Low operating voltage organic transistors and circuits with anodic titanium oxide and phosphonic acid self-assembled monolayer dielectrics

Hiroaki Jinno^a, Tomoyuki Yokota^a, Naoji Matsuhisa^a, Martin Kaltenbrunner^b, Yutaro Tachibana^a, and Takao Someya^{a,c,d,*}

^a Electrical and Electronic Engineering and Information Systems, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^b Department of Soft Matter Physics, Johannes Kepler University Altenbergerstrasse 69, 4040 Linz, Austria

^c Thin-Film Device Laboratory, RIKEN, 2-1, Hirosawa, Wako, Saitama, 351-0198, Japan.

^d Center for Emergent Matter Science, RIKEN, 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan.

Abstract

We fabricated organic thin-film transistors (OTFTs) with sub-1 V driving voltage enabled by a hybrid dielectric comprising high-k amorphous titanium oxide (TiO_x) and a phosphonic acid self-assembled monolayer (SAM). The p-type OTFTs show a high on/off ratio (10⁵), a near 0 V threshold voltage (−0.09 V), and a high mobility of 1.2 cm²/Vs when operated at 1 V. These OTFTs are readily employed in circuit applications, and we show pseudo-CMOS and CMOS inverters operating at 0.5 V as basic building blocks of low-voltage advanced organic logic circuits. We fabricate a five-stage CMOS ring oscillator that displays clear oscillation characteristics at a driving voltage of 0.5 V to highlight the potential of our hybrid dielectric for ultra-low-voltage integrated plastic circuitry.

titanium oxide thin-film transistors.

Keywords

Organic thin-film transistors; Low driving-voltage; Ring oscillators

1. Introduction

Organic thin-film transistors (OTFTs) are emerging electronic devices that have unique features such as low-temperature fabrication, printability, ultra-flexibility, and lightweight. When using these new features in practical devices, it is important to decrease the driving voltage of the OTFTs to achieve low-power-consumption electronics devices. Obtaining a sufficient carrier density to operate the device at a lower driving voltage requires an increase in interface capacitance (C_{OX}) and a decrease in the threshold voltage (V_{TH}). An increase in C_{OX} can be achieved by either decreasing the thickness of the dielectric or by increasing the dielectric constant k by employing high- k materials. This has been achieved in different ways for various dielectrics. For decreasing thickness, initiated chemical vapor deposition [1] and AlO_x with self-assembled monolayers (SAM) [2][3][4] were used. For high- k materials, TiO_2 with polystyrene [5], titanium oxide (TiO_x) with PMMA [6], and HfO_2 [7][8][9] are common. Electrical double layer (EDL) dielectrics is a common method that uses other kinds of dielectrics. For EDL dielectrics, ionic liquids [10], ion gels [11], and polar elastomers [12] have been reported. In terms of circuit applications, a ring oscillator with polyelectrolyte dielectrics showed a 100-Hz oscillation with 0.9 V [13], and that with AlO_x /SAM showed a 2-kHz oscillation at 1 V [14].

Hybrid dielectric layers of AlO_x modified with phosphonic acid self-assembled monolayers (PA-SAM) are especially suitable for low-operating-voltage circuit applications using OTFTs. Such a hybrid dielectric is a promising material for circuit applications owing to its favorable combination of mobility, on-off ratio [15][16], operational frequency [14], high temperature stability [17], and low-temperature processing that is compatible with soft plastic substrates. In a recent study, OTFTs with oxygen plasma formed ultrathin AlO_x /SAM dielectrics that were used for ring oscillators operating at 1 V. Here, decreasing the contact resistance with a suitable SAM (PA-SAM and fluorinated PA-SAM), in combination with an extremely short channel length (1 μm) [14], allowed for low-voltage, high-speed operation. Proper adjustment of V_{TH} was achieved using SAM layers with appropriate end groups.

