Chemistry Letters Vol.38, No.1 (2009)

Surface Modification of Organic–Inorganic Hybrid Insulator for Printable Organic Field-effect Transistors

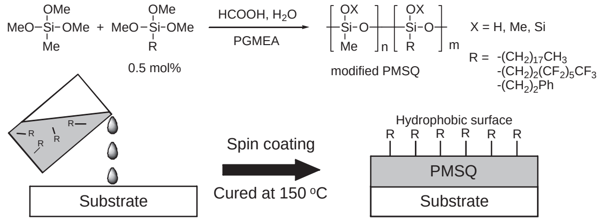
Mitsuru Watanabe,[1] Koji Muro,[2] Takashi Hamada,[3] Toshiyuki Tamai,[1]
Araki Masuyama,[2] Hiroyoshi Naito,[4] and Kimihiro Matsukawa*[1]
[1]*Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Jyoto-ku, Osaka 536-8553*
[2]*Department of Applied Chemistry, Osaka Institute of Technology, 5-16-1 Omiya, Asahi-ku, Osaka 535-8585*
[3]*Inovation Plaza Osaka, Japan Science and Technology Agency, 3-1-10 Technostage, Izumi 594-1144*
[4]*Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai 599-8531*

(Received October 16, 2008; CL-080995; E-mail: kmatsu@omtri.city.osaka.jp)

To improve the performance of organic field-effect transistors (OFETs) composed of poly(3-hexylthiophene) (P3HT) semiconductor and polymethylsilsesquioxane (PMSQ)-based insulator, surface modification of PMSQ insulator has been carried out. The modified PMSQ were synthesized by a sol–gel co-condensation of methyltrimethoxysilane and hydrophobic alkoxysilane. The thin films from these PMSQ had smooth and hydrophobic surface. Resulting OFET fabricated on the modified PMSQ insulator showed enhanced mobility. A clear relation could be seen between the mobility and the surface free energy of insulator.

Organic field-effect transistors (OFETs) have received considerable attention as a key technology for a wide range of applications, such as flexible displays, radio-frequency identification tags, and smart cards, owing to their flexible, light-weight, and low-cost characteristics.[1] Much effort has been focused on developing organic semiconductors for OFETs, and the potencial of mobility has been achieved comparable to amorphous silicon-based FETs.[2] For this purpose, some poly- or origothiophene derivatives and pentacene derivatives have been utilized as a semiconductor layer of OFETs via a wet film formation process.[3,4] The film formability by solution process is one of the most important functions of the materials for OFETs with low-cost manufacturing. Although various printable gate insulators with wet and low-temperature processes have been proposed,[5] the requirements for insulating layer are not only an excellent electronic resistivity but also appropriate surface properties. As the performance of OFET directly reflects the interfacial conditions between the organic semiconductor layer and the insulating layer, the surface properties of insulator are extremely important.[6–8] Surface roughness of the insulator would cause a defect of electronic fields on the channel and a decrease in the mobility of the OFETs.[3,9] Moreover, it was known that functional groups onto the surface of the insulator would control the crystal growth and structure ordering of the organic semiconductor.[6] The enhancement in the mobility of poly(3-hexylthiophene) (P3HT) on SAM-modified surfaces has been observed and explained by the improvement in the structural ordering of P3HT molecules on the hydrophobic surfaces.[6,10–13] Thus, the surface modification of the gate insulator is an important process for the fabrication of efficient OFETs.

Recently, we have investigated polymethylsilsesquioxane (PMSQ) dielectric as applied for a printable gate insulator in OFETs on plastic substrate. PMSQ dielectric film is a siloxane-based organic–inorganic hybrid, which can be prepared at 150 °C and shows high resistivity up to $10^{14}\ \Omega\,\mathrm{cm}$.[14] An OFET composed of PMSQ and P3HT showed higher mobility than that composed of SiO_2 and P3HT. However, the mobility of OFET from PMSQ/P3HT was lower than that from octadecyltrichlorosilane-modified SiO_2/P3HT,[14] indicating that the surface condition of PMSQ insulator is not yet sufficient for the structural ordering of P3HT. In pursuit of high-performance OFETs, we tried the surface modification of PMSQ insulator by a cocondensation with several alkoxysilanes. In this paper, we added alkoxysilanes with hydrophobic functional groups during sol–gel synthesis of PMSQ on the assumption that the hydrophobic groups will migrate to the surface of PMSQ insulator because of its low surface free energy character (Scheme 1). The hydrophobic surface of modified PMSQ will enhance the structural ordering of P3HT molecules. It is an advantage of this method that the performance of OFETs can be increased without additional surface modification step, such as alkyltrichlorosilane treatment.



