical microscopic images of TIPS-pentacene films on (c) the PVP layer and (d) the PVDF-TrFE layer. (e) AFM images (1 μm × 1 μm) of PVP and PVDF-TrFE layers baked at different temperatures. The insets indicate the root-mean-square roughness values.

morphologies of TIPS-pentacene films on these insulators, as shown in Figs. 2(c) and 2(d). Previously, it was reported that the molecular packing density in a thermally-evaporated pentacene film is strongly influenced by the surface energy of an underlying insulator [10, 11]. Likewise, the fact that TIPS-pentacene molecules formed larger needle-shaped crystals on the less wettable PVDF-TrFE film directly implies the surface energy-dictated crystallization of solution-processed TIPS-pentacene molecules. It is considered that TIPS-pentacene molecules on a wettable surface would have a little chance to be condensed into a crystal during the solvent evaporation, resulting in smaller crystals. Meanwhile, as shown in Fig. 2(e), there are no discernible effects of the baking temperature on the surface morphologies of polymeric insulators; the insets indicate the root-mean-square roughness values of polymeric layers. These are likely thought to be due to that the baking temperatures in this study are less than the characteristic temperatures of both polymers.

Figure 3 shows the XRD spectra of TIPS-pentacene films on the PVP and PVDF-TrFE layers according to the processing temperature of the TIPS-pentacene film. Note that the crystallinity of an organic semiconductor can be evaluated from the peak intensity in a XRD spectrum [12, 13]. In our results, the typical (001) diffraction peaks are observed at approximately 5.2°, which is in a good agreement with previous works [6, 13–15]. For the TIPS-pentacene film on the PVP layer, the intensities of the (00*l*) Bragg peaks significantly increased on increasing the processing temperature from RT to 60°C as shown in Figs. 3(a) and 3(b). However, all peaks for the PVDF-TrFE were less influenced by the processing temperatures (see Figs. 3(c) and 3(d)). In addition to the above optical microscopic images, the different dependence of the XRD peaks on the processing temperature of the TIPS-pentacene film can be also attributed to the effect of the surface wettability of a polymeric insulator. It is thus reasonable to state that the surface wettability of an underlying

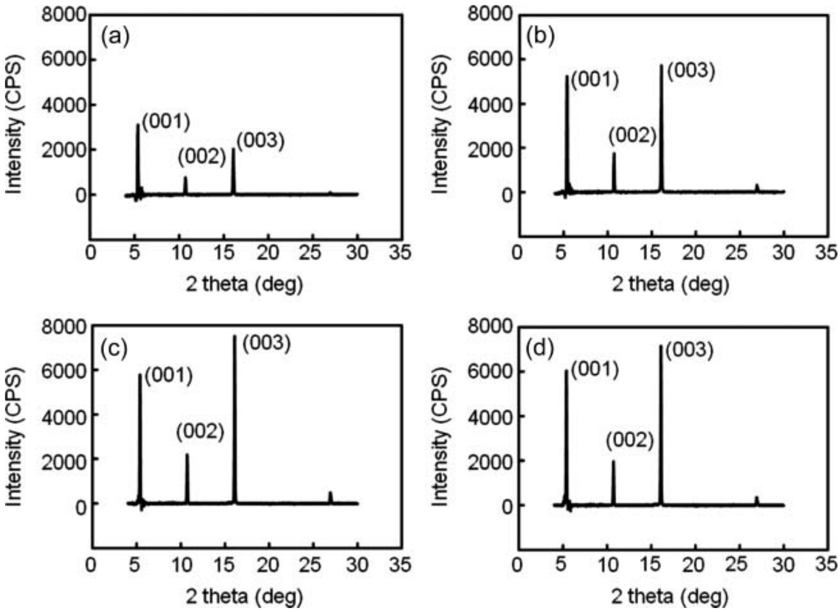

Figure 3. XRD spectra of TIPS-pentacene films formed on the PVP layer; the processing temperature of the TIPS-pentacene film are (a) RT and (b) 60°C and those on the PVDF-TrFE layer; the processing temperature of the TIPS-pentacene film are (c) RT and (d) 60°C.

