Available online at www.sciencedirect.com

ScienceDirect

Organic Electronics 8 (2007) 743–748

Organic Electronics

www.elsevier.com/locate/orgel

# Organic–inorganic hybrid materials as solution processible gate insulator for organic thin film transistors

Chaun Gi Choi, Byeong-Soo Bae *

*Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering,*
*Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Republic of Korea*

Received 17 September 2006; received in revised form 12 June 2007; accepted 19 June 2007
Available online 30 June 2007

## Abstract

We synthesized organic–inorganic hybrid materials (hybrimers) using a simple non-hydrolytic sol–gel reaction and applied the materials as gate insulators in organic thin film transistors (OTFTs). The hybrimer thin films had smooth and hydrophobic surfaces, and were stable with solvents. In addition, the hybrimer thin films had good electrical properties such as low leakage current and high dielectric strength. The performance of the OTFT with hybrimer gate insulator fabricated by drop casting of regioregular poly(3-hexylthiophene) (P3HT) was similar to that of OTFT with hexamethyldisilazane (HMDS) treated thermally grown $SiO_2$. The hysteresis of RR-P3HT based OTFT with hybrimer gate insulator was negligible.

*PACS:* 81.07.Pr; 85.30.Tv; 73.61.−r; 77.55.+f; 68.55.-a

*Keywords:* Organic thin film transistors; OTFTs; Organic–inorganic hybrid materials; Hybrimer gate insulators; P3HT organic semiconductor

## 1. Introduction

Organic thin-film transistors (OTFTs) have attracted a great deal of attention and have been utilized for integrated circuits and driving circuits for active matrix displays [1,2], sensors [3], and RFIDs [4] because OTFTs have many advantages for flexible electronics such as low temperature processibility, low cost, and flexibility compared with conventional Si technology. The performance of the OTFTs using a small molecule or polymer semiconductors is comparable to that obtained with hydrogenated amorphous silicon, which is being used for active matrix liquid-crystal displays.

Since field-induced carriers are confined to a very thin region close to the interface of the gate insulator and organic semiconductor [5], it is important to choose proper materials and to control the surface of the gate insulator to obtain a better performance of the OTFT. In order to improve the performance of the OTFT, the gate insulator requires such characteristics as a high dielectric constant, a

---

* Corresponding author. Tel.: +82 428694119; fax: +82 428693310.
*E-mail address:* bsbae@kaist.ac.kr (B.-S. Bae).

1566-1199/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2007.06.006

low leakage current, and a smooth surface [6]. For flexible electronics using plastic substrates, it is also preferred for gate insulators to be capable of being prepared by a solution process because they are desirable to be easily formed at low temperature. Hence, many solution processible polymer thin films have been used as the gate insulator in the OTFT instead of using inorganic insulators [6,7]. However, polymer gate insulators have limits to their practical use due to their restricted dielectric properties and low thermal stability.

The sol–gel derived siloxane based organic–inorganic hybrid materials (hybrimers), in which inorganic and organic components are intimately linked at the molecular scale by a covalent bond, have been widely studied with respect to new dielectric materials for applications in optics and electronics [8,9]. Such materials combine the characteristics of both glass and polymers, and they improve the thermal and mechanical properties of the final materials to be applied. By a suitable selection of precursors and optimization of processing parameters, we can easily control the properties of hybrimers such as dielectric constant, thermal stability, refractive index, surface roughness, and hydrophobicity [8,10] Especially, the methacrylate hybrimers synthesized using a precursor of methacryloxypropyl trimethoxysilane (MPTMS) have been widely investigated for many optical applications, since they show good optical characteristics and are photo-patternable, allowing easy fabrication for micro-optical devices. Thus, the hybrimers can be applied to the gate insulators in the OTFTs since they can control a wide range of electrical and surface properties with high thermal stability and are photo-patternable, as well as solution processible for easy fabrication of the OTFT. Recently, Bao et al. [11] reported that silsesquioxane based materials, which are another type of hybrid materials, could be potential candidates for gate insulators in low cost and low process temperature OTFTs.

