



## Effect of water in ambient air on hysteresis in pentacene field-effect transistors containing gate dielectrics coated with polymers with different functional groups

Se Hyun Kim<sup>a</sup>, Hoichang Yang<sup>b</sup>, Sang Yoon Yang<sup>a</sup>, Kipyong Hong<sup>a</sup>, Danbi Choi<sup>a</sup>, Chanwoo Yang<sup>a</sup>, Dae Sung Chung<sup>a</sup>, Chan Eon Park<sup>a,\*</sup>

<sup>a</sup> Polymer Research Institute, Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

<sup>b</sup> Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

### ARTICLE INFO

#### Article history:

Received 4 March 2008

Received in revised form 2 May 2008

Accepted 2 May 2008

Available online 13 May 2008

#### PACS:

72.20.Jv

72.80.Le

73.20.At

#### Keywords:

OFETs

Pentacene

Polymer dielectrics

Hysteresis

### ABSTRACT

We investigated the effect of water in ambient air on the hysteresis phenomena of pentacene field-effect transistors with polymer/SiO<sub>2</sub> gate dielectrics. The polarity of the polymer surface was controlled by using three different polymers: poly(styrene), poly(4-hydroxy styrene), and poly(4-vinyl pyridine). Water diffusion into the interface between the pentacene and the gate dielectric was driven by the polarity of the polymer surface, resulting in considerable hysteresis and degradation of device performances. The observed hysteresis behaviors can be explained in terms of donor- and acceptor-like trap formation by water molecules that have diffused between the pentacene and the gate dielectric. The different effects of these traps on hysteresis depending on the functional groups at the polymer surface were also investigated.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, organic field-effect transistors (OFETs) have received considerable interest because of their potential applications in low cost, large area and flexible electronics. The charge carrier mobility of OFET devices with a pentacene active layer has been shown to be comparable to those of amorphous silicon transistors ( $\sim 3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [1]. However, the utility of organic circuits has been hindered by the hysteresis phenomenon that is frequently observed during device operation. Therefore, minimizing the hysteresis effect in these circuits is a research priority in this area. When polymer layers were used as gate dielectrics, the hysteresis observed during device operation

was caused by slow polarization that occurred due to application of an electric field to a film comprised polymer molecules with polar groups on either the main or side chain, and/or to a film containing ionic impurities [2,3]. Also, the functional groups at the polymer surface, which can influence semiconductor/dielectric interface properties such as semiconductor morphology [1,4] and charge traps [5], results in specific hysteresis in accordance with the applied gate bias and operational environment. In particular, oxygen and water molecules in the air induce charge traps either in the semiconductor or at the semiconductor/dielectric interface, leading to a degradation of the device performance [6–11].

In the present study, we investigated the hysteresis phenomena of pentacene FETs by measuring the electrical characteristics of pentacene FETs with polymer/SiO<sub>2</sub> bilayer gate dielectrics having different surface properties

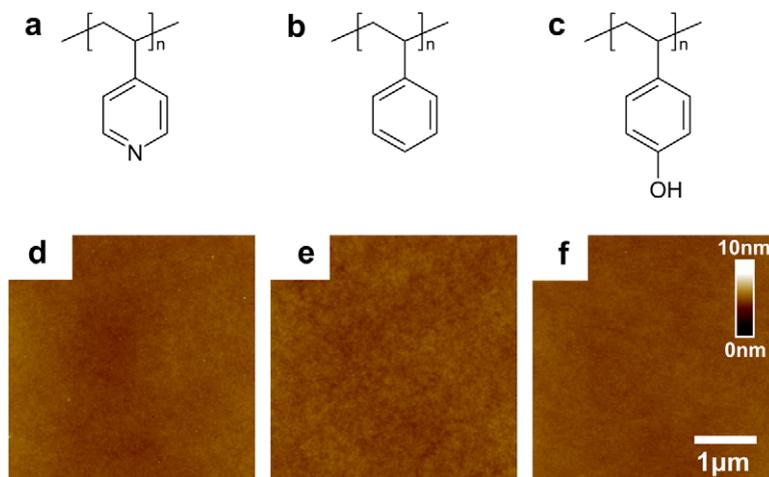
\* Corresponding author. Tel.: +82 54 279 2269; fax: +82 54 279 8298.  
E-mail address: [cep@postech.ac.kr](mailto:cep@postech.ac.kr) (C.E. Park).

