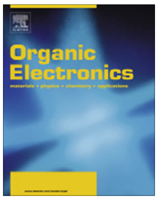
Organic Electronics 13 (2012) 1146–1151

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Forming semiconductor/dielectric double layers by one-step spin-coating for enhancing the performance of organic field-effect transistors

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ARTICLE INFO

Article history:
Received 1 December 2011
Accepted 13 March 2012
Available online 7 April 2012

Keywords:
Spin-coating
Small molecule semiconductor
Organic field-effect transistor
Performance enhancement
Interface modification
Crystal sizes

ABSTRACT

We report one-step formation of the gate dielectric and conduction channel for enhancing the performance of organic field effect transistors (OFETs). The resulting OFET with the semiconductor/dielectric bi-layers spun in ambient conditions exhibits μ_{FET} up to 1.6 $cm^2/V\,s$ and on–off ratio higher than 10^6, no additional treatment needed. Contact angle measurements and absorption spectra reveals that a well-defined semiconductor-top and dielectric-bottom film form after spin-coating the mixture of the two components, which is due to the surface induced self-organized phase separation. Compared to the single layer semiconductor film, the staggered film exhibits over 5 times higher mobility and nearly 90% reduced hysteresis in OFET. The higher performance is attributed to the simultaneous optimization in the dielectric interface and semiconductor crystallization. The approach is significant for the fabrication of low cost, easy processed and high performance OFETs.

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1. Introduction

Organic field effect transistors (OFETs) based on semiconducting small molecules have been intensively investigated [1]. Developing simple, reliable solution process to extract the intrinsic property of organic semiconducting molecules is one of the main goals. Generally, the semiconductor/dielectric interface are formed via successive deposition of films, e.g. by spin-coating, in solution processed OFETs [2]. This procedure yet may increase the risk of inducing impurities to the interface during the deposition of the second layer, especially when fabricated in air [3]. Hence forming the semiconductor/dielectric interface free of exposure to atmosphere would be beneficial for realizing reliable, high performance and simplifying the fabrication process.

At the meantime, the OFET fabrication also needs optimization in both the interfacial conditions and the semiconductor crystallinity, because few interfacial traps and crystal boundaries are considered to be crucial for high mobility charge transport [1]. The former is mostly achieved by growing self-assembly monolayers (SAMs) on the dielectric interface which block interfacial traps and lower polarity disorder [4], while the latter is usually controlled by post thermal or solvent annealing [5–7]. However, the use of SAMs may cause de-wetting in spin-coating [8], and shows limited impact on modifying the morphology of the spin-coated semiconducting layers [9]. Therefore simultaneous optimization of the dielectric interface and semiconductor crystallinity remains a challenge for solution processed OFETs.

Here we report the formation of the semiconductor and dielectric layers in one step spin-coating, with the dielectric interfacial conditions and semiconductor

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http://dx.doi.org/10.1016/j.orgel.2012.03.025

crystallinity simultaneously optimized. The semiconducting 2,7-didodecyl[1]benzothieno[3,2-b][1]benzothiophene (C12-BTBT) [10] and polymer dielectric poly(methyl methacrylate) (PMMA) self-organize into a staggering bi-layer structure after the spin-coating [11]. Compared to the as-spun C12-BTBT film on SiO_2, the OFETs with staggered film exhibit mobility more than 5 times higher and hysteresis nearly 90% reduced. With the film spun in ambient conditions, the FETs exhibit mobility up to 1.6 $cm^2/V\,s$ and on–off ratio higher than 10^6.

2. Experimental

2.1. Film fabrication and characterization

The semiconductor C12-BTBT was synthesized as described in [12]. The substrate Si/SiO_2 wafers were cleaned in an ultrasonic bath in a succession of acetone and isopropanol for 10 min each. For the single component film, the semiconductor C12-BTBT was dissolved in chloroform solution (0.4 wt.%) and spin-coated on Si/SiO_2 substrates (500 rpm for 5 s, 2000 rpm for 40 s). For the mixture film, C12-BTBT and PMMA (Fluka, Mw = 100 k) were mixed in the mass ratio of 1:1 and dissolved in chlorobenzene solvent (1.2 wt.% in total). Then the solution was spin-coated onto the substrates (500 rpm for 5 s, 2000 rpm for 40 s). The above procedures were all processed in ambient conditions.

