Synthesis of Fluorinated Polymer Gate Dielectric with Improved Wetting Property and Its Application to Organic Field-Effect Transistors

Jaewook Kim and Hee-Tae Jung

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

Sunyoung Ha and Mihye Yi

Information and Electronics Polymer Research Center, Korea Research Institute of Chemical Technology, Daejeon 305-610, Korea

Jae-eun Park, Hyojoong Kim, Youngill Choi, and Seungmoon Pyo*

Department of Chemistry, Konkuk University, Seoul 143-701, Korea

Abstract: We report the fabrication of pentacene organic field-effect transistors (OFETs) using a fluorinated sty-rene-*alt*-maleic anhydride copolymer gate dielectric, which was prepared from styrene derivatives with a fluorinated side chain [$-CH_2-O-(CH_2)_2-(CF_2)_5CF_3$] and maleic anhydride through a solution polymerization technique. The fluorinated side chain was used to impart hydrophobicity to the surface of the gate dielectric and maleic anhydride was employed to improve its wetting properties. A field-effect mobility of 0.12 cm^2/Vs was obtained from the as-prepared top-contact pentacene FETs. Since various functional groups can be introduced into the copolymer due to the nature of maleic anhydride, its physical properties can be manipulated easily. Using this type of copolymer, the performance of organic FETs can be enhanced through optimization of the interfacial properties between the gate dielectric and organic semiconductor.

Keywords: gate dielectric, organic field-effect transistor, fluorinated polymer.

Introduction

Over the past two decades organic materials have attracted remarkable attention as an active material for electronic applications due to their simple processability and flexible controllability of physical and chemical properties. In particular, remarkable achievement in the development of organic field-effect transistors (OFETs) has been made for the low-cost, light-weight and flexible organic electronics.[1-6] The performance of OFETs has been improved dramatically through intensive and focused research effort, and already reached the level of conventional hydrogenated amorphous silicon transistors.[4,7] Considering that charge transport occurs within a few monolayer of organic semiconductor, surface properties of gate dielectric could affect the growth mechanism of organic semiconductor and performance of OFETs.

Early work for OFETs employed Si/SiO_2 system as a substrate and gate dielectric. The surface of SiO_2 gate dielectric consists of hydroxyl groups[8,9] rendering the surface hydrophilic. Later Lin *et al.* reported OFETs with much improved performance by using modified SiO_2 treated by a self-assembling agent.[10] Since then, many research revealed that the performance of OFETs could be enhanced by modifying the surface of the SiO_2 with a hydrophobic primer, such as *n*-octadecyltrichlorosilane (OTS)[11,14-21] and hexamethyldisi-lazane (HMDS).[11-13,19] Compared with the extensive research on the surface modification of SiO_2, less work has been reported on the surface modification of polymeric gate dielectrics such as poly(vinylphenol),[22,23] poly(methylmethacrylate),[24] poly(vinylalcohol),[25] polyimide[26,27] and benzocyclobutene.[28] Unlike Si/SiO_2 system, polymeric gate dielectrics might not be treated by a primer because they usually do not have reaction site over their surface. Therefore, multi-layer approach was proposed to control the surface properties of the polymeric gate dielectric although some problems such as swelling and washing of the first layer can be generated.

Considering that well-defined control of the interface between gate dielectric and organic semiconductor is one of the key issues for the high performance OFETs, it is neces-

*Corresponding Author. E-mail: pyosm@konkuk.ac.kr

sary to develop a method to control the surface properties of the gate dielectric without using multi-layer approach. Recently, we have reported polyimide gate dielectrics with well-defined surface properties by introducing a long alkyl (C_{18}) side group to a polyimide main chain through a copolymerization and hybridization method. It was found that the performance of OFETs was enhanced dramatically due to the relatively hydrophobic long alkyl (C_{18}) side group.[26,27] Fluorinated polymers would be expected to serve as a good gate dielectric because they showed many advantages such as a good electrical and thermal properties and low surface energy.[29,30] However, their wettability on flexible and glass substrates is not good enough for the formation of a few hundreds of nanometer thick layer. In this manuscript, we report a fluorinated copolymer gate dielectric prepared from styrene derivatives with a fluorinated side chain [-CH_2-O-(CH_2)$_2$-(CF_2)$_5CF_3$] and maleic anhydride. The long fluorinated side chain moiety was introduced to impart hydrophobicity to the copolymer gate dielectric, and the maleic anhydride was employed as co-monomer to improve wetting properties. Additionally, we fabricated pentacene OFETs using the fluorinated copolymer as a gate dielectric and investigated their electrical characteristics.