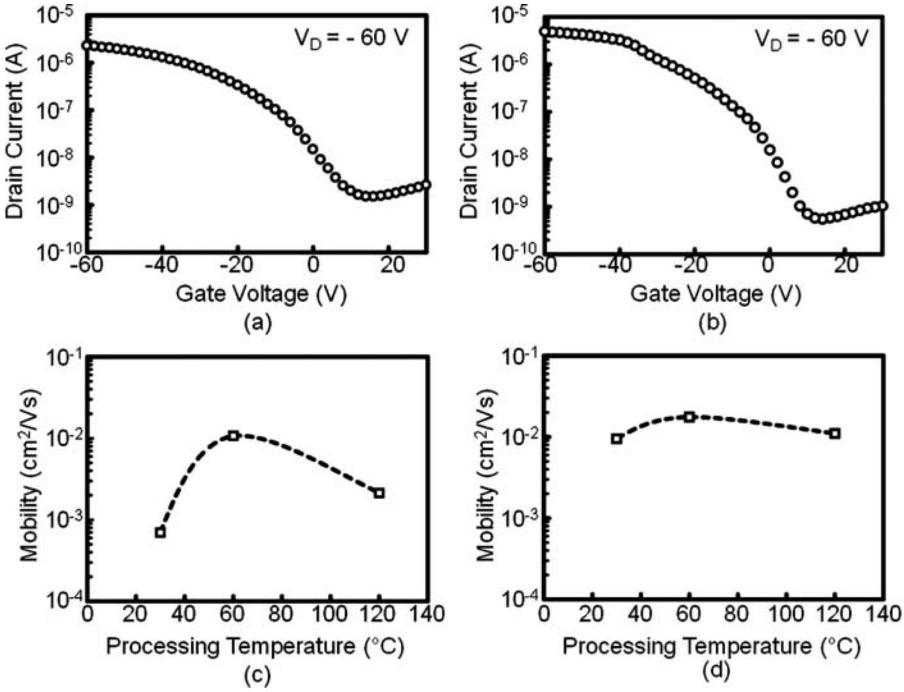

Figure 4. Transfer characteristics of TIPS-pentacene TFTs with (a) a PVP insulator and (b) a PVDF-TrFE insulator. The mobility variations for the TFTs with (c) a PVP insulator and (d) a PVDF-TrFE insulator as a function of processing temperature of TIPS-pentacene films.

insulator predominantly affects the crystallization of TIPS-pentacene molecules for solution processes.

Figures 4(a) and 4(b) show the transfer characteristics of the fabricated TIPS-pentacene TFTs in which TIPS-pentacene films were cured at 60°C. The gate voltage (V_G) was varied from 30 to -60 V in sweep steps of -2 V at a fixed drain voltage (V_D) of –60 V. The TIPS-pentacene TFT with the PVDF-TrFE insulator exhibited a larger drain current than that for the device with the PVP insulator. The field-effect mobility (μ_{sat}) in the saturation regime was calculated using the following equation [16]

$$\mu_{sat} = \frac{2L}{W \cdot C_i} \cdot \frac{I_D}{(V_G - V_T)^2},$$

where C_i is the dielectric capacitance of a gate insulator and V_T is the threshold voltage. As can be expected from well-defined TIPS-pentacene crystals on the PVDF-TrFE layer, the mobility of the TFT was higher (0.016 cm^2/Vs) than that for the device with the PVP insulator (0.011 cm^2/Vs). For the magnitude of the mobility, the mobility obtained from our study is relatively low, but it can be improved by optimizing the device structure, further purifications, and extra surface treatments. Considering the processing-temperature dependence of the crystallinity of the TIPS-pentacene film, more important observation was performed on aspects of processing temperatures of TIPS-pentacene films for both TFTs. Note that the mobility is invariably influenced by the crystallinity of an organic semiconductor [14, 17]

Table 1. The field-effect mobilities in TIPS-pentacene TFTs with two different polymeric insulators, PVP and the PVDF-TrFE are summarized as a function of the solvent processing temperature of the TIPS-pentacene films.

	Field-Effect Mobility (cm^2/Vs)	
Temperature	PVP	PVDF-TrFE
RT	6.9×10^{-4}	1.0×10^{-2}
60°C	1.1×10^{-2}	1.6×10^{-2}
120°C	2.1×10^{-3}	1.2×10^{-2}

Figures 4(c) and 4(d) show the mobility variation as a function of the processing temperature of the TIPS-pentacene film. The TIPS-pentacene TFT with the PVP insulator shows a significant dependence on the processing temperature; the highest mobility value was obtained at 60°C in Fig. 4(c). In contrast, for the PVDF-TrFE case, there was no critical dependence of the mobility on the processing temperature as shown in Fig. 4(d). The mobility variations of our TIPS-pentacene TFTs according to the processing temperature are summarized in Table 1. Noteworthy is that the mobility variations observed by us well correspond with the characteristic variations in the presented XRD results. Then, the observed mobility variation upon the processing temperature can be understood by reference to the surface wettablity of a polymeric insulator against the chemical solvent for TIPS-pentacene, DCB. A TIPS-pentacene solution would spread widely on the more wettable surface of the PVP layer, implying that TIPS-pentacene molecules would distribute over a large contact area. Under this circumstance, the condensation of TIPS-pentacene molecules into a crystal will be predominantly influenced by a solvent evaporation rate. This suggests that the processing temperature of the TIPS-pentacene film critically affects the crystallization of TIPS-pentacene molecules. Our explanation is also supported by the fact that solution-processed organic semiconductors are structurally oriented during the solvent evaporation [18].