The optical images of film were captured by using the microscope Nikon Eclipse LV100POL, with or without polarizer as described. The thicknesses of the films were measured by the surface profiler (Model P-16, KLA Tensor). The water contact angles of selected surfaces were measured by the contact angle goniometer (Imoto Corporation) with de-ionized water as the sessile drop. UV–Vis absorption spectra were measured from the film on glass substrates by the UV/Vis/NIR spectrophotometer JASCO V-570. The absorptions of glass substrate were deduced from the film signals.

2.2. Transistor fabrication and characterization

Highly doped n-type (100) silicon wafers with 50 nm SiO_2 layers were cleaned as described above. Films were deposited as stated above without any post annealing, followed by thermal evaporation of selected materials through shadow masks in vacuum ($<3 \times 10^{-4}$ Pa). For gold only contact, Au was evaporated in the rate of 0.1 Å/s and the final thickness is 40 nm. For contact doping, firstly $FeCl_3$ was evaporated in the rate of 0.1 Å/s to for 1 nm thick film and secondly Au was evaporated as stated above. Channel width (W) and channel length (L) of the device are 1200 μm and 300 μm, respectively. Then the FETs were measured under vacuum ($<4 \times 10^{-3}$ Pa) using an Agilent 4156C semiconductor parameter analyzer. The saturation mobility of OFET, μ_{FET}, and threshold voltage, V_{th}, are extracted from saturation regime in the transfer characteristics by fitting $-I_d = [W/(2L) \times C_i \times \mu_{FET}] \times (V_g - V_{th})^2$, where I_d is drain current, C_i is capacitance per unit area, V_g is gate voltage, and V_{th} is threshold voltage.

3. Results and discussions

3.1. Forming semiconductor and dielectric layers in one-step spin-coating

The C12-BTBT film spun from chloroform onto bare SiO_2 exhibit relatively low mobility in OFET with Au contact ($\mu_{FET} \sim 0.1$ $cm^2/V\,s$, data shown in the next section). Yet the μ_{FET} of vacuum deposited C12-BTBT film reaches 3.9 $cm^2/V\,s$ on the octadecyltrichlorosilane (ODTS) SAM layer [10], and has a theoretical limit of 40∼50 $cm^2/V\,s$ in the single crystalline state [13], implying possibility for further enhancement for the spin-coated film. However, spin-coating C12-BTBT onto the SiO_2 treated by hydrophobic hexamethyldisilazane (HMDS) causes severe de-wetting, not able to form a continuous film larger than 0.5 cm^2. Such de-wetting also happens when spin-coating onto bare SiO_2 in high boiling point solvent (e.g. chlorobenzene). Instead we adapt the polymer dielectric PMMA as the charge transport interface. To form the layers of C12-BTBT and PMMA in one step, we investigated the potential of self-organized phase separation method, i.e. the two solutes automatically separate and form bi-layer structure in spin-coating [11].

The mixture of C12-BTBT and PMMA in the chlorobenzene solvent was spin-coated onto the Si/SiO_2 substrates. The two components in the film are possibly evenly distributed in each other or phase separated, either laterally to form isolated domains or vertically to form staggered continuous layers [7]. We used orthogonal solvent to selectively dissolve the component and reveal the film structure. Firstly, the substrate was vertically held and partially immersed into acetone, which dissolve both C12-BTBT and PMMA, followed by drying with nitrogen air flow. This step exposed the SiO_2 surface (Fig. 1a, region I). Secondly, the substrate was partially immersed into cyclohexane, which dissolve C12-BTBT moderately (∼2 mg/ml) but not PMMA, and dried. This step forms the region II in Fig. 1a, next to which is the surface of the pristine film (region III). Under the cross-polarized microscope, the region II is totally dark and thus amorphous, while the region III exhibits strong birefringence and thus is crystalline (Fig. 1a, with polarizer). Surface profile scanning across the regional edges clearly reveals two staggering layers (Fig. 1b), each about 20∼40 nm thick. According to the solubility, the bottom layer is presumed to be PMMA and the top layer is presumed to be C12-BTBT. Therefore we propose a process of self-organized phase separation as illustrated in Fig. 1c.