(polarity and functionality) in various operational environments, including a vacuum ( $\sim 10^{-3}$  Torr), oxygen (99.9%), dry air (relative humidity (RH)  $\sim 0\%$ ) and ambient air (RH  $\sim 40\%$ ). The surface properties of the gate dielectric were controlled by applying three different ultra-thin polymer layers ( $\sim 15$  nm) on the SiO<sub>2</sub> dielectric. These systematic studies revealed that both the presence of water in the atmosphere and the polarity arising from the functional groups at the polymer surface determine the severity of hysteresis during device operation. Moreover, the observation of greater hysteresis in ambient air than in a vacuum can be accounted for in terms of the formation of long-lived donor- and acceptor-like traps by water molecules that have diffused into the interface between the semiconductor and gate dielectric, a process that is driven by the functional groups at the polymer surface.

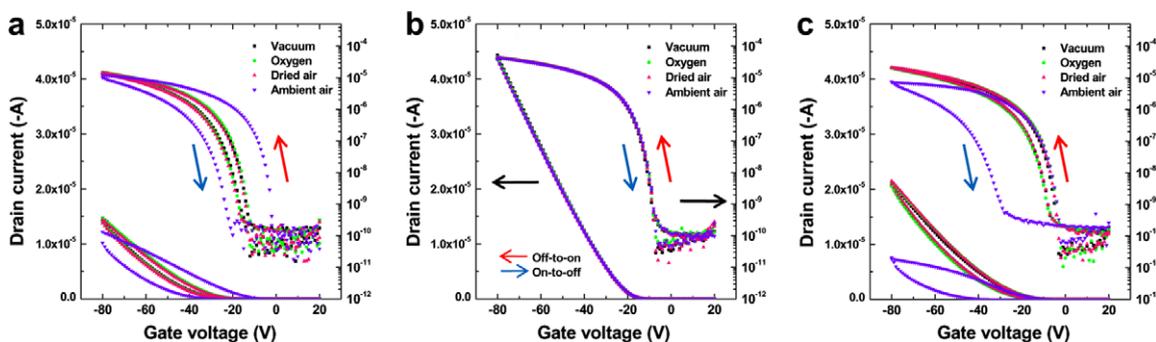
## 2. Experimental

Poly(4-vinyl pyridine) (PVP), polystyrene (PS) and poly(4-hydroxyl styrene) (PHS) thin layers (see Fig. 1a–c for their chemical structures) were spin-cast onto thermally grown 300-nm-thick SiO<sub>2</sub> substrates, followed by

annealing for 1 h at 90, 100, and 120 °C, respectively. The three types of polymer/SiO<sub>2</sub> bilayer gate dielectrics exhibited very smooth surfaces with root-mean-square roughnesses (Rq) of 3.6–4.5 Å, respectively, obtained by means of atomic force microscopy (AFM, Digital Instruments Multimode SPM, tapping mode, see Fig. 1d–f). The thickness of the polymer films measured by using an ellipsometer (J.A. Woollam Co. Inc.) was of about 10–15 nm. A 50-nm-thick pentacene active layer (Aldrich), patterned through a shadow mask, was deposited onto the gate dielectrics at a rate of 0.1–0.2 Å/s by organic molecular beam deposition. Finally, the source/drain electrodes were defined on the pentacene film by thermally evaporating gold through a shadow mask. The channel length ( $L$ ) and width ( $W$ ) were 100 and 1000  $\mu\text{m}$ , respectively. The electrical characteristics of the pentacene FETs were sequentially measured in vacuum ( $\sim 10^{-3}$  Torr), oxygen (99.9%), dry air (RH  $\sim 0\%$ ) and ambient air (RH  $\sim 40\%$ ) using Keithley 2400 and 236 Source Meter instruments. Prior to the electrical measurement, the devices were outgassed under vacuum ( $\sim 10^{-3}$  Torr) in the measurement chamber for at least 30 min, and then exposed to the operational environment for 30 min. The overall capacitance ( $C_i$ ) for all three of the bilayer gate



