Letter

Hybrid TiO$_x$/fluoropolymer bi-layer dielectrics for low-voltage complementary inverters

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**A B S T R A C T**

In this article, low temperature processed, reactively evaporated titanium oxide layers were utilized as gate dielectrics for achieving low voltage driven transistors and complementary inverters. The surface of the gate dielectric was modified by an ultra thin (~30 nm) fluoropolymer Cytop$^a$ layer which partially helped to reduce the leakage in the dielectric films and also enhanced the organic transistor performance. The current investigation demonstrates the ability of these high capacitance bi-layer dielectrics ($k$ ~ 20). The combined p-type and n-type field-effect transistors show similar saturation mobility $\mu_{sat}$ to achieve low voltage driven complementary circuits with output gain of 22. Low temperature processing of these dielectric layers make them easily integrated.

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1. Introduction

Recently, interest in organic electronics is rapidly emerging due to its easy processing routes and cheaper production costs. Organic solar cells, organic thin-film transistors (OTFTs), complementary inverters and light emitting diodes have been the focus of invention by majority of researchers in this area [1–3]. Various materials have been investigated as candidates for the active layers for organic/inorganic TFTs [4,5]. Among organic TFTs, Pentacene has derived much attention due to its planar structure and high mobility. Moreover, Pentacene can be easily evaporated so that the growth mechanisms are easily controlled through deposition rate, thickness and the substrate temperatures. When employed as active layers in a planar geometry, Pentacene based OTFTs have resulted in field-effect mobilities $\sim 1 \text{ cm}^2/\text{V s}$, ensuring that they can be the possible replacements for the amorphous Si transistors in near future [6,7]. However, one of the challenging issues in OTFTs is to reduce the operative voltages of the devices. Utilization of high dielectric constant oxides is the plausible route to achieve low voltage driven transistors and complementary inverters [8–10]. Some of the oxides which derived much attention as gate dielectrics are Ta$_2$O$_3$ [11,12], YO$_x$ [13], TiO$_2$ [8,14,15], MgO [16] etc. Roughness, density of surface traps and dielectric constants of the dielectric layer are the key issues to be addressed while designing the OTFTs [11,17]. It is anticipated that surface of these oxides can be modified by a thin polymer layer coating which eventually smoothen the dielectric surface and helps in increasing the breakdown field [18]. Utilization of such bi-layer dielectrics is the main topic of current investigation [11,15]. Because of their highly hydrophilic surfaces, these oxide films are not suitable for direct growth of the organic semiconductor due to the probable undesirable interface modifications [19]. The polymer
layers atop gate oxide ensures organic–organic interface between the active layers and gate dielectrics which is of non-interacting nature and provide better interface [20]. Considering all these factors, in this study, we have grown low temperature processed titanium oxide (TiO$_x$) dielectric layers by a simple reactive evaporation process. The surface modification was achieved by a solution processed fluoropolymer Cytop layers. We also have demonstrated the low-voltage operation of the complementary inverter consisting of Pentacene and PTCDI-C8 as p- and n-type semiconductors, respectively.

2. Experimental

The devices were fabricated on the indium tin oxide (ITO)-coated glass substrates (10–20 Ω/□, sheet resistance), acting as gate electrode. Prior to the device fabrication, the ITO substrates were cleaned by TFD4 detergent (Franklab, France) and deionized water in an ultrasonic bath and were treated with UV-ozone for 15 min. In order to implement low-voltage operation of the organic thin-film transistors, we used the high-$k$ metal oxides TiO$_x$ as gate insulators. The chamber was pumped down to $\sim$10$^{-6}$ Torr before the TiO$_x$ deposition. The films were deposited by reactive evaporation of Ti in an oxygen environment. The flow rate of the oxygen gas was maintained by means of a mass flow controller. During the TiO$_x$ deposition process, the partial pressure was optimized at 2 $\times$ 10$^{-4}$ Torr. The as-deposited films were subjected to post-deposition annealing process at a temperature of 150 $^\circ$C, and the evaporation rate of 1.0 Å was fixed during the deposition. However, the resultant TiO$_x$ dielectrics caused a high grain boundary leakage current. To reduce such leakage currents, a dilute 1 wt% Cytop$^\text{®}$ CTL-809 M (Asahi Glass, Tokyo, Japan) was spin-coated over the TiO$_x$-covered ITO glass substrates at a rotation speed of 2000 rpm for 60 s, followed by baking at 100 $^\circ$C to remove the residual solvent. The spin coating process was carried out under nitrogen environment in glove box. In order to achieve the low-voltage complementary circuits, p-type Pentacene and n-type N,N-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C8) were, respectively, patterned on the TiO$_x$ layer using shadow masks by thermal evaporation.