Conclusion

We presented the effects of the surface wettability of a polymeric gate insulator on the crystallization of TIPS-pentacene molecules and the performance of a TIPS-pentacene TFT. It is shown that the crystallization of TIPS-pentacene molecules is strongly influenced by the surface wettability of an underlying polymeric insulator. In our results, TIPS-pentacene molecules formed larges crystals with well-ordered structures on the PVDF-TrFE film which was less wettable against a chemical solvent of TIPS-pentacene, DCB, than that on the PVP film. Compared to the TIPS-pentacene TFT with the PVP insulator, the device with the PVDF-TrFE insulator also exhibited a higher mobility value, which was also found to be less influenced by the processing temperature of the TIPS-pentacene film. These results suggest that the control of the surface energy of a polymeric gate insulator will be essential to improve the crystallinity of a solution-processed organic semiconductor for TFTs. More works on wide range of polymeric insulator together with several solution-processable organic semiconductors remain to be performed for more systematic study.

Acknowledgement

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010–0012487). Dr. Park also appreciates the financial support from Green Smart Card Platform Technologies Based on 3D Printed Electronic Devices Project of MKE (Ministry of Knowledge Economy) and ISTK (Korea Research Council for Industrial Science and Technology) of Republic of Korea.

References

[1] Crone, B., Dodabalapur, A., Lin, Y.-Y., Filas, R. W., Bao, Z., LaDuca, A., Sarpeshkar, R., Katz, H. E., & Li, W. (2000). *Nature*, *403*, 521.
[2] Dimitrakopoulos, C. D., & Malenfant, P. R. L. (2002). *Adv. Mater.*, *14*, 99.
[3] Zhu, Z.-T., Mason, J. T., Dieckmann, R., & Malliaras, G. G. (2002). *Appl. Phys. Lett.*, *81*, 4643.
[4] Eum, K., Kim, K., Jam, J., & Chung, I. (2010) *J. Vac. Sci. Technol. A 28*, 873.
[5] Chen, J., Tee, C. K., Shtein, M., Martin, D. C., & Anthony, J. (2009). *Org. Electron.*, *10*, 696.
[6] Bae, J.-H., Park, J., Keum, C.-M., Kim, W.-H., Kim, M.-H., Kim, S.-O., Kwon, S. K., & Lee, S.-D. (2010). *Org. Electron.*, *11*, 784.
[7] Jiang, L., Zhang, J., Gamota, D., & Takoudis, C. G. (2010). *Org. Electron.*, *11*, 344.
[8] Bae, J.-H., Kim, W.-H., Yu, C.-J., & Lee, S.-D. (2009). *Jpn. J. Appl. Phys.*, *48*, 020209.
[9] Kim, W.-H., Bae, J.-H., Kim, M.-H., Keum, C.-M., Park, J., & Lee, S.-D. (2011). *J. Appl. Phys.*, *109*, 024508.
[10] Bae, J.-H., Kim, W.-H., Kim, H., Lee, C., & Lee, S.-D. (2007). *J. Appl. Phys.*, *102*, 063508.
[11] Park, J., Bae, H.-J., Kim, H.-W., Lee, D.-S., Gwag, J. S., Kim, D. W., Noh, J. C., & Choi, J. S. (2010). *Solid-State Electron.*, *54*, 1650.
[12] Komoda, T., Endo, Y., Kyuno, K., & Toriumi, A. (2002). *Jpn. J. Appl. Phys.*, *41*, 2767.
[13] Chung, S., Jang, J., Cho, J., Lee, C., Kwon, K.-S., & Hong, Y. (2011). *Jpn. J. Appl. Phys.*, *50*, 03CB05.
[14] Lee, W., Kim, D., Jang, Y., Cho, J., Hwang, M., Park, Y., Kim, Y., Han, J., & Cho, K. (2007). *Appl. Phys. Lett.*, *90*, 132106.
[15] Ohe, T., Kuribayashi, M., Tsuboi, A., Satori, K., Itabashi, M., & Nomoto, K. (2009). *Appl. Phys. Express*, *2*, 121502.
[16] Sze, S. M. (1985). *Semiconductor Devices*, Wiley, New York, (Chapter 5).
[17] Lee, S. H., Choi, M. H., Han, S. H., Choo, D. J., Jang, J., & Kwon, S. K. (2008). *Org. Electron.*, *9*, 721.
[18] Arena, A., PAtane, S., Saitta, G., & Bonavita, A. (2006). *Mater. Lett.*, *60*, 2171.