Scheme 1. Synthesis of modified PMSQ and fabrication of the hydrophobic insulator.

Octadecyltrimethoxysilane [$CH_3(CH_2)_{17}Si(OMe)_3$, OTS], (2-phenylethyl)trimethoxysilane [$Ph(CH_2)_2Si(OMe)_3$, PES], and (tridecafluoro-1,1,2,2-tetrahydrooctyl)trimethoxysilane [$CF_3(CF_2)_5(CH_2)_2Si(OMe)_3$, FOS] were used as hydrophobic alkoxysilanes. The octadecyl group is a common hydrophobic functional group for surface modification, and specific effects derived from phenyl group and fluorinated alkyl group would be expected from PES and FOS, respectively. The modified PMSQ was synthesized by allowing a mixture of methyltrimethoxysilane and hydrophobic alkoxysilane (0.5 mol %) for a sol–gel cocondensation with formic acid catalyst in propylene glycol methyl ether acetate (PGMEA). The modified PMSQ solutions were spin-coated onto a substrate and cured at 100 °C for 1 h and then 150 °C for 1 h. The surface properties of obtained modified PMSQ insulator were evaluated by surface free energy and AFM measurement. Surface free energy was calculated from the contact angle according to Kitazaki and Hata's equation.[15]

Although the water contact angles slightly increased by the addition of OTS and PES (Table 1), FOS-modified PMSQ showed remarkably high water contact angle. The surface free

Table 1. The surface properties of modified PMSQ insulators

Additive [R–Si(OMe)$_3$]		Contact angle (water) /degree	Surface free energy /mJ m^{-2}	Average surface roughness[a] /nm
R	Amount /mol %			
None	—	86.1	28.2	0.42
–(CH$_2$)$_{17}$CH$_3$	0.5	87.1	28.5	0.36
–(CH$_2$)$_2$Ph	0.5	89.6	27.1	0.48
–(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$	0.5	92.9	24.3	0.35
–(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$	1.0	97.1	22.3	—

[a] Measured by AFM analysis.

energy also indicated the similar tendency that the FOS-modified PMSQ exhibited lower surface free energy than that of the others. This indicates that fluorinated alkyl groups migrated and accumulated on the surface of the film and then decreased the surface free energy by only small amount addition of hydrophobic groups. The AFM surface images of nonmodified and FOS-modified PMSQ showed no significant difference (Figure S1 in Supporting Information),[15] and the values of average surface roughness were almost identical (Table 1). Adding 0.5 mol % of hydrophobic alkylsilanes to PMSQ does not affect the surface roughness of PMSQ, giving a smooth surface. However, increasing the amount of FOS addition prevents its film formation by reducing surface free energy. Therefore, P3HT-based OFETs were fabricated with the modified PMSQ containing 0.5 mol % hydrophobic alkylsilane. For precise comparison of the insulator surface condition, modified PMSQ insulators were spin-coated on a heavily doped silicon wafer with a thermally grown 140-nm-thick SiO$_2$ layer, and the device characteristics of modified PMSQ/P3HT OFET were evaluated.

The output and transfer characteristics of FOS-modified PMSQ/P3HT OFET are shown in Figure 1. The device showed p-type characteristics with clear transitions for linear saturation behavior and followed well the standard MOSFET gradual channel model. These device performances of modified PMSQ/P3HT OFETs are summarized in Table 2. The mobility μ and threshold voltage V_{th} were calculated using the standard equation from the transfer curves in the saturation. The device on the FOS-modified PMSQ exhibited the highest mobility, and that on the PES-modified PMSQ showed the second highest. This result was consistent with the result of the surface free energy analysis. Figure 2 shows the relation between the surface free energy and mobility of the OFETs fabricated on the modified PMSQ insulators. It can be clearly seen that the mobility increased as the surface free energy of the insulator decreased. This simple relation suggests that the hydrophobicity of the insulator surface enhances the structural ordering of P3HT, although direct evidence of P3HT ordering has not been obtained as yet.

