An organic thin-film transistor of high mobility by dielectric surface modification with organic molecule

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Organic thin-film transistors (OTFTs) based on pentacene semiconductor are elaborated on the plastic substrates through a four-level mask process without photolithographic patterning to yield a simple fabrication process. Octadecyltrimethoxysilane (OTMS) as an organic molecule for self-assembled monolayers is deposited on the surface of zirconium oxide dielectric layer. The effect of OTMS interlayer with gate dielectric surface modification on the field effect mobility of OTFTs has been examined and these prototype organic transistors showed excellent electrical characteristics with field effect mobility >0.66 cm^2/V s and $I_{on}/I_{off}>10.^5$ © *2004 American Institute of Physics*. [DOI: 10.1063/1.1841470]

Organic electronics based on the flexible transparent plastic substrates has recently attracted much attention because the glass and silicon wafer substrates which have been used conventionally as a supporting material do not exhibit any intrinsic flexibility.[1,2] Organic thin-film transistors (OTFTs) comprising flexible plastic substrates were reported to have such advantages in their electronic applications as simpler process, lower cost, and better flexibility over other conventional inorganic TFTs with great potential for foldable display applications.[3–6] The OTFTs also have substantial advantages over inorganic thin-film transistors with respect to processing cost, weight, and manipulation, but show comparatively lower electronic response time because of their low charge carrier mobility, which may typically be caused by interfaces with the substrate that are weakly bonded and poorly controlled.[7]

In this work, as an organic interlayer material for dielectric passivation of OTFT, octadecyltrimethoxysilane (OTMS) has been applied to improve the field effect mobility of OTFTs through the better quality of the organic active material/dielectric interface. The OTMS, which is well known as an important activator in the surface modification process, is one of the most widely used materials for the hydrophobic self-assembled monolayers (SAMs) containing alkyl silanes, resulting in the chemical bond formation by an intermolecular interaction between OTMS and zirconium oxide (ZrO_2).[8] We deposited the OTMS on a hydrophilic ZrO_2 surface so that the long alkyl tails form a tightly packed monolayer while the Si adheres to the surface of ZrO_2 through Si–O covalent bonds.[9,10]

In our process, a four-level mask process without any photolithography for the device patterning is employed to fabricate the flexible OTFTs with a self-aligned bottom-contact electrode structure on the plastic substrate. Pentacene ($C_{22}H_{14}$) composed of five benzene rings with a chain-like aromatic molecule was used for organic active layer.[11] At first, a flexible polyethersulfone (PES) substrate was preannealed for 1 h at 120 °C to minimize a shrinkage of polymer substrate during subsequent processing. A 200-nm-thick silicon dioxide (SiO_2) film for the adhesion layer is deposited on the bare plastic substrate by e-beam evaporator. Subsequently, the gold gate electrode was deposited. On the patterned gate electrode, a 250-nm-thick ZrO_2[12,13] for gate dielectric layer was deposited by the e-beam at relatively low temperature (<120 °C). Following the gate dielectric layer deposition, in order to have a good affinity of organic molecule on the surface of the dielectric layer, we modified the surface of ZrO_2 by using combinational SAMs of alkyl silanes. The SAMs deposition was performed by soaking a solution of OTMS/isopropanol (1:20/v:v) for 2–3 min under nitrogen atmosphere. For making the OTFTs of the bottom-contact structure, gold source and drain electrodes were deposited thermally through shadow-mask. Then, a 100-nm-thick pentacene film was evaporated through shadow-mask at average deposition rate of 0.5 Å/s at substrate temperature of 60 °C. For the evidence of the reaction of the OTMS with ZrO_2, we performed IR spectroscopy with the reaction mixture.

Figure 1(a) presents the structure of the bottom-contact electrode device fabricated for organic TFTs; Fig. 1(b) is the photograph of our completed device on the flexible substrate; Fig. 1(c) indicates the *C–V* characteristics of metal–insulator–semiconductor structure with a 250-nm-thick ZrO_2 film. The normalized value of the electrical capacitance was ranged to be within 1.00 (max) and 0.96 (min) when the voltage was applied from -10 to 10 V. The flatband voltage