In this study, we report on solution processible hybrimers as gate insulators to fabricate solution processed OTFTs with regioregular poly(3-hexylthiophene) (RR-P3HT) organic semiconductor. The photo-patternable hybrimers, which contain oligosiloxanes nanoclusters grafted by photo-polymerizable methacryl radicals, were synthesized using a simple non-hydrolytic sol–gel reaction. Electrical characteristics and surface properties of the hybrimer thin films were examined. In addition, the performance of the fabricated OTFT with hybrimer gate insulator was also investigated.

## 2. Experimental

We synthesized hybrimer resins containing oligosiloxanes grafted by methacryl radicals using a simple non-hydrolytic sol–gel reaction as shown in Fig. 1a. Methacryloxypropyl trimethoxysilane (MPTMS, Aldrich) and diphenylsilanediol (DPSD, TCI) were used as precursors without further purification, and barium hydroxide monohydrate ($Ba(OH)_2{\cdot}H_2O$, Aldrich) was used as a catalyst to promote a condensation reaction between the two precursors. The total proportion of MPTMS and DPSD together was 1:1 molar ratio. Detailed fabrication procedures, as well as structure and properties of the methacrylate hybrimer, were reported in previous report [10]. The hybrimer thin films were deposited on indium tin oxide (ITO) coated glass (sheet resistance of 15 $\Omega/\square$). The ITO coated glasses were cleaned with acetone, isopropylalcohol (IPA), and de-ionized (DI) water in ultrasonic, and were then exposed to oxygen plasma for 5 min at 200 W to remove organic contamination and to improve the wettability of hybrimers solution. The synthesized hybrimer resins were diluted with propylene glycol monomethyl ether acetate (PGMEA). The solutions were filtered through a 0.22 μm pore size polytetrafluoroethylene (PTFE) membrane syringe filter and spin cast at a spin rate of 5000 rpm for 30 s on the ITO coated glass. The deposited films were exposed to UV light ($\lambda = 365$ nm, Hg lamp) for 1 min 30 s and thermally cured at 150 °C for 2 h in air condition.

The electrical properties of the hybrimer thin films, such as dielectric constant and leakage current density, were measured using Al/hybrimers thin film/ITO structures with an HP4194A (Agilent Technologies) impedance/gain analyzer and a Keithley 237 source-measure unit (Keithley). We measured the surface roughness and water contact angle of the hybrimers thin films using atomic force microscopy (AFM) (XE/100,PSIA) and a contact angle analyzer (Phoenix 150, SEO), respectively.

OTFTs with the bottom contact geometry were fabricated. Gold was thermally evaporated on either hybrimer gate insulator/ITO or the hexamethyldisilazane (HMDS)-treated thermally grown $SiO_2$ on Si wafer (resistivity of 0.01 Ωcm) through a shadow mask to form source and drain electrodes. The OTFTs had a channel length of 50 μm and channel width of 3000 μm. RR-P3HT was used as received from Rieke Metals (Lincoln, USA) without further purification. Since the charge carrier mobility is

