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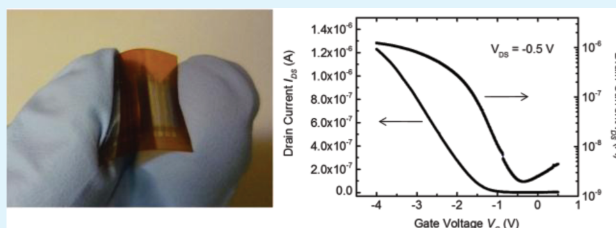
Flexible Low-Voltage Polymer Thin-Film Transistors Using Supercritical CO_2-Deposited ZrO_2 Dielectrics

Qingshuo Wei,[†] Eunyoung You,[‡] Nicholas R. Hendricks,[†] Alejandro L. Briseno,[†] and James J. Watkins*,[†]

[†]Department of Polymer Science and Engineering, University of Massachusetts Amherst, 120 Governors Drive, Amherst, Massachusetts 01003, United States

[‡]Department of Chemical Engineering, University of Massachusetts, 686 N. Pleasant Street, Amherst, Massachusetts 01003, United States

ABSTRACT: The fabrication of low-voltage flexible organic thin film transistors using zirconia (ZrO_2) dielectric layers prepared via supercritical fluid deposition was studied. Continuous, single-phase films of approximately 30 nm thick ZrO_2 were grown on polyimide (PI)/aluminum (Al) substrates at 250 °C via hydrolysis of tetrakis(2,2,6,6-tetramethyl-3,5-heptane-dionato) zirconium in supercritical carbon dioxide. This dielectric layer showed a high areal capacitance of 317 nF cm^{-2} at 1 kHz and a low leakage current of 1.8×10^{-6} A cm^{-2} at an applied voltage of −3 V. By using poly(3-hexylthiophene) (P3HT) as a semiconductor, we have fabricated flexible thin film transistors operating at V_{DS} = −0.5 V and V_G in a range from 0.5 V to −4 V, with on/off ratios on the order of 1×10^3 and mobility values higher than 0.1 cm^2/(V s).



KEYWORDS: *supercritical fluid deposition, zirconia, high-k, low voltage, organic transistors and polythiophene*

Organic thin-film transistors (OTFTs) have drawn tremendous attention because of their potential use in mechanically flexible, lightweight, and inexpensive electronic devices.[1] Low-voltage operation of OTFTs is necessary for practical applications, hence there is a need to develop stable dielectrics with low leakage current and a high areal capacitance.[2−4] High-*k* metal oxide dielectrics such as hafnia (HfO_2) and zirconia (ZrO_2) are attractive for this purpose because of the high dielectric constant, the robustness of the film and the possibility to functionalize the surface with self-assembled monolayers (SAMs) to control the threshold voltage of the transistors.[5,6] To date various methods have been used to fabricate high-*k* metal oxide films for the OTFT applications including metal anodization,[7] vacuum based depositions,[8−10] and sol−gel chemistry.[11,12] Supercritical fluid deposition (SFD) is a well-established technique for the reactive deposition of metal, metal oxide, and alloy thin films.[13,14] At present, there are no studies that report supercritical fluid deposited metal oxide layers for flexible TFT applications. SFD is comparable to the conventional thin film deposition techniques, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD), as it employs similar metal organic precursors and reaction chemistries. However, SFD offers advantages by providing a unique environment that allows solution-based chemistry in a supercritical fluid media where liquid-like densities and gas-like transport properties are present in the absence of surface tension.[13,14] Compared to the two aforementioned conventional deposition techniques, SFD has shown to deposit metal oxide films with relatively low substrate temperatures and exceptional step coverage, without the presence of strong oxidizing agents, such as peroxides and/or ozone. These considerations are especially important when device fabrication of a flexible polymer substrate is desired. Unlike ALD, which employs cyclic deposition of submonolayer quantities of oxide in each reaction cycle, depositions using batch SFD are not self-limiting and conformal films can be deposited in a single batch process at reasonable rate. In this letter, we describe the fabrication of flexible low-voltage OTFTs by using ZrO_2 dielectric material deposited with SFD.