The electrochemical preparation of alumina via potentiostatic anodization in conjunction with SAMs as dielectrics for OTFTs offers several distinct advantages such as room-temperature processing and the ability to grow dense, pinhole-free oxide layers [18][19]. Anodic AlO_x /SAM OTFTs can be prepared with a narrow performance distribution and high device yield rate on rough surfaces including 1- μm -thick substrates, and can show improved bending stability compared with plasma-grown AlO_x counterparts [20]. In addition, anodic AlO_x /SAM OTFTs typically achieve low off currents ($<10^{-11}$ A [20]), and the thickness of the oxide can be readily controlled by adjusting the anodization voltage. These advantages place anodic AlO_x /SAM OTFTs among the most promising

candidates for the development of well-organized large-area circuits on ultrathin substrates.

However, the application of AlO_x/SAM OTFTs to ultralow sub-1 V operation may be hindered owing to their somewhat large threshold voltage shift. For example, $V_{TH} = -0.61$ V [20] was found with anodic AlO_x/SAM , and $V_{TH} = -0.2$ V [21] with oxygen plasma-derived oxides. In ultralow sub-1 V operation, the V_{TH} of OTFTs naturally has to fall within the operating voltage window from 0 V to 1 V (−1 V for p-type OTFTs) to obtain sufficiently high on/off ratios. Ideally, V_{TH} should be around 0 V to obtain an off state at 0 V and an on state at 1 V, resulting in a maximized on/off ratio.

One way to increase the interfacial capacitance using potentiostatic anodization is to utilize higher- k oxides than AlO_x . Potential higher- k valve metals usable as OTFT dielectrics are HfO_x [22], TaO_x [23], and TiO_x [6][24]. Although TiO_x has the highest dielectric constant (40 [25]) of these materials, and anodic TiO_x is often used in nanotube array applications, there is no research focusing on OTFTs and their circuits including CMOS ring oscillator using anodic TiO_x modified with PA-SAM as dielectrics owing to the (for insulators) relatively small band gap of TiO_x . To overcome this issue, we introduce a low-driving-voltage transistor with hybrid dielectrics comprised of anodic TiO_x modified with PA-SAM. We find a threshold voltage of around 0 V for TiO_x/SAM OTFTs, and demonstrate pseudo-CMOS and CMOS inverters and ring oscillators employing TiO_x/SAM OTFTs that operate well below 1 V.

2. Material and Methods

A 125- μm polyethylene-naphthalate (PEN) or polyimide (PI) film was used as a substrate. A 50-nm-thick Ti gate electrode was deposited through a shadow mask onto the film substrate by electron beam evaporation with a deposition rate ranging from 1.5–2.5 nm/s. After evaporation of the Ti, the substrate was dipped into an electrolyte solution (0.01 mol/L citric acid [Citric acid monohydrate, Sigma Aldrich] in 18 MOhm water) where the Ti serves as the anode. A sufficiently large platinum electrode was used as the cathode. One edge of the Ti electrode was electrically contacted and connected to a digital multimeter (2400, Keithley). The distance between anode and cathode was approximately 2 cm. First, the anodization voltage was kept at 1 V for 1 min to initially form a thin TiO_x layer. Subsequently, the voltage was ramped up to 6 V with a rate of 100 mV/s. Reaching 6 V, the voltage was kept constant until the current decreased to approximately 1×10^{-4} A/cm² (8 min). For the ring oscillators, we used 8 V anodization voltage, resulting in a slightly thicker oxide and, in turn, lower leakage and higher stability. After anodization, the devices were rinsed with ultra-pure water. The color change from darkish gray Ti to the yellow of 40 nm anodized TiO_x was clearly observed. Subsequently, the TiO_x surface was activated with O_2 plasma (150 W for 3 min). Next, the device was dipped into octadecylphosphonic acid (C18-SAM) solution (5 mM/L, isopropanol) for 16 h to modify the surface of the TiO_x . To investigate the alkyl chain length