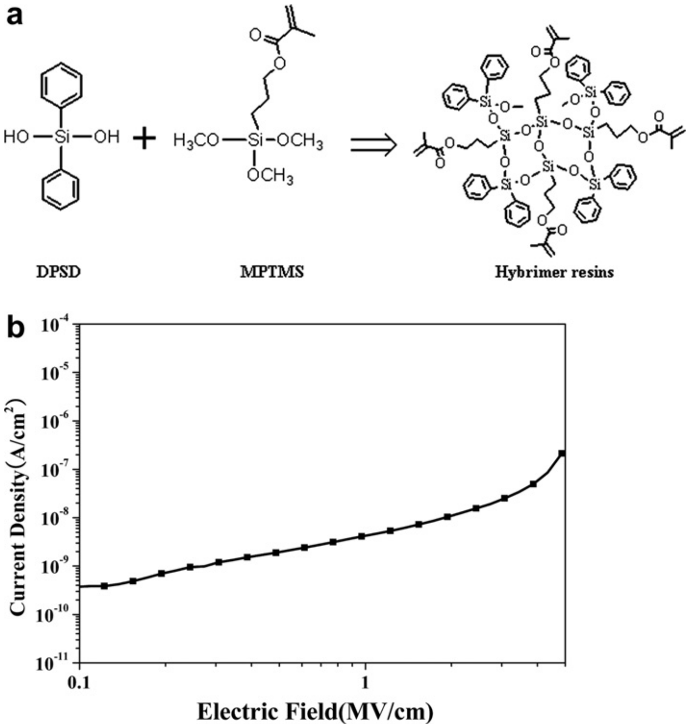

Fig. 1. (a) Schematic synthesis diagram of hybrimers by sol–gel reaction of DPSD and MPTMS, and (b) leakage current density of hybrimer thin film for the MIM structure.

enhanced when the evaporation rate of solvents is low [12], RR-P3HT was dissolved in chlorobenzene (concentration of 0.2 wt%). The solution was filtered through a 0.22 μm pore size PTFE membrane syringe filter, drop cast on the substrate in a nitrogen atmosphere. The thin films were dried overnight (10–12 h) at 100 °C in a vacuum oven. Electrical characteristics of the fabricated OTFTs were measured using an HP 4155 A semiconductor parameter analyzer (Agilent Technologies) under ambient laboratory conditions. In order to investigate the hysteresis of RR-P3HT based OTFT with hybrimer gate insulator, capacitance–voltage ($C$–$V$) characteristics were measured using metal–insulator–semiconductor (MIS) structure, Au/RR-P3HT/hybrimer gate insulator/ITO, with an HP4194A (Agilent Technologies) impedance/gain analyzer. The voltage was swept with 0.5 V step, starting from +40 V to −40 V and returning to +40 V at 100 kHz.

## 3. Results and discussion

The deposited hybrimer thin films were dense and pinhole free, as determined by scanning electron microscope (SEM, JEOL). In addition, the adhesion of the hybrimer films on the ITO coated glass was excellent. The dielectric constant ($\varepsilon_r$) of the hybrimer thin film is ∼3.1 at 100 kHz calculated from the thickness and capacitance. The $\varepsilon_r$ of hybrimer is lower than that of $SiO_2$ ($\varepsilon_r = 3.9$). The low $\varepsilon_r$ is attributed to the nonpolar phenyl group of DPSD and symmetrical structures of hybrimers.

Fig. 1b shows the dependence of leakage current density (J) of hybrimer thin film on the applied electric field ($E$) at room temperature. The leakage current density at 1 MV/cm of the hybrimer thin film is 4.1 nA/cm$^2$ and the dielectric strength of the hybrimer thin film, which was measured at current density of $10^{-6}$ A/cm$^2$ is about 5 MV/cm. The leakage current density and the dielectric strength of the hybrimer thin film are much better than those of the commonly used solution-processable polymer gate insulators in OTFT [13–15]. Polymer gate insulators were reported to have the relatively high leakage current density of $\sim 10^{-7}$ A/cm$^2$ at 1 MV/cm and the low dielectric strength of typically 0.1 ∼ 1 MV/cm [16]. This is due to the fact that they cannot yield conformal and pin-hole free film, and also a number of the polymers possess hydroxyl groups which act as trap sites [17].

Hybrimer thin film was fabricated by the condensation reaction between two precursors and by the polymerization of the methacryl groups. The condensation reaction between the methoxy groups of MPTMS and hydroxyl groups of DPSD forms the oligosiloxane networks. Oligosiloxane networks are cross-linked via polymerization under UV irradiation due to the photosensitivity of methacryl groups in MPTMS, which allowing the hybrimer thin film to be more dense and robust. Since the non-hydrolytic sol–gel reaction to fabricate the hybrimer does not use the water which is necessary to hydrolyze the precursor, there are few hydroxyl groups in the hybrimer gate insulator [10]. The formation of totally cross-linked 3-dimensional networks and few hydroxyl groups in hybrimer gate insulator give the low leakage current density and high dielectric strength of hybrimer thin film.