We further provide evidences to confirm the film structure by measuring water contact angles and absorption spectra of each region. As shown in Fig. 2, the water contact angle of the bottom layer (region II) resembles that of the as-spun PMMA film (∼68°), while the value measured on the top layer (region III) is almost the same with that on the as-spun C12-BTBT film (∼100°). In UV–Vis absorption spectra, the as-spun film of the C12-BTBT/PMMA mixture exhibits a strong absorption peak at

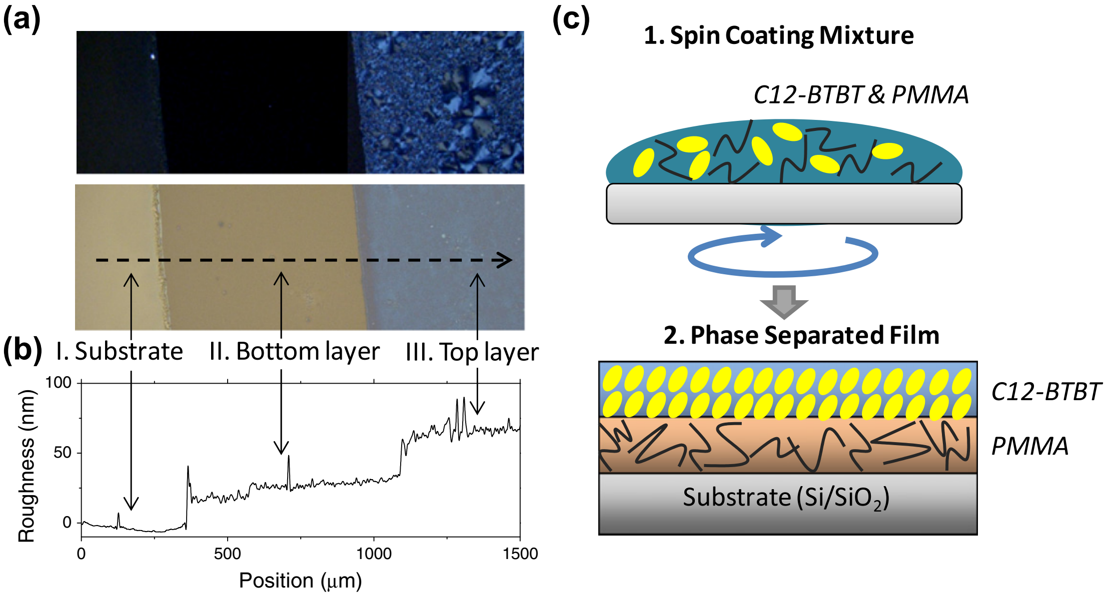

Fig. 1. (a) Microscope image of the self-organized phase separation film, with polarizer (up) and without polarizer (down). The film was partially cleaned by acetone (region I) and cyclohexane solvent (region II). The as-spun film surface is on the right (region III). (b) Roughness scans along the dash arrow in (a), indicating the self-organized bi-layer structure. (c) Scheme of the self-organized phase separation.

