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Abstract
A self-assembled monolayer of n-octylphosphonic acid (C8PA) is prepared from vapour phase in vacuum. C8PA thickness corresponding to several monolayers is deposited on aluminium oxide (AlOx) and subsequently heated to leave a monolayer of chemisorbed molecules.

The effect of C8PA deposition rate on a 15-nm-thick, bi-layer AlOx/C8PA dielectric and low-voltage p-channel organic thin-film transistors (OTFTs) is studied. The increase in the deposition rate from 0.1 to 7.0 Å/s leads to increase in the field-effect mobility from 0.039 to 0.061 cm2/Vs, while the threshold voltage remains around -1.55 V. At the same time, the off-current is reduced from $2.3 \times 10^{-12}$ to $1.3 \times 10^{-12}$ A. The subthreshold slope is lowered from 100 to 89 mV/decade and the on/off current ratio is increased from $1 \times 10^5$ to $10^8$.

The leakage current density of AlOx is reduced from $1 \times 10^{-7}$ to $4 \times 10^{-8}$ A/cm² at 3 V when C8PA monolayer is added on top of it. In addition, pentacene grain size on AlOx is larger than that on AlOx. The overall performance of AlOx/C8PA OTFTs is superior to that of AlOx OTFTs.

1. Introduction
Low processing temperature of organic thin-film transistors is compatible with plastic substrates for flexible active matrix displays [1]. Their high on/off current ratio and modest field-effect mobility are sufficient for non-emissive displays such as electrophoretic and liquid crystal [2]. Emissive displays, such as organic light-emitting diodes, require transistors with higher on-current and good bias stability. Since the drain current of a field-effect transistor is proportional to the capacitance of its gate dielectric, higher on-currents can be achieved by using dielectrics with high capacitance. Ultra-thin dielectrics based on materials with high- to moderate-k values, for example aluminium oxide [3, 4], lead to high capacitance; however, their leakage current must be controlled. The leakage current in excess of $10^8$ A/cm² [5] of ultra-thin oxides can be reduced by functionalizing them with self-assembled monolayers (SAM) [6–11]. Along with the suppression of the leakage current, SAMs provide higher field-effect mobility than oxide surfaces [7, 11, 12]. Organic thin-film transistors (OTFTs) with SAMs achieved operating voltages less than 3 V [6–11].

The fabrication of display backplanes requires processes that produce layers with very high uniformity over large areas. Here, layer depositions with large process windows and self-limiting growth mechanisms provide an advantage. We developed a vacuum process for fabrication of an ultra-thin, bi-layer dielectric consisting of aluminium oxide (AlOx) and n-octylphosphonic acid (C8PA). AlOx is prepared by UV/ozone oxidation of thermally evaporated aluminium [13]. C8PA monolayer is prepared in two steps: firstly several monolayers are vapour-deposited on AlOx in vacuum and then the substrate is heated to remove all physisorbed molecules [14]. However, the kinetics of the chemisorption process of the phosphonate group to AlOx and the molecular alignment of C8PA molecules are affected by the deposition temperature [15] and the post-annealing treatment [14]. This paper studies how the deposition rate of C8PA affects the performance of organic thin-film transistors (OTFTs) and the corresponding metal-insulator-metal (MIM) structures.

2. Experimental details
MIM structures and OTFTs were fabricated side by side on Eagle 2000 glass substrate. Approximately a 15-nm-thick AlOx was obtained by UV/ozone oxidation of thermally evaporated aluminium [13]. C8PA corresponding to several monolayers was thermally evaporated at rates of 0.1, 1, 3, and 7 Å/s, respectively. Each C8PA layer was desorbed at ~ 160°C for an hour. In OTFT structures, 50-nm-thick, four-time purified pentacene was deposited at room temperature. Finally, 50-nm-thick gold contacts were evaporated to complete the MIM and OTFT structures. The fabrication used vacuum-grown processes only, applying shadow masks where needed. The maximum process temperature was 160°C. The fabricated transistors have channel lengths of 30, 50, 70, and 90 µm and the channel width of 1000 µm. The transistor cross-section is shown in Figure 1. The reference MIM structures and OTFTs without C8PA monolayer were also prepared. The dielectric with and without C8PA monolayer is referred to as AlOx/C8PA and AlOx, respectively.