It is well known that the surface energy and surface roughness of the gate insulator play important roles in the performance of OTFT [7,15,16,18]. The gate insulators should have smooth and hydrophobic surface, and chemical stabilities with the solvents used to dissolve RR-P3HT. The water contact angle of the hybrimer thin film was as high as ~80°, which indicates that it has a hydrophobic surface. The hydrophobic surface of the hybrimer thin film is attributed to the methacryl and phenyl groups grafted to the oligosiloxanes networks. The hydrophobic characteristics of hybrimer film can remove the additional works such as self assemble monolayers treatment to improve the performance of OTFTs.

The solvent used in the solution processing of the organic semiconductor layer affects the underlying polymer gate insulators and, consequently, affects the device performance significantly [15]. The hybrimer thin films were treated with various solvents, which can dissolve the RR-P3HT, to examine the chemical stabilities of the hybrimer thin films although the solvents could not dissolve the hybrimer thin films. Fig. 2 shows the AFM surface images of the hybrimer thin films as deposited and after dipping in the solvent for 5 min and drying the solvents. The as-deposited hybrimer thin film shows a smooth surface with a RMS roughness of 0.38 nm. The hybrimer solution fills up the valley region on the rough ITO substrate during the spin coating due to the low viscosity of the solution, which makes ITO surface planar. This is consistent with other groups' results using polymer to flatten the ITO surface [19,20]. The RMS roughness of the solvent treated thin films is around 0.3–0.4 nm, which is almost identical with as deposited hybrimer thin films. Thus, we concluded that the hybrimer thin films are stable with the solvents for RR-P3HT due to the cross-linked 3-dimensional networks consisting of inorganic and organic networks.

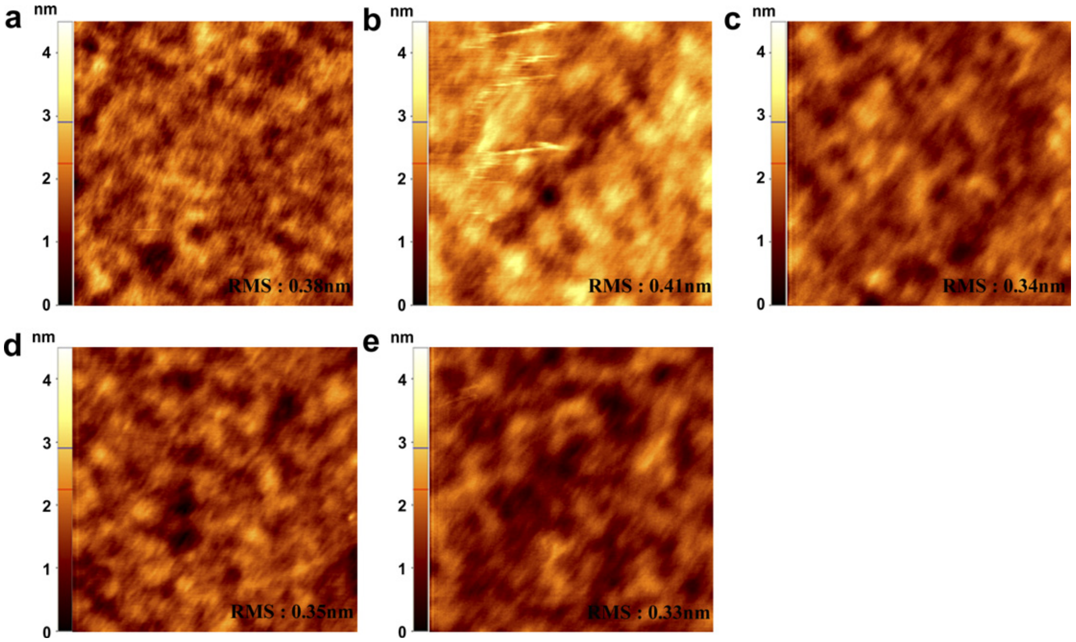

Fig. 2. AFM surface images of the hybrimer thin films (a) as deposited, and after treated with (b) chlorobenzene, (c) *p*-xylene, (d) trichloroethylene, and (e) toluene. All images are 5 μm × 5 μm in size.