The deposition rate was fixed to 0.5 Å/s for the evaporation of both Pentacene and PTCDI-C8 which were deposited onto the gate dielectric under a high vacuum 10$^{-6}$ Torr. Both the thicknesses of Pentacene and PTCDI-C8 films were 50 nm. Finally, the metal (Au) was deposited on semiconductors through a shadow mask as the contact electrodes. The current–voltage ($I−V$) characteristics of OTFTs were measured in N$_2$ by Keithley semiconductor analyzer (4200-SCS). The $C−V$ measurement was performed by a HP 4980A precision LCR meter. The films were subjected to X-ray diffraction (XRD) to ascertain nature of crystallinity.

![Fig. 1. UV–vis transmission spectra for TiO$_x$ thin film. Inset: photographic images of the TiO$_x$ films grown on glass and a bare glass.](image1)

![Fig. 2. X-ray photoelectron spectroscopic (XPS) spectra of TiO$_x$ thin film. Inset: X-ray diffraction (XRD) spectra of TiO$_x$ thin film with/without annealing.](image2)

![Fig. 3. (a) Current density vs. electric field characteristics of the TiO$_x$ and TiO$_x$/polymer gate dielectrics. (b) Capacitance vs. voltage curves measured at 100 kHz for TiO$_x$ and TiO$_x$/polymer.](image3)
in the films. The XRD measurements were performed using a Philips X’ Pert-Pro diffractometer with Cu Kα radiation of wavelength \( \lambda = 1.54 \) Å.

3. Results and discussion

Optical band gap of TiO\(_x\) without intentional doping is \(~3.4\) eV [21]. Its wide band gap makes it transparent in the visible region of the electromagnetic spectrum and hence are suitable for the transparent electronics applications. Fig. 1 displays the transmission spectrum of the reactivity evaporated TiO\(_x\) films grown on glass. Inset provides the photographic images of the TiO\(_x\) films grown on glass and that of a bare glass. The highly transparent nature of the films is clearly visible from the figure. Thickness of the layer was \(~350\) nm as measured from the thickness profilometer. The optical transmission spectra of the reactivity evaporated TiO\(_x\) films are highly transparent (transmittance >78%) in the visible region. The high transmittances indicate fairly smooth surfaces and relatively good film homogeneity.

In order to further characterize the oxide films, X-ray photoelectron spectroscopy was carried out. Fig. 2 shows the high resolution XPS spectra of the TiO\(_x\) films deposited on glass substrate. As shown in the figure, titanium peaks were located 458 eV (Ti 2p\(_{3/2}\)) and 464 eV (Ti 2p\(_{1/2}\)), the oxygen peak (O 1S) was positioned at 530 eV. The elemental analysis of the films resulted in corresponding atomic composition of 66.3 and 33.7 for titanium and oxygen, respectively. Hence, it was found that the composition is...
close to the ideal value of 2, indicating that the films are stoichiometric in nature and the current reactive evaporation is desired for the effective conversion of Ti into TiO$_x$ films at room temperature. Fig. 2 inset shows the X-ray diffraction pattern of TiO$_x$ thin films grown on glass substrates by reactive evaporation. The absence of any well defined diffraction peaks indicates that the films are amorphous in nature. For comparison both unannealed and annealed films are shown in the figure. As can be seen from the figure, annealing at 150 °C did not help in inducing any crystallinity in the films. In the case of oxides, the grain size tends to increase with increasing annealing temperatures as a result of which the surface roughness also increases. Since the higher surface roughness is not desired for the gate dielectric applications, high-temperature annealing process was not carried out for the films. Amorphous nature of the oxide films ensures that the grain boundary effects will be minimal. Hence, it is expected to lead to reduced charge trapping at the interface. Amorphous nature of the gate dielectric films is also found in the literature.