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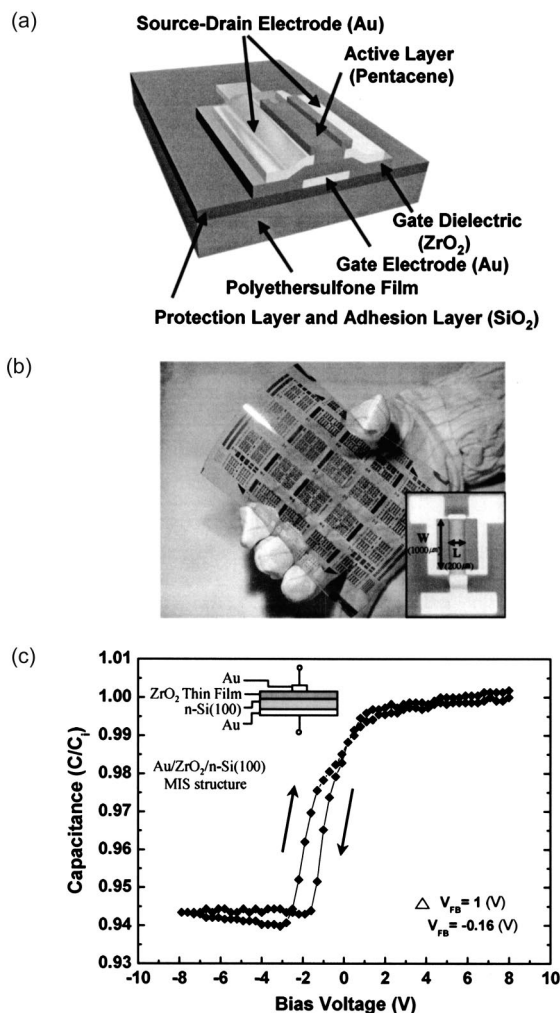
FIG. 1. (a) Schematic three-dimensional structure of the bottom-contact electrode device, (b) photograph of the pentacene TFTs on the flexible PES substrate ($W=1000$ μm, $L=200$ μm), and (c) high frequency (1 MHz) C–V characteristics of a 250-nm-thick ZrO_2 thin film deposited on n-type Si (100) substrate.

FIG. 2. (a) Electrical characteristics of drain current (I_D) vs drain voltage (V_D) at various gate voltages (V_G) obtained from the pentacene TFT prepared in the absence of OTMS treatment of the gate dielectrics. (b) Electrical characteristics of I_D vs V_G and field effect mobility at drain voltage (V_D) of 0.1 V obtained from the pentacene TFT prepared in the absence of OTMS treatment of the gate dielectrics.

of the ZrO_2 was found to be approximately -0.16 V in these characteristic curves.

Figure 2 shows electrical characteristics of the organic pentacene TFTs with a channel width of 1000 μm and length of 200 μm in the absence of the OTMS treatment. The kink phenomena shown in Fig. 2(a) are attributable to the increased surface potential barrier height between a pentacene organic layer and a gate dielectric layer, resulting in the serious device degradation. Figure 2(b) illustrates the electrical characteristics such as on/off current ratio of 10^4 and the field effect mobility of 0.12 cm^2/V s in the linear region. Therefore, considering the possible positive effect of the organic molecules modifying the surface of gate dielectrics, we applied OTMS as the organic molecules on the surface of the gate dielectric layer.[14–17]

In the absence of the OTMS treatment on the gate dielectrics as shown Fig. 3(a), we obtained the irregular pentacene grain film, which is due to the low organic electrostatic interaction between the ZrO_2 and the pentacene. However, it can be seen that application of the OTMS shows better surface morphology because the OTMS makes organic electrostatic interaction of the surface between them stronger based on the lipophilic aggregation effect [see Fig. 3(b)]. The
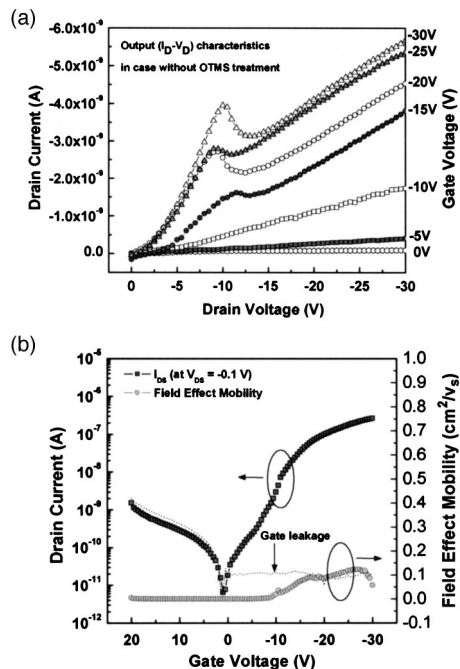
OTMS deposited on the ZrO_2 surface was confirmed by IR spectroscopy as shown in Fig. 4. Two sharp stretching bands at 2921 and 2850 cm^{-1} indicate that the sample has an aliphatic C–H which comes from the reacted OTMS. Two peaks at 1459 and 1431 cm^{-1} are for the aliphatic C–H bending. In addition, one sharp stretching band at 1083 cm^{-1} is for C–O single bond.

Figure 5(a) I_D-V_D and Fig. 5(b) I_D-V_G show electrical characteristics for the organic pentacene TFTs in the presence of the OTMS surface treatment on the gate dielectrics. The mobility increased up to 0.66 cm^2/V s and the on/off current ratio of 10^5 has been obtained from the linear region.
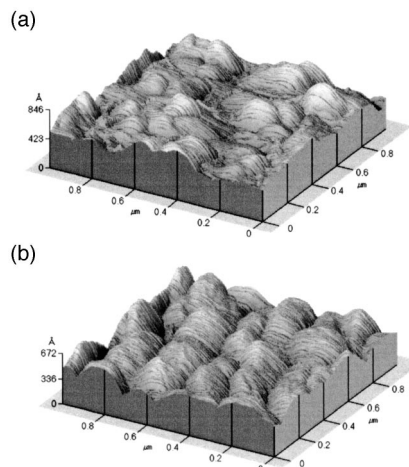