One major problem in using polymeric gate insulators is the hysteresis problem. It is desirable that the hysteresis of OTFTs is as small as possible for organic circuit applications. Fig. 3 shows *C–V* hysteresis behavior of hybrimer gate insulator in MIS structure at 100 kHz is negligible. It is well known the hysteresis of OTFTs with polymeric gate insulator is caused by two mechanisms: (1) slow polarization of the dipolar groups or molecules such as hydroxyl groups in the gate insulator and/or (2) charge injection from gate, movement, and storage in gate insulator [21]. Thus, we conclude that the small hysteresis is attributed to the hydrophobic surface which prevents the water from penetrating into the gate insulator [22], the low contents of hydroxyl groups which act as electron traps in the gate insulators, and low leakage current density of hybrimer gate insulator.

RR-P3HT based OTFTs with the bottom contact geometry were fabricated to investigate the performance of the OTFTs with either the hybrimer gate insulators or HMDS-treated thermally grown $SiO_2$. Fig. 4 shows the transfer characteristics of the OTFTs with the hybrimer gate insulator and the HMDS-treated thermally grown $SiO_2$. The electrical performance parameters are summarized in Table 1. The carrier mobility was determined from a plot of $(-I_D)^{1/2}$ vs. $V_G$ on the basis of the following relationship in the saturation regime:

$$I_D = \frac{WC_i}{2L}\mu(V_G - V_{th})^2 \qquad (1)$$

where $I_D$ is the drain current, $W$ and $L$ are the channel width and length, respectively, $\mu$ is the field-effect mobility, $C_i$ is the capacitance per unit area, and $V_{th}$ is the threshold voltage. The saturation regime mobility was determined at drain–source voltage ($V_D$) of −40 V. The measured capacitance of the hybrimer gate insulator and $SiO_2$ was 7.2 nF/cm$^2$ and 10 nF/cm$^2$ at 100 kHz, respectively. The subthreshold slope, S, is defined as the voltage required to increase the drain current by a factor of 10. Since the surface properties of hybrimer gate insulators are analogous to that of HMDS-treated $SiO_2$ such as the hydrophobicity and surface roughness, the

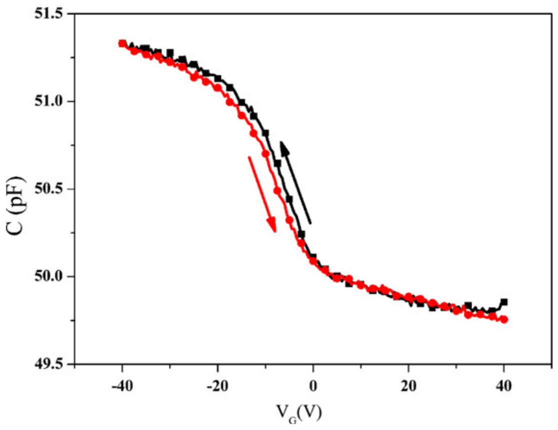

Fig. 3. *C–V* hysteresis behavior of hybrimer gate insulator in MIS structure. RR-P3HT was drop cast on the hybrimer gate insulator.