![Figure 1: OTFT cross-section.](image)

The capacitance of AlOx and AlOx/C8PA dielectrics was measured from 1 kHz to 1 MHz and the current-voltage characteristic between 3 and -3 V.

OTFT transfer characteristics were measured at drain-to-source voltage ($V_{DS}$) of -0.1 and -3 V while sweeping the gate-to-source voltage ($V_{GS}$) from 1 to -3 V. The OTFT field-effect mobility ($\mu$) and threshold voltage ($V_{TH}$) were calculated from the transfer characteristics using the standard MOSFET equations. We define the off-current ($I_{OFF}$) and the on-current as the minimum and maximum drain current at $V_{DS} = -3$ V, respectively. The subthreshold slope ($S = \partial V_{GS}/\partial \log(I_D)$) is extracted from the slope of log $I_D$ versus $V_{GS}$. The output characteristics were measured for $V_{GS}$ of 0, -0.5, -1.0, -1.5, -2.0, -2.5, and -3.0, while sweeping $V_{DS}$ between 0 and -3 V. Finally, the surface topography of pentacene was studied by atomic force microscopy (AFM) using the tapping mode.
3. Results and discussion
This section presents the properties of MIM and OTFT devices with AlO<sub>x</sub>/C<sub>x</sub>PA dielectric. Their properties were studied with respect to C<sub>x</sub>PA deposition rate and the reference AlO<sub>x</sub> devices.

3.1 Dielectric Properties
The mean and standard deviation of capacitances were calculated from several MIM structures and the values at 100 kHz are shown in Figure 2(a). Figure 2(b) presents the gate leakage current density of AlO<sub>x</sub>/C<sub>x</sub>PA and AlO<sub>x</sub> dielectrics.

![Figure 2: Capacitance (a) and leakage current density (b) of AlO<sub>x</sub>/C<sub>x</sub>PA bi-layer dielectric.](image)

The capacitance of the AlO<sub>x</sub>/C<sub>x</sub>PA bi-layer dielectric is ~ 0.34 μF/cm<sup>2</sup> for C<sub>x</sub>PA deposition rate of 0.1 Å/s. The capacitance slightly decreases with increasing C<sub>x</sub>PA deposition rate, reaching a value of ~ 0.30 μF/cm<sup>2</sup> at the rate of 7 Å/s. The reference capacitance of AlO<sub>x</sub> is ~ 0.41 μF/cm<sup>2</sup>. The lower dielectric capacitance of AlO<sub>x</sub>/C<sub>x</sub>PA versus AlO<sub>x</sub> confirms the presence of C<sub>x</sub>PA for all deposition rates. Previously, we confirmed that C<sub>x</sub>PA deposited in vacuum at a rate of 3 Å/s is chemically bonded to AlO<sub>x</sub> [15]. Since the post-deposition annealing of the C<sub>x</sub>PA layer at the temperature of ~ 160°C previously led to removal of all physisorbed C<sub>x</sub>PA molecules, one would conclude that C<sub>x</sub>PA molecules are chemically bonded to AlO<sub>x</sub> regardless of their deposition rate. Nevertheless, the slightly lower capacitance obtained for higher deposition rate suggests a slightly larger thickness and/or lower relative permittivity of the organic monolayer.

The gate leakage current density of AlO<sub>x</sub>/C<sub>x</sub>PA and AlO<sub>x</sub> are ~ 4×10<sup>-8</sup> and ~1×10<sup>-7</sup> A/cm<sup>2</sup> at 3 V, respectively. There is no observable difference in the gate leakage current density with deposition rate. The leakage current obtained with our vapour-deposited C<sub>x</sub>PA monolayer is comparable to the solution processed alkyl phosphonic acid monolayers by Jedaa et al [6], Wöbkenberg et al. [10], Ma et al [11], and Klauk et al. [16].