dependence using Ti/TiO_x/Au capacitors, the same concentration of n-hexyl (C6-SAM), n-octyl (C8-SAM), decyl (C10-SAM), dodecyl (C12-SAM), tetradecyl (C14-SAM), hexadecyl (C16-SAM) phosphonic acid solution was used to form SAM layers. After dipping, the devices were rinsed with isopropanol and heated at 100 °C for 10 min. As a p-type organic semiconductor, dinathto-thieno-thiophene (DNTT) [26] (Nihon kayaku) was deposited and *N, N'*-bis (n-octyl) - (1,7 & 1,6), dicyanoperylene -3,4:9,10-bis (dicarboximide) (PDI-8CN2) [27] (ActivInk™ 1200, Polyera) was deposited as an n-type semiconductor (30 nm thick, respectively). Finally, a 70-nm Au layer was deposited as source and drain electrodes. A schematic illustration of fabricated TiO_x/SAM OTFT is shown in Fig. 1 (a). For the fabrication of inverters and ring oscillators, via holes through the Ti gate electrode were formed by a green laser (T-Centric Laser marker MD-T1010W, Keyence). The microscopic images of a p-type and an n-type TFT top-view are shown in Fig. 1 (b), (c).

The electrical characteristics of the OTFTs and inverters were evaluated with a semiconductor parameter analyzer (B1500, Agilent). The capacitances of the devices were measured with a precision LCR meter (4284A, Agilent). The dynamic response of the inverters and ring oscillators were measured with an oscilloscope (DSO6054A, Agilent) and a waveform generator (33220A, Agilent).

3. Results

Typical transfer curves of a p-type (DNTT) OTFT show sufficiently low leakage current (I_{leak}), around 0 V V_{TH} and require low drain-source voltage V_{DS} to drive the transistors (Fig. 1 (d)). The estimated saturation-mobility of the p-type TiO_x/SAM OTFTs is 1.2 cm²/Vs with a V_{TH} as low as -0.09 V. A high on-off ratio ($\sim 10^5$) at -1 V V_{DS} is obtained. The output characteristics show a clear saturation at -1 V V_{GS} and V_{DS} (Fig. 1 (e)). N-type TiO_x/SAM OTFTs with PDI-8CN2 as the semiconductor exhibit equally low leakage currents around 10⁻¹⁰ A (Fig. 1 (f)). Here, the leakage current increases in V_{GS} regions lower than 0 V. The calculated effective mobility is 0.021 cm²/Vs and the on/off ratio is 10³ at 1 V. These n-type OTFTs have a V_{TH} as small as 0.03 V. Characteristic transfer curves of an n-type OTFT are shown in Fig. 1 (f), the output characteristics in Fig. 1 (g).

We initially evaluate our TiO_x/SAM hybrid dielectric layers using capacitor structures (Fig. 2). First, we optimize the anodization conditions using Ti/TiO_x/Au test capacitors (Fig. 2 (a), (b)). As expected, the capacitance inversely scales with the dielectric thickness, determined in turn by the applied anodization voltage (Fig. 2 (a)). Using 2 V anodized TiO_x, a high capacitance per unit area of up to 3.0×10³ nF/cm² is achieved. We further confirm that the capacitance is independent of the anodization time, as long as the oxide is given enough time to form in the high-field growth region (typically, potentiostatic anodization for 8 min is sufficient) (Fig. 2 (b)). A large frequency-independent dielectric function of up to at least 100 kHz regime is required for dielectrics