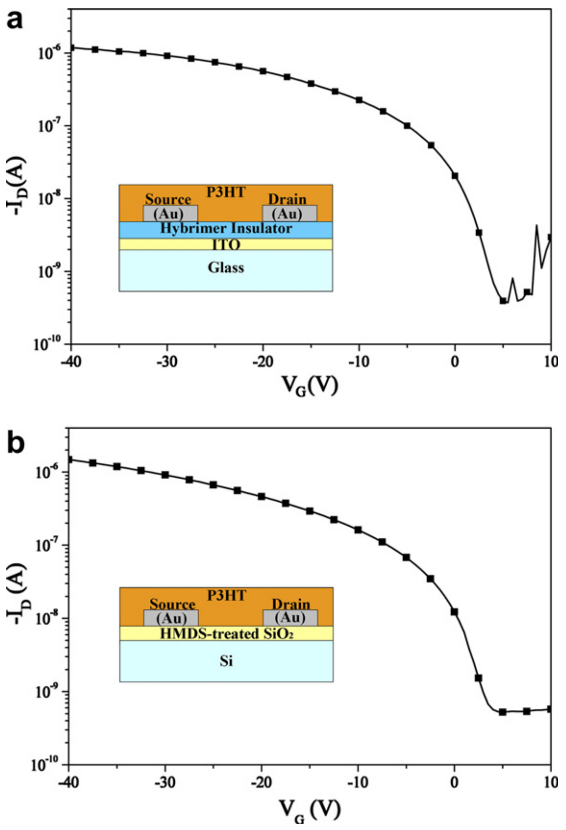

Fig. 4. Transfer characteristics of RR-P3HT based OTFT (a) with hybrimer gate insulator and (b) with HMDS-treated $SiO_2$ gate insulator. Inset: the schematic transistor structure with different gate insulators.

Table 1
Electrical performance of OTFTs with the hybrimer gate insulator and HMDS-treated thermally grown $SiO_2$

| Insulators | μ (cm$^2$/V s) | $V_{th}$ (V) | S (V/dec.) | On/off ratio |
|---|---|---|---|---|
| Hybrimer gate insulator | $4.6 \times 10^{-3}$ | 5.0 | 2.3 | $3.2 \times 10^3$ |
| HMDS-treated thermally grown $SiO_2$ | $2.8 \times 10^{-3}$ | 4.6 | 2.4 | $2.8 \times 10^3$ |

OTFT with hybrimer gate insulator shows similar electrical performance to that of the OTFT with HMDS-treated thermally grown $SiO_2$.

## 4. Conclusion

We synthesized the hybrimers using a non-hydrolytic sol–gel reaction of MPTMS and DPSD and characterized the electrical and surface properties of hybrimer thin film for the low temperature and solution-processable gate insulator in OTFTs. The hybrimer thin film had a low dielectric constant of 3.1 at 100 kHz, low leakage current density of 4.1 nA/cm$^2$ at 1 MV/cm, high dielectric strength of 5 MV/cm, a smooth and hydrophobic surface, and chemical stability against the solvent for dissolving RR-P3HT. The *C–V* hysteresis of MIS capacitor with hybrimer gate insulator is negligible due to the hydrophobic surface, the low contents of hydroxyl groups, and low leakage current density of hybrimer gate insulator. The performance of the OTFT with hybrimer gate insulator was similar to that of OTFT with HMDS treated $SiO_2$.

## Acknowledgement

This work was financially supported by the Basic Research Program (Grant No. R01-2003-000-10125-0) of the Korea Science and Engineering Foundation (KOSEF). Byeong-Soo Bae acknowledges the financial support of the LG Yonam Foundation for his visit to Flexible Display Center at Arizona State University.

## References

[1] G.H. Gelink, H.E. Huitema, E. van Veenendaal, E. Cantatore, L. Schrijnemakers, J.B.P.H. Van Der Putten, T.C.T. Geuns, M. Beenhakkers, J.B. Giesbers, B.-H. Huisman, E.J. Meijer, E.M. Benito, F.J. Touwslager, A.W. Marsman, B.J.E. Van Rens, D.M. de Leeuw, Nat. Mater. 3 (2004) 106.

[2] C.D. Sheraw, L. Zhou, J.R. Huang, D.J. Gundlach, T.N. Jackson, M.G. Kane, I.G. Hill, M.S. Hammond, J. Campi, B.K. Greening, J. Francl, J. West, Appl. Phys. Lett. 80 (2002) 1088.