In order to achieve low-voltage operation in OTFTs, the high-$k$ materials are always used as the gate insulators, which can afford greater surface charge density and also reduce the operating voltages of OTFTs. The TiO$_x$ has lately been used as a high-$k$ gate dielectric material and many groups have researched about this metal oxide [14,15,20]. In general, the TiO$_x$ films have usually fabricated through rf/dc sputtering, sol–gel, solution processing, and were used as dielectrics for OTFTs. However, almost such methods need to high-temperature annealing. Their dielectric constant values of the TiO$_x$ films are in the range of 11–41. In the present study, the TiO$_x$ films are deposited by reactive evaporation of Ti without any high-temperature treatment. The electrical properties of the films are investigated by current–density–voltage $J$–$V$ and capacitance–voltage $C$–$V$ characteristics of the Au/Cytop$^\circledR$/TiO$_x$/ITO sandwich structures. As shown in Fig. 3b, the TiO$_x$ film has relatively high capacitance ($C = 129$ nF/cm$^2$) and the dielectric constant of the TiO$_x$ extracted from capacitance–voltage ($C$–$V$) measurement is as high as 51. In order to avoid leakage current and surface modification, the fluoropolymer Cytop$^\circledR$ thin film is used to stack on the TiO$_x$ film through solution processing. The leakage current density of the bi-layer dielectric has successfully compressed than that of the single TiO$_x$ layer as seen in Fig. 3a. For the bi-layer insulator, the bottom layer of the thick TiO$_x$ enhances the dielectric constant of the insulator, and the top layer of the ultrathin Cytop$^\circledR$ acts as a roughness-smoothing layer and hydrophobic surface treatment. As the metal–insulator–metal capacitors, we have measured the capacitance of 48.3 nF/cm$^2$ for an Au/Cytop$^\circledR$/TiO$_x$/ITO sandwich, and the total dielectric constant of the dual-layered gate dielectric was 20. Hence, in order to reconcile the advantages of high dielectric constant for operating at low operating voltages and polymer dielectric for better interface, it is desirable to employ bilayer gate dielectrics as demonstrated by the electrical properties.

OTFTs were fabricated using the above mentioned bilayer dielectrics using a top contact geometry with a channel length ($L$) of 120 μm and width ($W$) of 2 mm. While the Pentacene OTFTs exhibited a typical p-channel conduction, PTCDI-C8 OTFTs resulted in a n-type OTFT characteristics. It is worth noting that the operative voltages for both the devices is only 5 V depicting that these devices can be operated at low voltages. Output curves are the plots of drain current as a function of source to drain voltages are shown in Fig. 4b and d. Maximum saturation drain current of 0.5 μA for PTCDI-C8 transistor and 0.3 μA for Pentacene transistor are achieved under a gate bias of ±5 V. The field-effect mobility ($\mu$) and threshold voltage ($V_T$) were extracted from the measured transfer curve (Fig. 4a and c) by comparing it with the standard current–voltage equation for a transistor in the saturation regime [22]. The PTCDI-C8 and Pentacene OTFTs had high field-effect mobilities of 0.33 and 0.31 cm$^2$/Vs, and exhibited low threshold voltage of 2.7 and –3.1 V, respectively. It reveals that the high-performance and low-voltage organic thin-film transistors can be accomplished though the high-$k$ metal oxide. The PTCDI-C8 OTFTs exhibited a slightly higher on/off ratio ($\sim 10^4$) compared to the Pentacene OTFTs ($\sim 10^3$). Overall, the values of the filed-effect mobilities are relatively high both in n-channel transistors and p-channel transistors operating at low voltages, and the low threshold voltage will enable us to achieve the low-voltage operation of the inverter.

Finally, we have also demonstrated the organic complementary inverters with PTCDI-C8 and Pentacene OTFTs, fabricated on TiO$_x$/Cytop$^\circledR$ double dielectric layers. The static inverter characteristic of a complementary Pentacene/PTCDI-C8 is shown in Fig. 5, and the inverter operated at low voltages ($V_{DD}$) in the range of 4–7 V. When the organic complementary inverters operated at a low voltage of 5 V, it shows a maximum voltage gain of 22. Thus, we conclude that our TiO$_x$/Cytop$^\circledR$ double layer is a promising
new gate dielectric for realizing a low-operating-voltage PTCDI-C8 and Pentacene OTFTs and subsequent complementary inverters. Therefore, the logic circuits operating at low voltage can be realized by these low-voltage devices.

4. Conclusion

In summary, we have successfully implemented low-voltage operation organic thin-film transistors by using the high-$k$ metal oxides TiO$_x$/thin polymer as gate insulators. The titanium oxide films are deposited by reactive evaporation of Ti in an oxygen environment without high-temperature annealing. The total dielectric constant of the dual-layered gate dielectric is 20 enabled us to achieve a high capacitance dielectric for low-voltage operation. By using TiO$_x$/Cytop as insulator, we were able to manufacture high quality PTCDI and Pentacene organic OTFTs with exceptionally low leakage and relatively low operating voltage. The PTCDI-C8 and Pentacene OTFTs possess field-effect mobilities of 0.33 and 0.31 cm$^2$/Vs, and threshold voltage of 2.7 and $-3.1$ V, respectively. In addition, the organic complementary inverters operated at a low voltage of 5 V with a voltage gain of 22. Thus, we conclude that our TiO$_x$/Cytop double layer is a promising new gate dielectric for realizing a low voltage driving OTFTs.

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