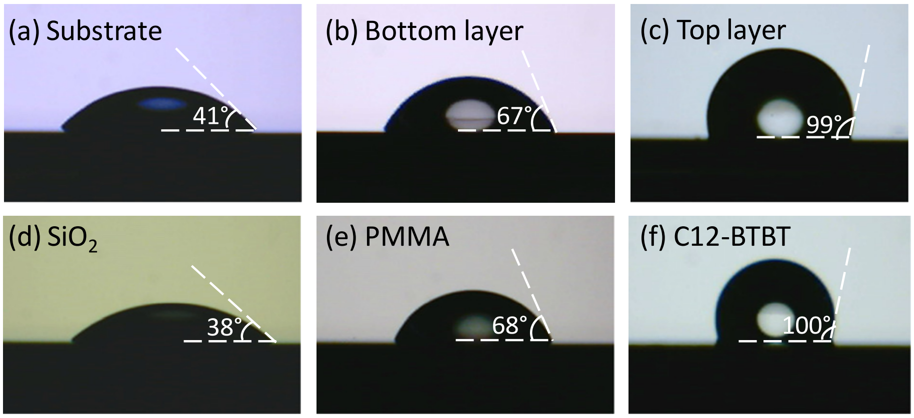

Fig. 2. Water contact angles of the film layer shown in Fig. 1b: (a) substrate, (b) bottom layer and (c) top layer. Water contact angles of single component film: (d) bare SiO_2, (e) as-spun PMMA film, and (f) as-spun C12-BTBT film. Measurement errors of the angles are 2°.

362 nm (Fig. 3, open squares), which is the main characteristic peak of C12-BTBT (Fig. 3, solid triangles). This peak disappears after the same sample was soaked into cyclohexane for 30 s to expose the whole, continuous bottom layer (Fig. 3, open triangles), indicating the absence of C12-BTBT in the bottom layer. The above characterizations confirm the process proposed in Fig. 1c, in which well-defined vertical segregation is formed after spin-coating, with the top-C12-BTBT and the bottom-PMMA.

The reason for forming such structure is attributed to either kinetics or energetic [14]. In the former case, as solvent evaporates, component with higher solubility will condense in the free surface and form a homogeneous layer on the top of the component with lower solubility [15]. Yet since in chlorobenzene PMMA is much more soluble (>30 mg/ml) than C12-BTBT (<10 mg/ml) but actually forms the bottom layer, this explanation is excluded. In the latter case, the component which has a lower energy to coat the substrate surface will wet the substrate and form the bottom layer [14]. This mechanism agrees well with our experimental results. According to Fig. 2, the surface energy of the film decreases in the sequence of SiO_2, PMMA and C12-BTBT. In fact, directly spin-coating C12-BTBT in chlorobenzene de-wets on the SiO_2 surface, whereas spin-coating PMMA solution completely wets the surface and forms a homogeneous film. Therefore when spin-coating the mixture, the less hydrophobic PMMA component is preferentially adsorbed onto the hydrophilic substrate SiO_2

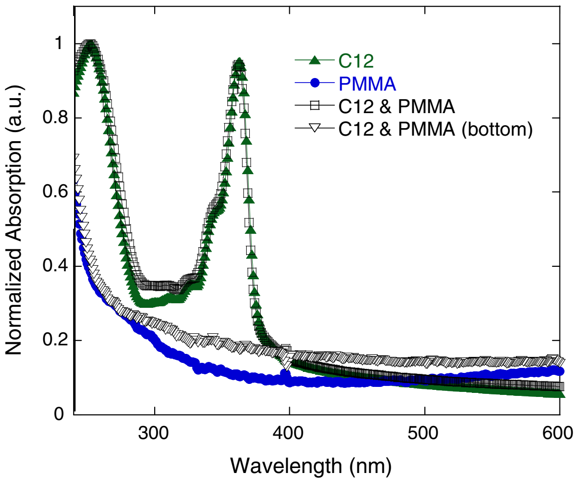

Fig. 3. UV–Vis absorption spectra of the films of: C12-BTBT (solid triangles), PMMA (solid circles), C12-BTBT and PMMA (open squares), and C12-BTBT and PMMA washed by cyclohexane (open triangles).

and form the bottom layer [16]. Whether the resulting semiconductor/dielectric interface is suitable for charge transport will be investigated in the next section.