FIG. 3. AFM images of thermally evaporated thin film pentacene surface on ZrO_2 dielectrics. 100 nm thickness of the pentacene film deposited with the deposition rate of 0.5 Å at the substrate temperature of 60 °C: (a) pentacene film deposited on the non-OTMS-treated ZrO_2, (b) pentacene film deposited on the OTMS-treated ZrO_2.
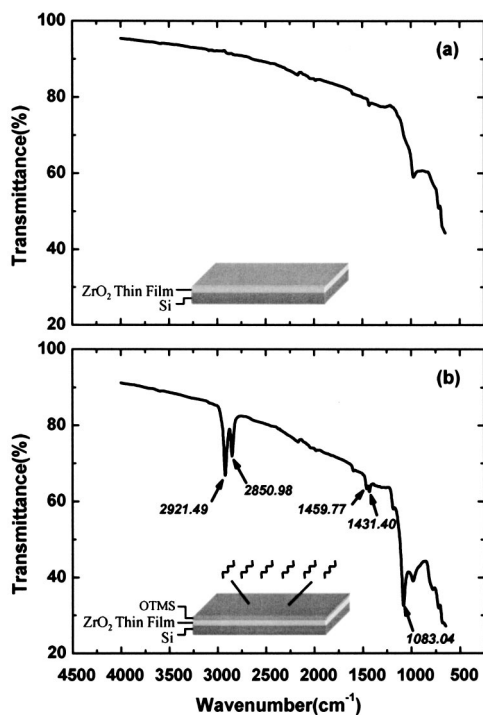
FIG. 4. Infrared spectra of the ZrO$_2$–OTMS film. Sample was prepared by deposition of ZrO$_2$ on the silicon wafer followed by surface treatment of the OTMS: (a) untreated surface, (b) treated surface.

The I_D at high V_G is increased in the case of OTMS-treated gate dielectric because of the higher packing of the pentacene crystallites in the channel. While the gate-leakage currents in the surface-untreated dielectric layer are at around 10^{-11} A, those in the surface-treated dielectric layer are near 10^{-12} A. Such an improvement of gate-leakage current characteristi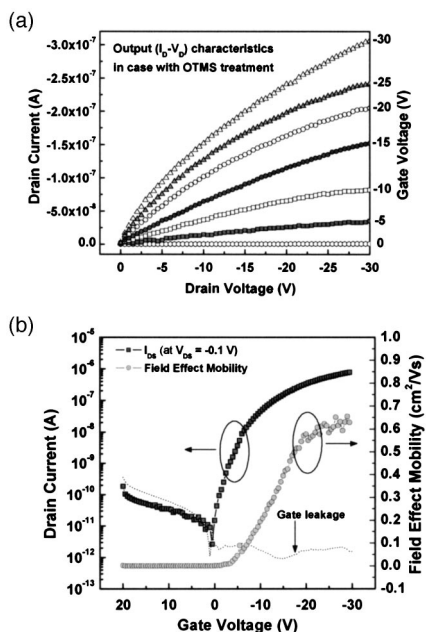cs in dielectric surface-treated OTFT is attributable to the reduction of surface defect density. In addition, the chemically enhanced contact between pentacene grains and dielectric layer increases an overall electrical conductivity of the channel during the charge accumulation in the interfacial surface state. These remarkably improved electrical characteristics of the OTFT seem to be ascribed to the uniformity of the pentacene grain as well as the enhanced contact edge effect between the surface modified gate dielectrics and organic pentacene molecules as mentioned earlier [Fig. 3(b)]. Also, the hydrophobic pentacene molecules became more feasible to bind with the hydrophobic tails of organic molecules on the surface-treated gate dielectric layer.

So, it should be noticed that the intermolecular chemical reaction between the OTMS and ZrO$_2$ brings much improved device performance. It can also be expected that a substitution reaction of the –OCH$_3$ group of the OTMS with the ZrO$_2$ would give a ZrO$_2$–OTMS compound on which the organic pentacene molecule would be easily deposited because the van der Waals lipophilic attraction force between the OTMS and the pentacene, which seems to reduce the contact resistance between dielectric layer and the pentacene, is strong enough to have an intermolecular interaction, providing the excellent adhesion of the organic pentacene molecules on gate dielectric films.

In this letter, we report the electrical characteristics of the organic pentacene thin-film transistors fabricated on flexible polyethersulfone film by a four-level mask process. It is found that chemical treatment of the gate dielectric surface with OTMS gives rise to a remarkable increase of field effect mobility. It is thus concluded that the organic pentacene thin-film transistors show the dependence of field effect mobility on the interface surface state of gate dielectric/pentacene, which may be modified by chemical properties in the gate dielectric surface.

FIG. 5. (a) Electrical characteristics of drain current (I_D) vs drain voltage (V_D) at various gate voltages (V_G) obtained from the pentacene TFT with OTMS-treated gate dielectrics, (b) I_D vs V_G and field effect mobility at V_D of 0.1 V obtained from the pentacene TFT with OTMS-treated gate dielectrics.

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