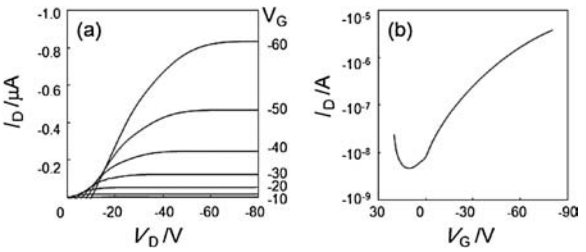


Figure 1. Output characteristics (a), and transfer characteristics (b) of FOS-modified PMSQ/P3HT OFET.

Table 2. Device performances of modified PMSQ/P3HT OFETs

Additive [R–Si(OMe)$_3$] R	μ /cm^2 V^{-1} s^{-1}	V_{th} /V	On/off ratio
None	6.9×10^{-3}	−25	485
–(CH$_2$)$_{17}$CH$_3$	6.2×10^{-3}	−20	774
–(CH$_2$)$_2$Ph	9.1×10^{-3}	−8	1586
–(CH$_2$)$_2$(CF$_2$)$_5$CF$_3$	1.1×10^{-2}	−20	461

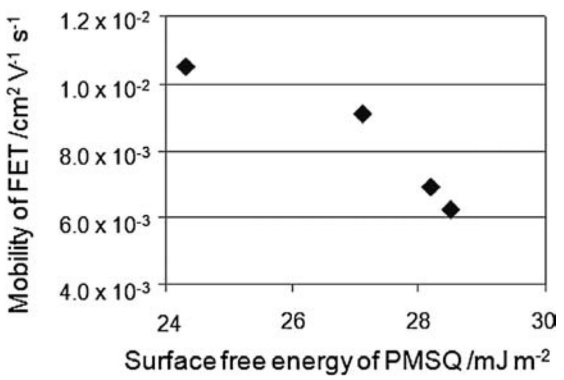


Figure 2. Relationships between mobility of OFETs and surface free energy of insulator.

In conclusion, printable insulator layer having hydrophobic surfaces was fabricated by adding 0.5 mol % of FOS during the sol–gel synthesis of PMSQ. The mobility of FOS-modified PMSQ/P3HT OFET was higher than that of nonmodified OFET, indicating the enhancement of structural ordering of P3HT by hydrophobic surface. Moreover, clear negative relation was exhibited between the mobility of OFETs and the surface free energy of insulators. The simple method employed here will provide a promising technique to improve the performance of OFETs.

This study was supported by the Science and Technology Incubation Program in Advance Regions, Japan Science and Technology Agency.

References and Notes

1 C. D. Dimitrakopoulos, D. J. Mascaro, *IBM J. Res. Dev.* **2001**, *45*, 11.
2 H. E. Katz, *Chem. Mater.* **2004**, *16*, 4748.
3 D. Knipp, R. A. Street, A. R. Völkel, *Appl. Phys. Lett.* **2003**, *82*, 3907.
4 A. R. Murphy, J. M. J. Frěchet, *Chem. Rev.* **2007**, *107*, 1066.
5 Z. Bao, J. A. Rogers, H. E. Katz, *J. Mater. Chem.* **1999**, *9*, 1895.
6 J. Veres, S. Ogier, G. Lloyd, *Chem. Mater.* **2004**, *16*, 4543.
7 A. Salleo, M. L. Chabinyc, M. S. Yang, R. A. Street, *Appl. Phys. Lett.* **2002**, *81*, 4383.
8 K. P. Pernstich, S. Haas, D. Oberhoff, C. Goldmann, D. J. Gundlach, B. Batlogg, A. N. Rashid, G. Schitter, *J. Appl. Phys.* **2004**, *96*, 6431.
9 D. Knipp, R. A. Street, A. R. Völkel, J. Ho, *J. Appl. Phys.* **2003**, *93*, 347.
10 S. Grecu, N. Roggenbuck, A. Opitz, W. Brütting, *Org. Electron.* **2006**, *7*, 276.
11 L. A. Majewski, M. Grell, *Synth. Met.* **2005**, *151*, 175.
12 D. H. Kim, Y. Jang, Y. D. Park, K. Cho, *Macromolecules* **2006**, *39*, 5843.
13 A. Zen, D. Neher, K. Silmy, A. Holländer, U. Asawapirom, U. Scherf, *Jpn. J. Appl. Phys.* **2005**, *44*, 3721.
14 K. Tomatsu, T. Hamada, T. Nagase, S. Yamazaki, T. Kobayashi, S. Murakami, K. Matsukawa, H. Naito, *Jpn. J. Appl. Phys.* **2008**, *47*, 3196.
15 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) November 29, 2008; doi:10.1246/cl.2009.34