3.2. Enhancement in the performance of OFET

The bottom-gate, top-contact FETs were fabricated by covering the film with Au source/drain contact as shown in Fig. 4a. The transfer characteristics measured at −40 V source/drain voltage (V_d) are illustrated in Fig. 4b. Although the PMMA layer decreases the total capacitance, the FET with self-organized film exhibits current level (61 μA at $V_g = -40$ V, Fig. 4, circles) over 5 times higher than that of the single layer film of C12-BTBT (12 μA at $V_g = -40$ V, Fig. 4b, squares). As the interface roughness strongly influences the field-effect mobility [17], these results indicate the abruptness and high quality of the interface between the top-C12-BTBT and the bottom-PMMA. The capacitance per unit area (C_i) of the self-organized film is 48 nF/cm^2, calculated from capacitance–voltage measurements, corresponding to an about 20 nm thick PMMA film on 50 nm thick SiO$_2$. The mobility in saturation regime (μ_{FET}) and threshold voltage (V_{th}) are 0.71 cm^2/V s and −9.8 V, respectively for the bi-layer device, whereas the single layer device exhibits μ_{FET} of 0.13 cm^2/V s and V_{th} of −9.4 V. More than 8 samples of each type are measured and the average values of the C12-BTBT/PMMA device are $\mu_{FET} = 0.63 \pm 0.18$cm^2/V s and $V_{th} = -9.1 \pm 1.5$ V, whereas the values of the C12-BTBT only devices are $\mu_{FET} = 0.11 \pm 0.02$ cm^2/V s and $V_{th} = -11.3 \pm 5.2$ V.

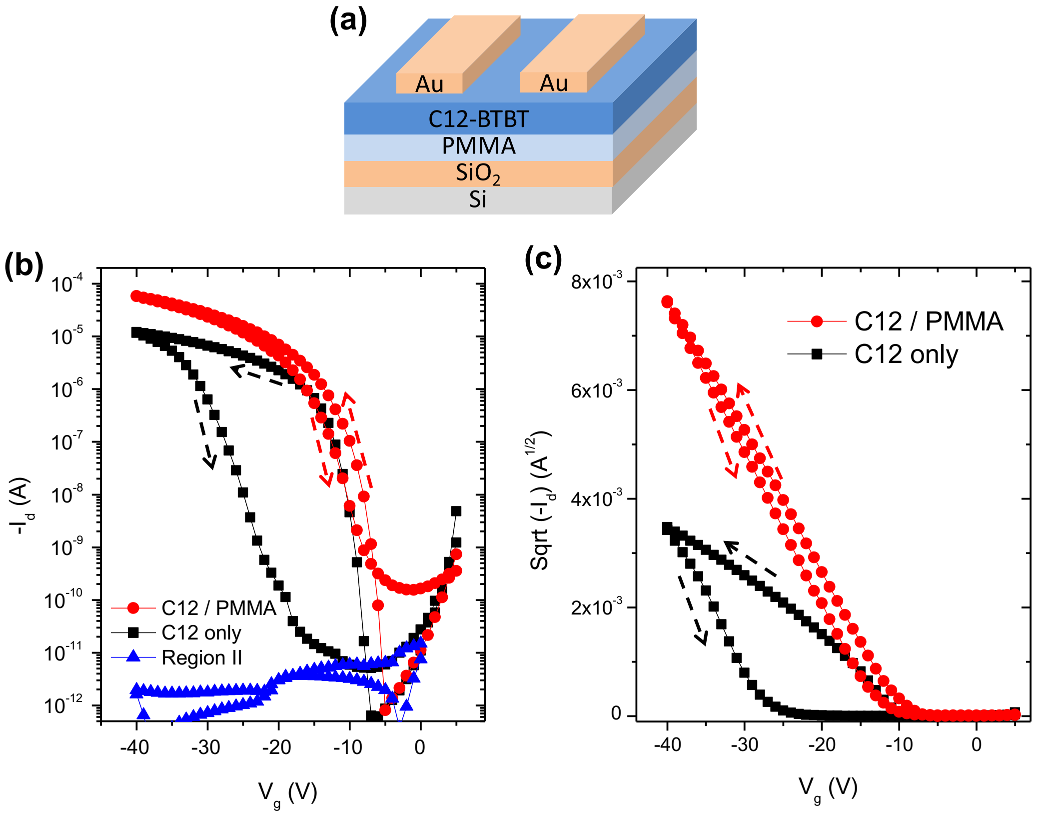

Fig. 4. (a) Device configuration. (b) Transfer characteristics of FETs made with C12-BTBT and PMMA (red curves) and C12-BTBT only film (black curves). The transistor in region II in Fig. 1b is shown for reference, indicating good insulating properties. (c) Square root of drain current of C12-BTBT and PMMA (red curves) and C12-BTBT only film (black curves). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