**Fig. 1.** Chemical structures of the polymer gate dielectrics employed in this experiment are (a) PVP, (b) PS and (c) PHS. Their surface morphologies are present in the AFM images of (c) and (d), respectively.



**Fig. 2.** Transfer characteristics of pentacene FETs in the linear regime (drain voltage,  $V_D = -8$  V) using the polymer/SiO<sub>2</sub> bilayer gate dielectrics with various operational environments, specifically vacuum ( $\sim 10^{-3}$  Torr), oxygen (99.9%), dry (RH  $\sim 0\%$ ) and ambient air (RH  $\sim 40\%$ ): (a) PVP, (b) PS and (c) PHS devices.

dielectrics, measured using an Agilent 4284 precision LCR meter, was  $10 \text{ nF/cm}^2$ .

### 3. Results and discussion

Fig. 2 shows the influence of operational environment on hysteresis in the linear regime (drain voltage  $V_D = -8 \text{ V}$ ) transfer characteristics of the devices with PVP, PS and PHS/SiO<sub>2</sub> bilayer gate dielectrics, and Fig. 3 shows a comparison of the device performance when the three devices were operated in the different environments. The PVP and PHS devices showed considerable hysteresis in ambient air but little hysteresis in the other environments (Fig. 2a and c). Also, operation in ambient air led to a degradation of the drain current ( $I_D$ ), which resulted in a reduction in charge

carrier mobility ( $\mu$ ) and changes in device performance indicators such as the turn-on voltage ( $V_{\text{turn-on}}$ ), threshold voltage ( $V_{\text{th}}$ ) and subthreshold swing (SS). On the other hand, compared to operation in a vacuum, devices operated in oxygen showed slightly increased  $I_D$  and SS, and shifts in  $V_{\text{turn-on}}$  and  $V_{\text{th}}$  toward more positive voltages. These effects of oxygen on device performance are attributed to the acceptor-like traps created by oxygen in both pentacene films and pentacene/polymer interfaces, which attract electrons from the pentacene layer, thereby increasing the hole density in the channel region [6–8]. However, on going from a vacuum to an oxygen atmosphere, the hysteresis was not enlarged (see Fig. 2a and c), indicating that the hysteresis observed in these devices was not due to oxygen but rather to water molecules in