Experimental

Chemicals. All the chemicals used for the synthesis and purification of monomer and copolymer were purchased from Aldrich Chemical Co. Maleic anhydride was recrysal-lized from methanol prior to use. The initiator, 2,2-azobis-isobutyronitrile (AIBN), was recrystallized from chloroform and dried in a vacuum desiccator for 24 h and stored in the refrigerator. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-octanol [$CF_3(CF_2)_5CH_2CH_2OH$], tetrabutylammonium hydrogensul-fate (TBAHS) and pentacene (98% purity) were used as received. Fluorinated styrene monomer and fluorinated sty-rene-*alt*-maleic anhydride copolymer were synthesized for this study.

Synthesis of Fluorinated Styrene Monomer (1). A solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (2.5×10^{-2} mol), TBAHS (2.5×10^{-2} mol) and an aqueous solution of 6 N NaOH was stirred at 50 °C under N_2 for 10 min. p-Vinyl-benzylchloride (p-VBC) (2.5×10^{-2} mol) was added to the solution and stirred for additional 6 h. When reaction was completed, 20 mL of CH_2Cl_2 and 20 mL of H_2O were added to the solution and the organic layer washed several times with an aqueous solution of 0.1 N HCl. The organic layer was dried over $MgSO_4$ and filtered. Solvent was removed by a rotary evaporator to give a final product (1). The product (1) was purified by column chromatography using ethylacetate/hexane (10/90 v/v) as an eluent. ^{1}H NMR (δ, CDCl$_3$), 7.28 (d, 2H, Ar*H*), 7.17 (d, 2H, Ar*H*), 6.5 (dd, 1H, CH$_2$=C*H*-Ar-), 5.64 (d, 1H, C*H$_2$*=CH-Ar-), 5.13 (d, 1H, C*H$_2$*=CH-Ar-), 4.4 (s, 2H, -Ar-C*H$_2$*-O-), 3.6 (t, 2H, -Ar-CH$_2$-O-C*H$_2$*-), 2.4-2.2
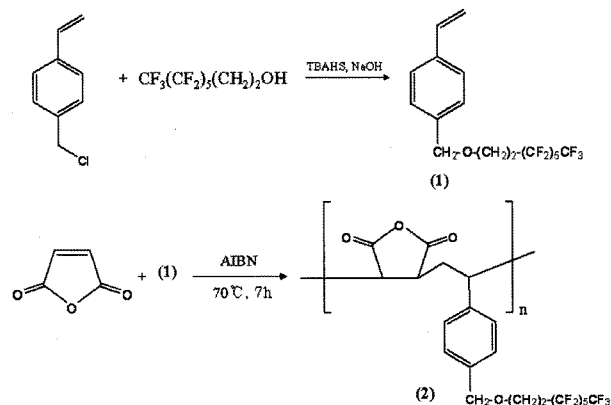

Figure 1. The reaction scheme for the preparation of fluorinated styrene monomer (1) and copolymer gate dielectric, fluorinated styrene-*alt*-maleic anhydride copolymer (2). The copolymer (2) was prepared by a solution copolymerization.

(m, 2H, -O-CH$_2$-C*H$_2$*-C$_6$F$_{13}$).

Preparation of Copolymer Gate Dielectric (2). Fluorinated styrene-*alt*-maleic anhydride copolymer was prepared by a solution copolymerization. Maleic anhydride (0.03 mol) was dissolved in 100 mL of methylethylketone in a 250 mL 3-neck-round-bottom flask fitted with a condenser. The synthesized fluorinated styrene monomer (1) (M.W. 480 g/mol) (0.03 mol) and AIBN (1.5×10^{-4} mol) was added to the solution which was deoxygenated with nitrogen. The mixture was heated up to 70 °C and stirred for 7 h. The mixture was poured to 500 mL of diethyl ether and the precipitate was washed with diethyl ether several times. The final product (2) was gathered and dried in a vacuum oven for 24 h. Figure 1 shows reaction scheme for the preparation of fluorinated styrene monomer (1) and copolymer gate dielectric (2).