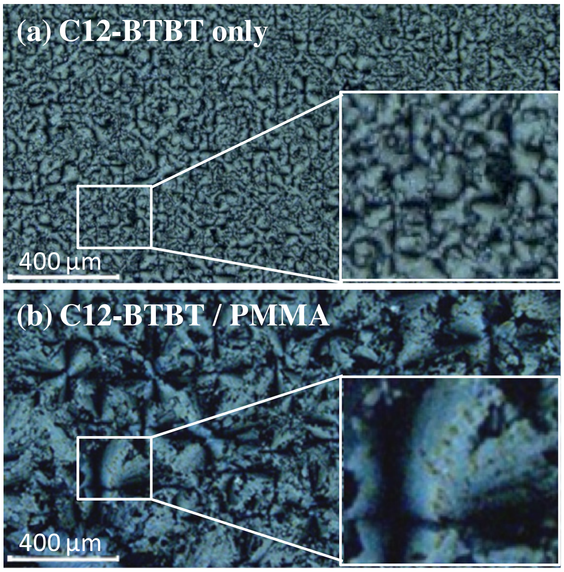

Fig. 5. Images of films spun from: (a) C12-BTBT in chloroform (b) and mixture of C12-BTBT and PMMA in chlorobenzene, taken from a cross-polarized microscope. The zoomed in images are shown as the inset.

The enhanced performance is most probably the result of reduction of traps in the dielectric interface [18]. This is supported by the analysis on the hysteresis behaviors. The self-organized phase separated film exhibits a much reduced hysteresis window (difference of V_{th} between the forward and backward scan), $\Delta V_{th} = -2.9$ V (Fig. 4b, circles), compared to $\Delta V_{th} = -17.4$ V in the single layer film (Fig. 4b, squares). Correspondingly, the density of the effective trapped charges is $N_Q = -C_i\,\Delta V_{th}/q = 8.8 \times 10^{11}$ cm^{-2} in phase separated film, 88% decreased compared to 7.5×10^{12} cm^{-2} of the single layer film on bare SiO_2 [19]. As the charge traps generally come from impurities or water contamination, this result indicates that using less polar dielectric and forming interface by one-step spin-coating instead of two successive steps, is much less susceptible to traps that are gradually filled in the gate field [2].

Besides the interface modification, the presented methods also affect the morphology of the semiconductors, which should also be taken into account to understand the enhanced performance [20]. According to the images of the film under the cross-polarized microscope, the sizes of crystals are several microns to tens of microns in the single layer film (Fig. 5a), while those of bi-layer film are about generally tens to hundreds of microns (Fig. 5b). The enhanced crystal sizes are mainly attributed to the elongated drying time in spin-coating when using the higher boiling point chlorobenzene (131 °C) as solvent instead of the lower boiling point chloroform (61 °C) [21]. Note that the solution of C12-BTBT in chlorobenzene