of field effect transistors. We characterize the frequency dependence of our dielectric (Fig. 2 (c)): the capacitor with TiO_x/SAM dielectric layers exhibits a stable C - f curve with sufficiently low dielectric loss ($\tan \delta$). Finally, we measure J - V curves of the fabricated capacitors (Fig. 2 (d)). As a comparison, we show capacitors with plasma-treated TiO_x dielectric layers and ones with anodized TiO_x dielectric layers. Figure 2 (d) clearly shows that anodized TiO_x dielectric layers have superior dielectric properties as compared to plasma-treated ones. The leakage current further decreases by around one order of magnitude when applying SAM onto the anodized TiO_x surfaces. Figure 2 (e) shows C - V curves obtained from these capacitors. The capacitances are independent of applied voltage within the TFT operation region and the voltage window becomes broader with the SAM treatment since the leakage current decreases. When comparing the dielectric properties of the TiO_x/SAM hybrid dielectrics with SAMs of different alkyl chain length, we find that the current density of Ti/anodic $\text{TiO}_x/\text{SAM}/\text{Au}$ capacitors with varying SAMs does not show an obvious difference under small forward (1V) bias voltage (V_{Ti}), (Fig. S1). However, a decrease of current density with increasing SAM alkyl chain length is observed at a reverse bias of -1V, and for both higher reverse and forward bias of -3V and 3V. Since longer alkyl chains lead to lower leakage current density, and simultaneously result in a densely packed monolayer [28], in turn crucial for the fabrication of OTFTs with high yield and good stability, C18-SAM seem an optimal choice. Specifically, when comparing the present TiO_x/SAM and the prior AlO_x/SAM dielectrics as shown in Fig. 2 (f), the capacitance of TiO_x/SAM with shorter alkyl chain SAM (C6, C8 and C10) shows a higher per-unit-area capacitance than plasma-treated AlO_x/SAM dielectrics, while the capacitance of $\text{TiO}_x/\text{C18-SAM}$ is equivalent to that of plasma-treated $\text{AlO}_x/\text{C18-SAM}$ and higher than that of anodic $\text{AlO}_x/\text{C18-SAM}$ (280 nF/cm²). The relative ease of patterning and processing of the here presented Ti/ TiO_2 systems is very comparable to the prior Al/ AlO_x systems, we thus conclude that anodic AlO_x & TiO_x take up complementary roles in circuit design. While anodic AlO_x systems are appropriate for circuit components that require very low leakage current and high on/off ratio, anodic TiO_x systems are best suited where low driving voltage & high capacitance is paramount.

We continued to fabricate pseudo-CMOS inverters[29] with our TiO_x/SAM OTFTs. A circuit schematic and corresponding microscopic image of the pseudo-CMOS inverter are shown in Fig. 3 (a), and (b). The output characteristics of the pseudo-CMOS inverter is shown in Fig. 3 (c). The pseudo-CMOS inverter was operated successfully even at a remarkably small operating voltage of 0.3 V. We obtained good on-off switching with a large gain of 26 at an operation voltage of 0.5 V. The dynamic response of the inverter was evaluated by applying a rectangular wave with 10 Hz frequency at the input of the inverter, and the output waveform was monitored with an oscilloscope (Fig. 3 (d)). We observed an output voltage of 0.37 V and an estimated delay time of 15.2 ms for an input voltage of 0.5 V.

We also fabricated CMOS inverters; a circuit diagram is shown in Fig. 4 (a). The W/L ratio of

n-type OTFT was 4 times larger than the p-type OTFT as shown in Fig. 4 (d). The W/L of p-type and n-type OTFT was $800\text{ }\mu\text{m} / 25\text{ }\mu\text{m}$ and $3200\text{ }\mu\text{m} / 25\text{ }\mu\text{m}$, respectively. Our CMOS inverters exhibited clear on-off switching with a gain of 29 at 0.5 V supply voltage (V_{DD}), confirming steep switching of the CMOS inverter. Furthermore, we fabricated a five-stage ring oscillator comprising these CMOS inverters to evaluate the operation speed of the devices (Fig. 4 (d)). Oscillation characteristics at 0.5 V supply voltage are shown in Fig. 4 (e). The output wave has a frequency of 14.93 Hz and an amplitude of 179 mVpp. Estimated signal delay per stage was 13.4 ms at 0.5 V supply voltage.