Device Fabrication. The geometry of OTFTs for all electrical characterizations was top-contact. Figure 2 shows the schematic diagram for the structure of top-contact OFET with the chemical structure of pentacene and the copolymer gate dielectric. Indium tin oxide (ITO) on a glass substrate was patterned by a conventional lithographic method for a
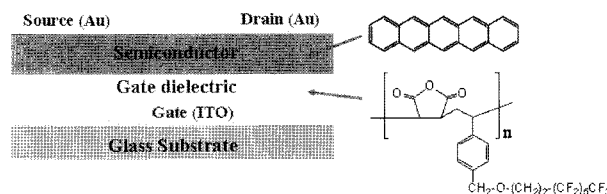
Figure 2. Schematic device structure of pentacene field-effect transistors (FETs) with the copolymer (2) gate dielectric fabricated on the cleaned ITO/Glass substrate. The final thickness of the pentacene and the copolymer (2) was about 60 and 300 nm, respectively. The 50 nm-thick gold film were deposited as the source and drain electrodes (L=50 μm, W=1,000 μm).

gate electrode, and cleaned using the general cleaning process for electronic applications; sonication in detergent, deionized water, acetone and isopropanol in that order for 20 min at room temperature. The copolymer gate dielectric solution in methylethylketone was spin-coated on top of the gate electrodes and dried at 120, 150 and 180 °C for 2 h. The final thickness of the gate dielectric was controlled to about 300 nm. A 60 nm-thick pentacene layer was deposited on top of the gate dielectric through a shadow mask by a thermal evaporation at a pressure of 1×10^{-6} torr. The evaporation rate and substrate temperature were 1 Å/s and 90 °C, respectively. OFETs were then completed by thermally evaporating 50 nm thick source and drain gold electrodes through a shadow mask with channel length (L) of 50 μm and width (W) of 1,000 μm. Metal-Insulator-Metal (MIM) devices were prepared for capacitance measurement of the copolymer gate dielectric. Bottom gold electrode was formed by a thermal evaporation though a shadow mask on the pre-cleaned glass substrate. The copolymer solution was spin-coated on top of the bottom electrode and dried at 90, 120 and 180 °C for 2 h. MIM devices were completed by evaporating top gold electrode with right angle to the bottom electrode. The final thickness of the copolymer film was controlled to 300 nm. The active area of the MIM device was 63 mm².

Characterizations. The thickness of the polymer films was determined using alpha-step (KLA-Tencor α-step DC 50) surface profiler. The output (I_{ds} vs V_{ds}) and transfer (I_{ds} vs V_{gs}) characteristic curves of OFETs were recoreded using an Agilent E5272 semiconductor parameter analyzer. The capacitance of the copolymer gate dielectric was measured with an HP 4294A LCR meter. Surface tension was calculated from a contact angle of water and diiodomethane on the copolymer gate dielectric using PHONIX 300 contact angle analyzer. All electrical measurements of the devices were carried out in air without any encapsulation.

Results and Discussion

The fluorinated styrene monomer (**1**) was successfully synthesized from the reaction of p-VBC with 3,3,4,4,5,5, 6,6,7,7,8,8-tridecafluoro-1-octanol. ^{1}H NMR spectrum for fluorinated styrene monomer (1) is shown in Figure 3. Fluorinated styrene-alt-maleic anhydride copolymer (2) was prepared by a solution copolymerization. The copolymerization of styrene and maleic anhydride has long been regarded as a classical example of an alternating radical copolymer system.[31-34] The alternating tendency in copolymerization has been explained by the participation of a 1:1 charge-transfer complex of styrene and maleic anhydride in the propagation step.[35,36] This is due to the fact that maleic anhydride does not homopolymerize under normal conditions and styrene forms a donor-acceptor complex with anhydride.