The transistors were fabricated on polyimide (PI) substrates and 20 nm of aluminum (Al) was evaporated on the PI substrate through a 6 mm ×13 mm shadow mask prior to the ZrO_2 deposition. The ZrO_2 depositions, as previously reported by our group,[15] were performed in a cold-wall, high pressure reactor with an internal volume of 110 mL. The PI/Al substrates were mounted on an aluminum stage within the reactor, which was later heated to and maintained at a set temperature. Before the reactor was sealed, 0.025 mmol of tetrakis(2,2,6,6-tetramethyl-3,5-heptane-dionato) zirconium ($Zr(tmhd)_4$, Strem Chemicals) was added. The system was purged with nitrogen (N_2) for 1 h while the reactor was heated to 60 °C. Supercritical carbon dioxide, $scCO_2$, was delivered at 60 °C using a high-pressure syringe pump (ISCO, Teledyne Tech. Inc.) until the reactor pressure was 110 bar. After the precursor was dissolved in $scCO_2$, the deposition reaction via hydrolysis with trace water present in the $scCO_2$ was initiated

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by setting the Al stage temperature to 250 °C. After 15 min, the stage heater was turned off, and the reactor was depressurized and purged with fresh $scCO_2$. The recovered ZrO_2 films have an average film thickness of approximately 31 nm as measured by ellipsometry.

X-ray photoelectron spectroscopy (XPS) was used to characterize the films deposited by SFD. As shown in Figure 1a, the survey spectrum shows only Zr, O and C peaks at the surface, and C peaks were almost completely removed after Ar^+ sputtering of the dielectric film surface. This indicates that high purity continuous films were deposited onto the substrates. The atomic ratio between Zr and O is 1:2.01 in the bulk, and the binding energy measured for the Zr $3d_{5/2}$ peak was approximately 181.6 eV as shown in Figure 2(b), indicating Zr oxides were deposited in the 4^+ oxidation states. X-ray diffraction (XRD) analysis does not reveal any significant peak, thereby suggesting that the film was amorphous. This result is consistent with our previous studies.[15] The morphology of the deposited film was examined by atomic force microscoppy (AFM). As shown in Figure 1c, the deposited films were uniform with a mean roughness (Ra) of 1.68 nm.

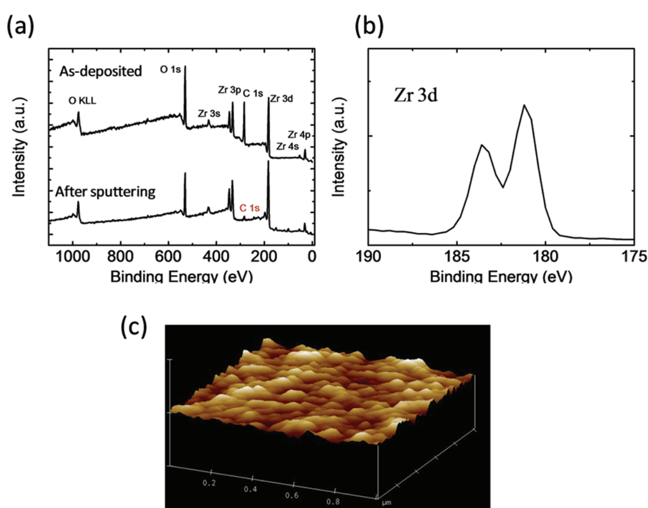

Figure 1. (a) XPS survey spectrum of the as-deposited ZrO_2 layer and after sputtering; (b) Zr 3d core-level photoemission spectrum of as-deposited ZrO_2 layer; and (c) AFM height image of the as-deposited ZrO_2 layer. The scale is 1 μm × 1 μm; the height scale is 0 to 50 nm (a *Ra* of 1.68 nm).