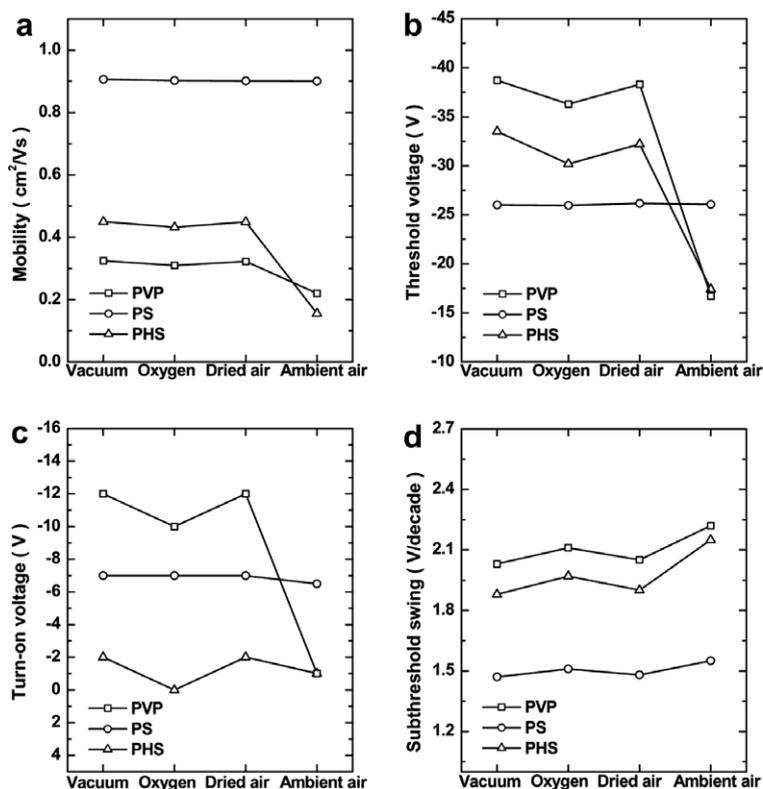


Fig. 3. Variation of the device performance characteristics for each operational environment in the PVP, PS and PHS devices. The mobility ( $\mu$ ) and threshold voltage ( $V_{\text{th}}$ ) were calculated in the linear regime. All electrical parameters were extracted from the off-to-on sweep curves.

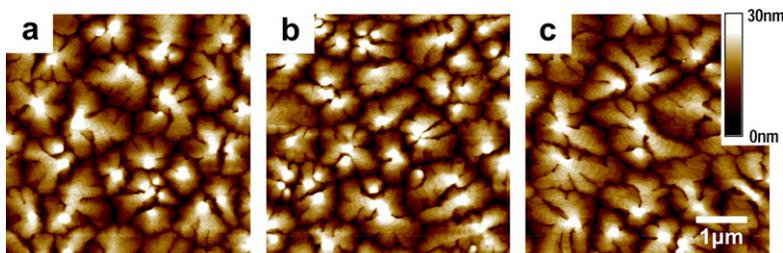


Fig. 4. AFM images in (a), (b) and (c) show the morphologies of pentacene layers (50 nm thick) on PVP, PS and PHS films, respectively.

ambient air. The influence of water in ambient air on OFETs has been previously reported [7–11]. It was found that water molecules in humid air diffuse into the grain boundary of the polycrystalline semiconductor layer and/or the interface between the semiconductor and gate dielectric, where they create both donor- and acceptor-like traps, leading to significant degradation of device performance [7]. In the present work, however, the PS device did not exhibit hysteresis in any of the operational environments (Fig. 2b), and other electrical parameters also showed almost no dependence on environment (Fig. 3). These findings indicate that the hysteresis and device performance characteristics may be crucially affected by the absorbed water in the semiconductor and the interface between the semiconductor and the gate dielectric. In addition, the diffusion of water molecules is intimately related to the density of grain boundaries in the pentacene film because small molecules migrate into the channel region through such defects [12]. As shown in Fig. 4a–c, the density of grain boundaries on the pentacene surface is similar for all of the polymer/SiO<sub>2</sub> bilayer gate dielectrics; thus the grain boundary effect can be excluded in our study.

To demonstrate how the functional groups at the polymer surface interact with diffusing water molecules, we investigated the surface energies of the polymers by measuring the contact angles of two test liquids, namely water and diiodomethane. Surface energy is a direct indication of intermolecular force, and consists of the sum of dispersion and polar components which are calculated by the following equation [13]:

$$1 + \cos \theta = \frac{2(\gamma_s^d)^{1/2}(\gamma_{lv}^d)^{1/2}}{\gamma_{lv}} + \frac{2(\gamma_s^p)^{1/2}(\gamma_{lv}^p)^{1/2}}{\gamma_{lv}},$$