[3] Z.-T. Zhu, J.T. Mason, R. Dieckmann, G.G. Malliaras, Appl. Phys. Lett. 81 (2002) 4643.

[4] P.F. Baude, D.A. Ender, M.A. Haase, T.W. Kelley, D.V. Muyres, S.D. Theiss, Appl. Phys. Lett. 82 (2003) 3964.

[5] G. Wang, D. Moses, A.J. Heeger, H.-M. Zhang, M. Narasimhan, R.E. Demaray, J. Appl. Phys. 95 (2004) 316.

[6] A. Facchetti, M.-H. Yoon, T.J. Marks, Adv. Mater. 17 (2005) 1705.

[7] J. Veres, S. Ogier, G. Lloyd, D.D. Leeuw, Chem. Mater. 16 (2004) 4543.

[8] (a) E.S. Kang, T.H. Lee, B.S. Bae, Appl. Phys. Lett. 81 (2002) 1438;
(b) O.H. Park, S.Y. Seo, J.H. Shin, B.S. Bae, Appl. Phys. Lett. 82 (2003) 2787;
(c) W.S. Kim, K.S. Kim, Y.J. Eo, K.B. Yoon, B.S. Bae, J. Mater. Chem. 15 (2005) 465;
(d) D.J. Kang, W.S. Kim, B.S. Bae, Appl. Phys. Lett. 87 (2005) 21106;
(e) D.J. Kang, J.K. Kim, B.S. Bae, Optics Express 12 (2004) 3947.

[9] R. Buestrich, F. Kahlenberg, M. Popall, P. Dannberg, R. Müller-Fiedler, O. Rösch, J. Sol–Gel. Sci. Technol. 20 (2001) 181.

[10] (a) Y.J. Eo, T.H. Lee, S.Y. Kim, J.K. Kang, Y.S. Han, B.S. Bae, J. Polym. Sci. Polym. Phys. 43 (2005) 827;
(b) Y.J. Eo, J.H. Kim, J.H. Ko, B.S. Bae, J. Mater. Res. 20 (2005) 401.

[11] Z. Bao, V. Kuck, J.A. Rogers, M.A. Paczkowski, Adv. Func. Mater. 12 (2002) 526.

[12] J.-F. Chang, B. Sun, D.W. Breiby, M.M. Nielsen, T.I. Sölling, M. Giles, I. McCulloch, H. Sirringhaus, Chem. Mater. 16 (2004) 4772.

[13] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, W. Weber, J. Appl. Phys. 92 (2002) 5259.

[14] S.W. Pyo, D.H. Lee, J.R. Koo, J.H. Kim, J.H. Shim, J.S. Kim, Y.K. Kim, Synth. Met. 154 (2005) 141.

[15] J. Park, S.Y. Park, S.-O. Shim, H. Kang, H.H. Lee, Appl. Phys. Lett. 85 (2004) 3283.

[16] L.L. Chua, P.K.H. Ho, H. Sirringhaus, R.H. Friend, Adv. Mater. 16 (2004) 1609.

[17] S. Jeong, D. Kim, S. Lee, B.-K. Park, J. Moon, Appl. Phys. Lett. 89 (2006) 092101.

[18] S. Steudel, S.D. Vusser, S.D. Jonge, D. Janssen, S. Verlaak, J. Genoe, P. Heremans, Appl. Phys. Lett. 85 (2004) 4440.

[19] G. Wantz, L. Hirsch, N. Huby, L. Vignau, J.F. Silvain, A.S. Barriere, J.P. Parneix, Thin Solid Films 485 (2005) 247.

[20] C.S. Kim, S.J. Jo, J.B. Kim, S.Y. Ryu, J.H. Noh, H.K. Baik, S.J. Lee, K.M. Song, Semicond. Sci. Technol. 22 (2007) 691.

[21] G. Gu, M.G. Kane, Proc. SPIE 6336 (2006) 63360H.

[22] T. Jung, A. Dodabalapur, R. Wenz, S. Mohapatra, Appl. Phys. Lett. 87 (2005) 182109.