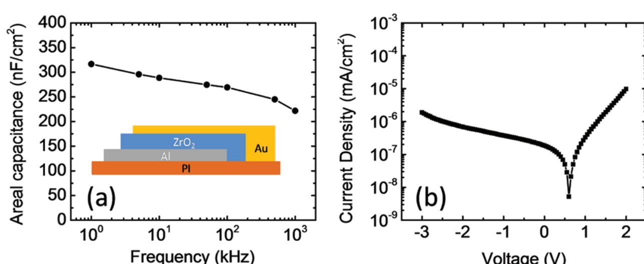

Figure 2. (a) Areal capacitance as a function of frequency. The device structure for the measurement is shown in the inset; (b) Leakage–current density as a function of bias voltage measurement.

Chemical passivation of ZrO_2 was carried out before device fabrication. A phosphonic acid self-assembled monolayer (SAM) was deposited on the ZrO_2 dielectric by immersing the samples in a 5×10^{-3} M n-octadecylphosphonic acid (ODPA) solution in 2-propanol.[12] The substrates were left in solution, at room temperature, overnight and successively sonicated in pure 2-propanol for 20 min and blown dry with nitrogen. Figure 2a shows the capacitance measurement of the ZrO_2/ODPA dielectric. The capacitance was 317 nF cm^{-2} at 1 kHz which is smaller than the calculated value for 31 nm crystalline ZrO_2 (664 nF cm^{-2}, by assuming $k = 25$).[16] This can be explained by the amorphous nature of ZrO_2 film deposited by SFD and/or the introduction of the low permittivity ODPA layer. The leakage current through the capacitor was approximately 1.8×10^{-6} A cm^{-2} at an applied voltage of −3 V (1 MV/cm) as shown in Figure 2(b), and this value is slightly higher than the ZrO_2 layer prepared with atomic layer deposition at a substrate temperature of 225 °C (1×10^{-7} to 1×10^{-6} A cm^{-2}).[17] We believe that if the ZrO_2 layer is crystalline, the leakage current should be even lower.

Figure 3a shows the structure of the devices used in this study. Transistors with a channel length (L) of 100 μm and width (W) of 3 mm were fabricated in a bottom-gate configuration on the PI substrates using Al as the gate electrode and ZrO_2/ODPA as dielectrics. An approximate 10 nm thick poly(3-hexylthiophene) (P3HT) film was transferred by the contact film transfer (CFT) method on top of the dielectric layer.[18,19] By using this transfer method, the dielectric and charge transport layers can be prepared separately. Previous studies have shown that the OTFTs prepared by CFT have higher mobility values than those of the conventional spin-coated devices. This is because the polymer/air interface induces a greater degree of molecular orientation and the interchain $\pi - \pi$ interactions are more extensive than those at the polymer/dielectric interface.[20] Briefly, water-soluble polymers, such as sodium poly(styrenesulfonate) (PSS), act as a "sacrificial layer" in the transfer process. A film with glass/PSS/P3HT structure was prepared by successive spin-coating of an aqueous solution of PSS and a chlorobenzene solution of P3HT (2 mg/mL). This polymer film was gently brought into contact with the surface of dielectric with the polymer facing down. One drop of water was placed on the edge of the stacked substrates. After the water moved from one side of the substrate to the other, the glass substrate was detached from the organic layer, resulting in the transfer of the polymer film from the glass to the surface of dielectric layer. Gold electrodes (4 mm ×100 μm) were then evaporated onto the surface through a shadow mask. The photograph of the fabricated flexible transistor is shown in Figure 3b.