where  $\gamma_s$  and  $\gamma_{lv}$  are the surface energies of the sample and test liquid, respectively, and the superscripts d and p refer to dispersion and polar components, respectively. Also, the values of  $\gamma_{lv}$ ,  $\gamma_{lv}^p$  and  $\gamma_{lv}^d$  for the test liquids and the procedure to solve the equation are provided in Ref. [13]. In particular, the polar component ( $\gamma_s^p$ ) of the surface energy is attributed to polar forces arising from permanent and induced dipoles, as well as hydrogen-bonding, whereas the dispersion component ( $\gamma_s^d$ ) is due to instantaneous dipole moments [13]. Therefore, the interaction between a polymer surface and diffusing water molecules will exhibit a greater dependence on  $\gamma_s^p$  rather than  $\gamma_s^d$ . Table 1 shows the measured contact angles of the test liquids, as well as the surface energy and polarity  $\chi_p$  (i.e. the ratio of the polar component to the total surface energy) for the polymer/SiO<sub>2</sub> bilayer gate dielectrics. The  $\gamma_s^p$  and  $\chi_p$  of the PS polymer are remarkably smaller than those of the PVP and

PHS polymers, indicating that the surface of the PS film is more non-polar than those of the PVP and PHS films. In other words, the functional group of PS, the phenyl moiety, interacts only weakly with water molecules compared with the pyridine group in PVP and the phenol in PHS. On the other hand, the pyridine and phenol functional groups of PVP and PHS interact strongly with water molecules through hydrogen-bonding. These results indicate that the surface polarity arising from the functional group in the polymer plays an important role in determining the device performance in ambient air.

The similar surface polarities of the polymers in the PVP and PHS devices mean that the diffused water molecules give rise to hysteresis loops in the same (anticlockwise) direction (Fig. 2a and c). However, significantly different features were observed in the hysteresis depending on the functional groups at the polymer surface: In the off-to-on gate sweep of the PVP device in ambient air, a large shift of the transfer curve toward positive  $V_G$  direction is observed, whereas the on-to-off gate sweep curve is slightly moved toward the opposite direction, as compared with non-humid conditions (Fig. 2a). When the hysteresis of the PHS device in ambient air is compared with that under non-humid conditions, by contrast, the transfer curve is hardly altered during the off-to-on gate sweep, but is shifted toward negative  $V_G$  when the gate voltage is swept from on to off (Fig. 2c). These deviations of the transfer curves in ambient air from those under non-humid conditions can be attributed to the water molecules that have diffused into the interface between the semiconductor and gate dielectric, which can act as both acceptor- and donor-like traps at the interface. According to the report by Gu et al., acceptor-like traps can result in hysteresis during the off-to-on gate sweep because negative charges accumulate at the interface by filling the acceptor-like traps with electrons for positive  $V_G$ , inducing more holes than those required by the  $V_G$  and  $C_i$  to balance the stored negative charges [14]. On the contrary, the donor-like traps are occupied by holes induced by the negative  $V_G$  applied during the off-to-on gate sweep. The long life-times of the donor-like traps result in keeping the traps filled during the on-to-off gate sweep, thereby reducing  $I_D$  during the on-to-off gate sweep. In other words, the donor-like traps contribute to hysteresis during the on-to-off gate sweep [14].

Therefore, in the case of the PHS device in ambient air, the acceptor-like trap effect due to water molecules is smeared during the off-to-on gate sweep because water molecules have the same effect as the hydroxyl groups of PHS which can function as acceptor-like traps [15], making the donor-like trap effects dominate in comparison to the