4. Discussion

We observe that the leakage current density of anodized TiO_x dielectrics is around 10^{-7} A/cm^2 when operated up to 1 V, which is consistent with previous results [6]. With SAM modification, the current density further decreases to around 10^{-10} A/cm^2 . This effect is presumably not only a result of the SAM being an additional insulator, but also because of its intrinsic dipole effect. The head group of PA-SAMs is strongly positively charged and has a tendency to lower the energy band of the dielectric (for example, $\delta = 0.87\text{ eV}$ on AlO_x [30]). For TiO_x/SAM , electron injection is blocked because this dipole band bends and the typical Schottky-like diode behavior in J - V scans is suppressed, resulting in a broader insulating window. We find a higher built-in voltage for TiO_x/SAM capacitors. Because of these effects on the leakage current, TiO_x/SAM dielectrics result in OTFTs with low leakage current and a high on-off ratio (Fig. 1 (e) and (g)).

N-type OTFTs show higher leakage currents than p-type OTFTs when a negative gate voltage is applied (Fig. 1 (e) and (g)). This is presumably the result of different energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) between DNTT and PDI-8CN2. TiO_2 has deep HOMO-LUMO levels of 7.0 eV and 3.8 eV [31]. For DNTT and PDI-8CN2, HOMO-LUMO levels are 5.1 eV and 1.8 eV in DNTT [26], and 6.5 V and 4.2 V in PDI-8CN2 [32], respectively. When an electron injection is blocked from the gate to the source electrode for TiO_x/SAM OTFTs with DNTT (because of the large energy barrier of electrons between the LUMO level of DNTT and TiO_x), electron injection is more favorable for PDI-8CN2 owing to the smaller energy barrier between PDI-8CN2 and TiO_x .

In previous reports on anodic AlO_x/SAM OTFTs, the experimental V_{TH} are found to be -0.61 V [20] and -1.2 V [33]. Compared with these V_{TH} values, we find a clear shift in V_{TH} toward 0 V when using TiO_x/SAM as the dielectric layer. Identifying the origin of the threshold voltage shifts is challenging because several parameters are influential [34][35]. Here, the main difference between AlO_x and TiO_x OTFTs can be narrowed down to three factors: the gate electrode, the oxide layer, and the SAM layer. Several groups reported that the work function (WF) of the gate electrode can

affect the threshold voltage [34]. In these cases, the change in ΔV_{TH} is consistent with the change in the gate electrode WF: a shallower WF causes positive shifts of threshold voltage. Although the shifts obtained are similar in their tendencies in our devices, ΔV_{TH} is much larger than the difference in WF of Al and Ti.

The difference between the threshold voltage of TFTs with a Ti gate and that of TFTs with an Al gate as reported in our previous work [20] is 0.52 V, whereas the WFs of Ti and Al are 4.28 eV and 4.33 eV ($\Delta WF = 0.05$ eV), respectively. This implies that other physical or chemical differences between Al/ AlO_x and Ti/ TiO_x affect the threshold voltage of our TFTs. One possibility is the lack of oxygen in the oxide-metal dielectric layers. Lack of oxygen in a high- k oxide layer induces dipoles at the interface of the oxide, which cause shifts of V_{TH} in Si MOSFETs [36][37] and is dependent on differences in oxygen density between AlO_x and TiO_x [37]. In OTFTs, similar effects appear, such as the oxygen plasma dependence of V_{TH} [38] or the effects of the dipole of a SAM on WF shifts [39]. This may be one of the origins of the observed V_{TH} shift in our TiO_x/SAM OTFTs.