Panels c and d in Figure 3 show the electrical properties of the fabricated flexible OTFTs. Figure 3c shows the typical output characteristics of the device. A clear field-effect and well-resolved linear and saturation regions were observed from the output curves with 0.1 V step. It is important to note that there was little drain current offset in a low gate bias suggesting a low leakage current from gate electrode to source electrode. This is reasonable because the thin ZrO_2 layer deposited by SFD was continuous and homogeneous, and should exhibit exceptional step coverage on the gate electrode.[21] Figure 3d shows the transfer characteristics scans from 0.5 V to −4 V at drain-source voltage (V_{DS}) = −0.5 V. The transistor exhibited a threshold voltage of −1.4 V, a subthreshold swing of 0.5 V and an on/off ratio greater than 1×10^3. The mobility calculated from the linear region is μ_{lin} = 0.11 $cm^2/(V\ s)$. The mobility value was almost identical with that of the device fabricated on silicon by using contact film transfer methods which suggest that the

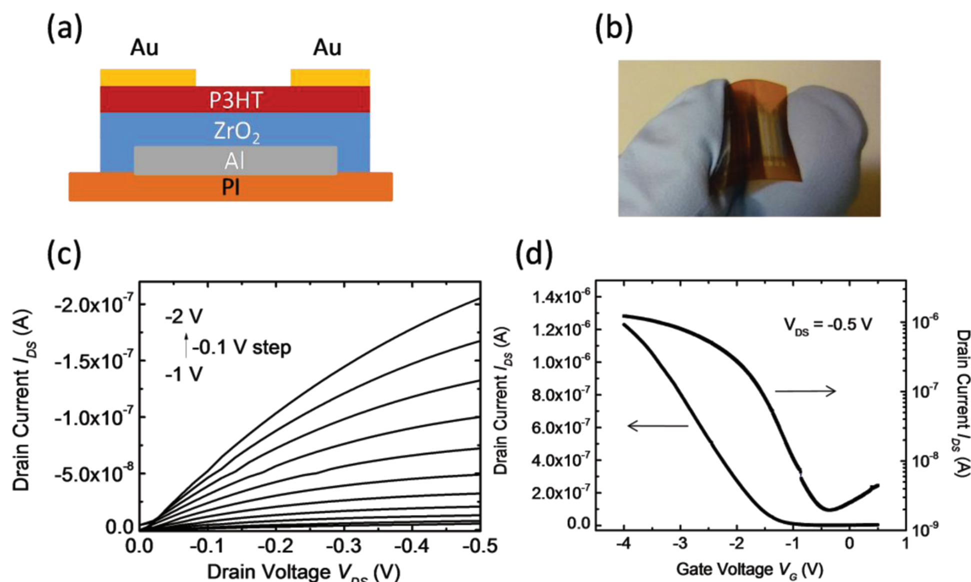

Figure 3. (a) Schematic representation of the bottom-gate, top-contact flexible transistors using ZrO_2 dielectric layers; (b) photograph of the fabricated flexible transistor; (c) output curve of prepared transistors; and (d) transfer curve of prepared transistors, measured at V_{DS} = 0.5 V.

dielectric layers show less effect on the mobility values compared with the molecular ordering in charge transport layers.[22,23] Our devices also show good reproducibility. More than 10 samples on ZrO_2/Al/PI substrates were prepared by using the same process, and over 90% of them exhibited a subthreshold swing of 0.25−0.6 V, a mobility value of 0.05 − 0.20 cm^2/(V s) and an on/off ratio of 1×10^2 to 1×10^4.

In conclusion, we have demonstrated the fabrication of flexible low-voltage OTFTs by using $scCO_2$ deposited ZrO_2 dielectric films for the first time. The mobility values of these flexible OTFTs were similar to the device fabricated on Si/SiO_2 substrates. By using P3HT as a semiconductor, we have achieved devices operating at V_{DS} = 0.5 V and V_G in a range from 0.5 V to −4 V, with on/off ratios of the order of 1×10^3, a subthreshold swing of 0.5 V and a mobility higher than 0.1 cm^2/(V s). We are currently working on the synthesis of high-k metal oxide nanoparticles using supercritical fluids such that the entire process can be performed in solution and ultimately compatible with roll-to-roll fabrications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: watkins@polysci.umass.edu.

Notes

The authors declare no competing financial interest.

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