**Table 1**  
Surface energy and polarity of polymer/SiO<sub>2</sub> bilayer gate dielectrics

Gate dielectric	Contact angle (°)		$\gamma_s^p$ (mJ m <sup>-2</sup> )	$\gamma_s^d$ (mJ m <sup>-2</sup> )	$\gamma_s(\gamma_s^p + \gamma_s^d)$ (mJ m <sup>-2</sup> )	$\chi_p(\gamma_s^p/\gamma_s)$
	Water	Diiodomethane				
PS	90	31	0.55	43.28	44.19	0.012
PHS	56	37	17.58	32.10	49.18	0.357
PVP	49	13	18.49	39.05	57.59	0.321

non-humid conditions (Fig. 2c). On the other hand, the PVP device in ambient air shows hysteresis caused by the diffused water molecules, which act as both acceptor- and donor-like traps: the transfer curve of the PVP device in ambient air is shifted toward positive  $V_G$  in the off-to-on sweep and toward negative  $V_G$  in the on-to-off sweep, as compared with non-humid conditions. In this case, the acceptor-like trap effect on hysteresis (shift toward the positive  $V_G$  direction) is larger than the donor-like trap effect (shift toward the negative  $V_G$  direction) (Fig. 2a). The decrease of  $I_D$  in the PVP device was smaller than that in the PHS device in ambient air because the acceptor-like traps created by the water molecules were more dominant than the donor-like traps in the PVP device (see Fig. 2a and c).

#### 4. Conclusion

In conclusion, we have demonstrated the influence of water in ambient air and the functional groups at the polymer surface on the hysteresis of pentacene FETs. The polarity of the polymer surface can determine the interaction with diffused water molecules, resulting in considerable hysteresis and a degradation of device performance. Moreover, the charge traps arising from water molecules have different effects on the hysteresis depending on the functional groups at the polymer surface.

#### Acknowledgment

This work was supported by Grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy (MOCIE).

#### References

- [1] H.C. Yang, T.J. Shin, M.M. Ling, K. Cho, C.Y. Ryu, Z.N. Bao, *J. Am. Chem. Soc.* 127 (2005) 11542.
- [2] J. Veres, S. Ogier, S.W. Leeming, D.C. Cupertino, S.M. Khaffaf, G. Lloyd, *Proc. SPIE* 147 (2003) 5217.
- [3] T.B. Singh, N. Marjanović, P. Stadler, M. Auinger, G.J. Matt, S. Günes, N.S. Sariciftci, R. Schwödiauer, S. Bauer, *J. Appl. Phys.* 97 (2005) 083714.
- [4] S.Y. Yang, K. Shin, C.E. Park, *Adv. Funct. Mater.* 15 (2005) 1806.
- [5] K. Shin, S.Y. Yang, C. Yang, H. Jeon, C.E. Park, *Org. Electron.* 8 (2007) 336.
- [6] A.R. Volkel, R.A. Street, D. Knipp, *Phys. Rev. B* 66 (2002) 195336.
- [7] D. Knipp, A. Benor, V. Wagner, T. Muck, *J. Appl. Phys.* 101 (2007) 044504.
- [8] O.D. Jurchescu, J. Baas, T.T.M. Palstra, *Appl. Phys. Lett.* 87 (2005) 052102.
- [9] T. Jung, A. Dodabalapur, *Appl. Phys. Lett.* 87 (2005) 182109.
- [10] D. Li, E. Borkent, R. Nortrup, H. Moon, H. Katz, Z. Bao, *Appl. Phys. Lett.* 86 (2005) 042105.
- [11] C. Goldmann, D.J. Gundlach, B. Batlogg, *Appl. Phys. Lett.* 88 (2006) 063501.
- [12] B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H.E. Katz, A.J. Lovinger, Z. Bao, *Appl. Phys. Lett.* 78 (2001) 2229.
- [13] A.J. Kinloch, *Adhesion and Adhesives: Science and Technology*, Chapman and Hall, 1987. (pp. 18–32, Chap. 2).
- [14] G. Gu, M.G. Kane, J.E. Doty, A.H. Firester, *Appl. Phys. Lett.* 87 (2005) 243512.
- [15] L.L. Chua, J. Zaumseil, J.F. Chabng, E.C.-W. Ou, P.K.-H. Ho, H. Sirringhaus, R.H. Friend, *Nature* 434 (2005) 194.