The molecular weight of the copolymer was determined by a gel permeation chromatography (GPC). Number average molecular weight ($\overline{M_n}$) and weight average molecular weight ($\overline{M_w}$) were 16,800 g/mol and 47,600 g/mol, respectively. Polydispersity index defined by $\overline{M_n}/\overline{M_w}$ was 2.8. The measured surface tension of the copolymer gate dielectric calculated from the contact angle of water (70°) and diiodomethane (60°) was 37 dyne/cm. For comparison, we measured the surface tension of two popular polymer gate dielectrics, polyvinylphenol (PVP) and cross-linked PVP. The surface tension of the PVP and cross-linked PVP is 39.2 dyne/cm and 39.8 dyne/cm, respectively. Although maleic anhydride, hydrophilic moiety, is used as a comonomer for the preparation of copolymer (2), its surface tension is still hydrophobic compared with that of PVP and cross-linked PVP. This indicates that the introduced fluorinated alkyl chain plays a major role in making the surface of the copolymer gate dielectric (2) hydrophobic. In case of amorphous fluoropolymer, Cytop™ (Asahi Glass), which is highly transparent fluoropolymer used as a gate dielectric for OFETs
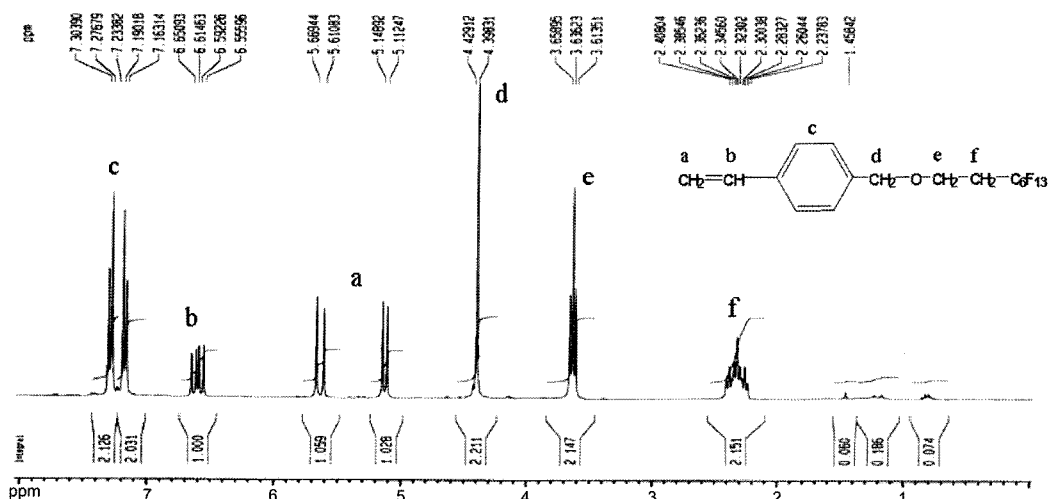
Figure 3. Nuclear magnetic resonance (^{1}H NMR) spectrum of fluorinated styrene monomer (1).

due to its excellent resistance to chemical attack and swelling by common organic solvents[29,30] the use of a specially designed solvent (such as CTX-809L, CT-Solv. 180) from a commercial company is required to make a uniform thin-film on a substrate. In addition, the surface of Cytop™ is highly hydrophobic, which make it difficult to completely wet its surface with solution processable organic semiconductor for the fabrication of OFETs. On the other hand, we could get high quality uniform thin films easily on the cleaned ITO/glass from the copolymer gate dielectric solution even though fluorinated alkyl chain was incorporated, indicating that the wetting property of the copolymer was improved by the introduced maleic anhydride moiety.

The measured capacitance and dielectric constant cured at 180 °C for 2 h were obtained from metal-insulator-metal (MIM) type device and they were 76.8 pF/mm^2 and 2.6, respectively. The low dielectric constant is due to the fluorinated long alkyl chain. This value is comparable to that (44~27 pF/mm^2 and 2.1~2.2, respectively) of Cytop™. We fabricated three kinds of top-contact pentacene OFETs with the copolymer gate dielectric cured at 90, 120, 180 °C for 2 h. The best performance was extracted from OFETs with copolymers cured at 180 °C for 2 h. The performance of OFETs with the copolymer cured at 90 and 120 °C was found to be bad. In particular, the leakage current of the OFETs was so high around 10^{-7}~10^{-8} A. We believe that this is due to the residual solvent inside the copolymer gate dielectric. The output characteristic (for drain current vs drain voltage, I_{ds} vs V_{ds}) curves of the pentacene OFETs (length, L=50 μm and width, W=1,000 μm) with the copolymer cured at 180 °C for 2 h at various gate voltages were shown in Figure 4(a). The OFETs showed typical p-type characteristics with a clear transition from linear to saturation behavior. At a given negative gate voltage (V_{gs}), I_{ds} initially increased linearly with small negative V_{ds} and then saturates due to a pinch-off of the accumulation layer.