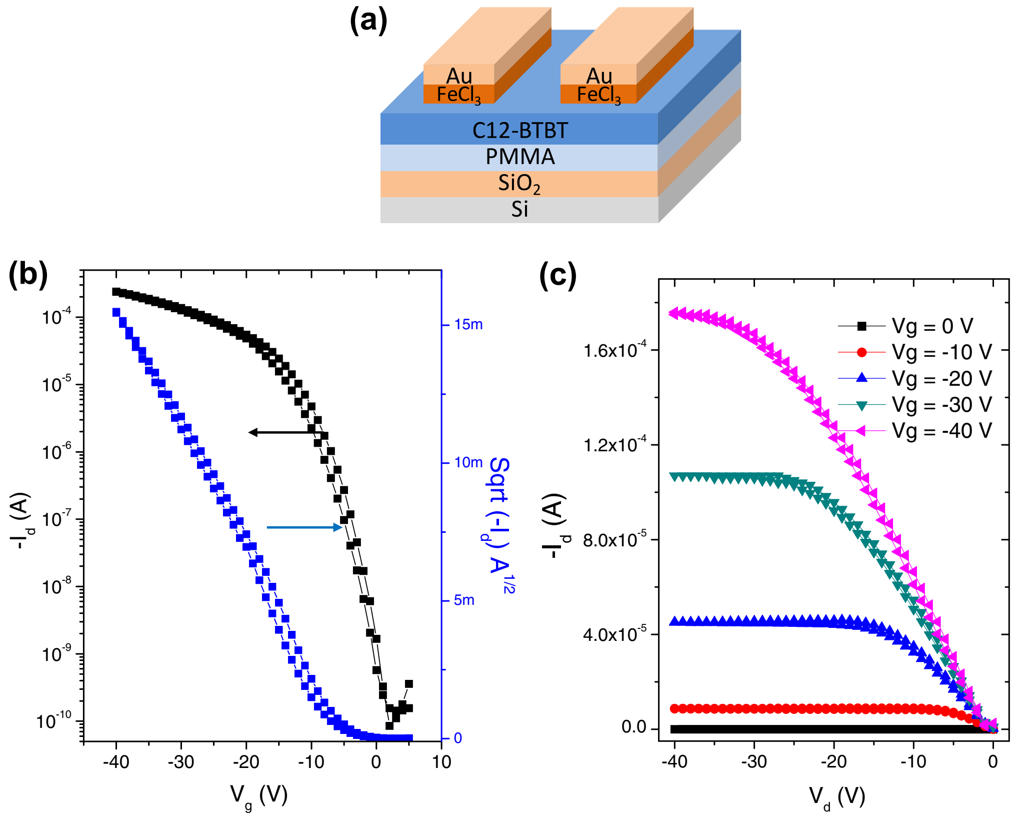

Fig. 6. (a) Device configuration of FETs with $FeCl_3$ doping the contact region. (b) Transfer characteristics (black squares) and square root of drain current (blue squares). (c) Output characteristics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

de-wets on SiO_2 and cannot form uniform film by spin-coating. Thus enabling usage of high boiling point solvent to allow better crystallization is also an important benefit of the presented method.

We note that the above OFETs have relatively large V_{th} (~ -9 V) and improve it with contact doping. A strong acceptor donating material, $FeCl_3$ [22], is used as the doping material to improve charge injection. Previous studies have shown that adding $FeCl_3$ into the semiconductor region-regular P3HT (rr-P3HT) leads to improvement in V_{th} and mobility, but suffers high current at $V_g = 0$ V [23]. Instead, we evaporate $FeCl_3$ onto C12-BTBT in the contact area only before gold deposition to avoid doping in the channel and increasing off-current. The performance of resulting transistor is shown in Fig. 6, in which V_{th} is shifted to -4.3 V and μ_{FET} is further enhanced to 1.6 cm^2/V s, compared to the value of -9.8 V and 0.71 cm^2/V s in device with gold contact. The results make the devices based on C12-BTBT more promising in the electronic application.

4. Conclusion

In summary, we present the large enhancement of performance OFETs with C12-BTBT by one-step formation of the semiconductor and dielectric layers. We used orthogonal solvent to selectively dissolve the component of the film and confirm that a vertical segregation is formed after spin-coating the mixture of C12-BTBT and PMMA. FETs based on these films exhibit strong gate-modulation, indicating the high quality of the interface for charge transport. The extracted field-effect mobility is more than 5 times higher than that of as-spun C12-BTBT film and the hysteresis is reduced by nearly 90%. The enhanced performance is mainly attributed to the PMMA-modified interface. The easy-processed approach allows large C12-BTBT film formation on hydrophobic dielectric, interface formation avoiding contamination, and usage of high-boiling point solvent for larger crystal sizes, all leading to the highly improved performance of OFETs. This method is compatible with traditional patterning techniques and significant for general fabrication of organic electronics by spin-coating.

Acknowledgment

This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology of Japan. It was also supported in part by a Grant for Advanced Industrial Technology Development (No. 11B11016d) from the New Energy and Industrial Technology Development Organization, Japan.

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