Another possibility is the SAM layer itself. The V_{TH} shifting effect of a SAM has two origins: the dipole-moment-induced electrostatic voltage of the SAM layer and a space charge layer at the semiconductor-dielectric interface. In previous research, relationships dependent on and independent of the dielectric capacitance (C_{diel}) [30] were reported. Considering a dependence on the capacitance, the higher interfacial capacitance of our TFTs (610 nF/cm²) compared with that of AlO_x/SAM (280 nF/cm²) simultaneously leads to a decrease in our TFT V_{TH} . Although at this point it is unclear whether our OTFTs have a V_{TH} dependence on C_{diel} , the V_{TH} dependence observed in SAM OTFTs supports our results with a near-0 V V_{TH} in OTFTs with TiO_x/SAM dielectrics.

5. Conclusion

We have succeeded in the fabrication of anodized TiO_x/SAM transistors with both p- and n-type semiconductors. Our hybrid dielectrics have a per-unit-area capacitance as high as oxygen plasma AlO_x/SAM dielectrics, with adjustable capacitance and low leakage currents at high yields. The OTFTs are applicable for circuits such as pseudo-CMOS and CMOS inverters and ring oscillators. Our pseudo-CMOS inverter can operate below 0.5 V with a high dynamic response and a delay time of 15.2 ms. The fabricated CMOS inverters have an operating voltage of less than 0.5 V, and the ring oscillators oscillate at 14.93 Hz when driven at only 0.5 V. These results corroborate the advantages of TiO_x/SAM dielectrics for low-driving-voltage applications such as implantable devices or low-power-consumption energy harvesting devices.

6. Author contribution

H.J., T.Y., N.M., M.K. and T.S. designed the transistors and circuits structure. H.J. and Y.T. fabricated the devices and measured the electrical characteristics. T.S. supervised the project. The authors declare no conflicting interests.

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Caption legends

Fig. 1. TiO_x/SAM TFTs with p- and n-type organic semiconductors. (a) Cross-section schematics of a TiO_x/SAM TFT, Microscopic top-view images of (b) a p-type (DNTT) TFT and (c) an n-type (PDI-8CN2) TFT, (d) Transfer curves of a p-type TiO_x/SAM TFT, (e) Output curves of a p-type TiO_x/SAM TFT, (f) Transfer curves of an n-type TiO_x/SAM TFT, (g) Output curves of an n-type TiO_x/SAM TFT

Fig. 2. TiO_x anodization condition and SAM modification effects on a $\text{Ti}/\text{TiO}_x/\text{Au}$ capacitor. (a) Capacitance versus anodization voltage (b) Capacitance versus anodization time (c) Capacitance-frequency ($C-f$) curves of the capacitor (d) Current density-Voltage ($J-V$) curves of the capacitor (e) Capacitance-Voltage ($C-V$) curves of the capacitor (f) Capacitances of $\text{Ti}/\text{TiO}_x/\text{SAM}/\text{Au}$ and $\text{Al}/\text{AlO}_x/\text{SAM}/\text{Au}$ capacitors with SAM alkyl chains

Fig. 3. Pseudo-CMOS inverter with TiO_x/SAM TFTs. (a) Circuit schematic of a TiO_x/SAM pseudo-CMOS inverter (b) Microscopic image of a TiO_x/SAM pseudo-CMOS inverter (c) Output characteristics of a TiO_x/SAM pseudo-CMOS inverter (d) Dynamic responses of a TiO_x/SAM pseudo-CMOS inverter with a rectangular wave input

Fig. 4. CMOS inverter and a ring oscillator with TiO_x/SAM TFTs. (a) Circuit schematic of a TiO_x/SAM CMOS inverter (b) Microscopic image of a TiO_x/SAM CMOS inverter (c) Output characteristics of a TiO_x/SAM CMOS inverter (d) Microscopic image of a TiO_x/SAM CMOS ring oscillator (e) Oscillation characteristics of a TiO_x/SAM CMOS ring oscillator

Fig. 1

Fig. 2

Fig. 3

Fig. 4