Figure 4(b) showed the transfer characteristics (for drain current vs gate voltage, I_{ds} vs V_{gs}) of the OFETs with the copolymer gate dielectric, where V_{gs} was swept from +20 to

-50 V and V_{ds} was set at -40 V. The field effect carrier mobility (μ) was extracted from the plot of $\sqrt{I_{ds}}$ versus V_{gs} in a saturation regime based on the following equation.

$$I_{ds} = \frac{WC_i}{2L}\mu(V_{gs}-V_T)^2 \tag{1}$$

where, I_{ds} is the drain current, W and L are, respectively, the channel width and length, C_i is the capacitance per unit area of the gate insulator layer, and V_{gs} and V_T are the gate voltage and the threshold voltage, respectively. V_T of the device in the saturation regime was determined from the plot of the square root of the drain current ($\sqrt{I_{ds}}$) and the gate voltage (V_{gs}) by extrapolating the measured data to I_{ds}=0. The inverse subthreshold swing (ss), which is a measure of how sharply the device transits from the off to the on state, is given by ss = $[d \log(I_{ds})/dV_{gs}]^{-1}$. The μ and V_T of OFETs with the copolymer was 0.12 cm^2/Vs and -7.7 V, respectively. The value of s.s. and current modulation ratio (I_{ON}/I_{OFF}) was 6.7 V/dec and 6.8×10^3, respectively. The I_{ON}/I_{OFF} value is relatively low. We think that the value can be increased by the optimization of processing condition of the copolymer gate dielectric and the interface between the copolymer and pentacene through the modification of the fluorinated polymer. The μ of the OFETs with the copolymer gate dielectric was comparable to that (0.26 cm^2/Vs) of OFETs with Cytop™.[30]

Conclusions

A fluorinated styrene-alt-maleic anhydride copolymer gate dielectric was synthesized through a solution copolymerization for the fabrication of OFETs. For the preparation of the copolymer, fluorinated styrene was synthesized from the reaction of p-VBC with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol. The copolymer showed hydrophobic surface property due to the fluorinated side chain and it formed a uniform layer on ITO/galss substrate due to the maleic anhydride moiety. OFETs with the copolymer showed good electrical properties. The μ and V_T of pentacene OTFTs with the copolymer were 0.12 cm^2/Vs and -7.7 V, respectively.
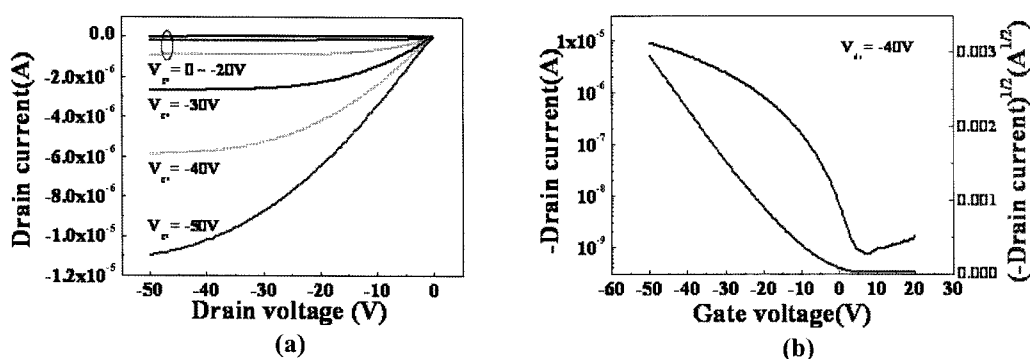
Figure 4. The output (a) and transfer (b) characteristic curves of pentacene OFETs with the copolymer gate dielectric. For transfer curves, V_{gs} was swept from +20 to -50 V and V_{ds} was set at -40 V.

The μ is comparable to that (0.26 cm²/Vs) of OFETs with Cytop™. The value of *s.s.* and current modulation ratio (I_{ON}/I_{OFF}) were 6.7 V/dec and 6.8×10^3, respectively. Since various functional group could be introduced to the copolymer main chain due to the reactive nature of maleic anhydride, we believe that the performance of OFETs can be enhanced by optimizing the interfacial properties between gate insulator and organic semiconductors.

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