3.2 OTFT characteristics
Figure 3 shows the transfer and output characteristics of OTFTs with C<sub>x</sub>PA deposited at the rate of 7 Å/s. The channel width (W) and length (L) is 1000 and 30 μm, respectively. The drain current of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs is about four orders of magnitude higher than the gate current at V<sub>DS</sub> = V<sub>DS</sub> = -3.0 V. Also, the transistors have good linear and saturation characteristics.

![Figure 3: Transfer (a) and output (b) characteristics of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs.](image)

The mean and standard deviation of field-effect mobility, threshold voltage, subthreshold slope, and off-current are presented in Figure 4 (a)-(d), respectively. On/off current ratio of transistors with 30 μm channel length is shown in Figure 5. Figure 6(a) shows the AFM surface image of 50-nm-thick pentacene deposited on AlO<sub>x</sub>. Figure 6(b) shows the surface of the same pentacene layer grown on AlO<sub>x</sub>/C<sub>x</sub>PA deposited at the rate of 7 Å/s.

As shown in Figure 4(a), the field-effect mobility of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs increases from 0.039 to 0.061 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> as the C<sub>x</sub>PA deposition rate increases from 0.1 to 7 Å/s. The mean field-effect mobility of the reference AlO<sub>x</sub> OTFTs is ~ 0.038 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The threshold voltage is ~1.55 V for all AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs regardless of the C<sub>x</sub>PA deposition rate. The mean threshold voltage of the reference AlO<sub>x</sub> OTFTs is -1.75 V. The lower threshold voltage of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs is an advantage for low-voltage device operation [17].

The off-current of OTFTs with AlO<sub>x</sub> is 3.2×10<sup>-12</sup> A. The off-current is lower for AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs; it decreases from 2.3×10<sup>-12</sup> to 1.3×10<sup>-13</sup> A with increasing C<sub>x</sub>PA deposition rate. Similarly, the subthreshold slope of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs is reduced from 104 to 89 mV/decade with increasing C<sub>x</sub>PA deposition rate, while the reference AlO<sub>x</sub> OTFTs have the subthreshold slope of 105 mV/decade. At the deposition rate of 7 Å/s, the subthreshold slope is close to the best reported value for pentacene-based organic thin-film transistors [11, 16] and slightly higher than that reported by Acton et al. [18].

Figure 5 shows that the on/off current ratio is higher than 10<sup>5</sup> for all OTFTs with L = 30 μm and W = 1000 μm. At the lowest deposition rate, the current ratio of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs is an advantage for low-voltage device operation [17].

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3.3 OTFT parameters and pentacene morphology
The mean and standard deviation of field-effect mobility, threshold voltage, subthreshold slope, and off-current are presented in Figure 4 (a)-(d), respectively. On/off current ratio of transistors with 30 μm channel length is shown in Figure 5. Figure 6(a) shows the AFM surface image of 50-nm-thick pentacene deposited on AlO<sub>x</sub>. Figure 6(b) shows the surface of the same pentacene layer grown on AlO<sub>x</sub>/C<sub>x</sub>PA deposited at the rate of 7 Å/s.

As shown in Figure 4(a), the field-effect mobility of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs increases from 0.039 to 0.061 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> as the C<sub>x</sub>PA deposition rate increases from 0.1 to 7 Å/s. The mean field-effect mobility of the reference AlO<sub>x</sub> OTFTs is ~ 0.038 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The threshold voltage is ~1.55 V for all AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs regardless of the C<sub>x</sub>PA deposition rate. The mean threshold voltage of the reference AlO<sub>x</sub> OTFTs is ~1.75 V. The lower threshold voltage of AlO<sub>x</sub>/C<sub>x</sub>PA OTFTs is an advantage for low-voltage device operation [17].

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of 7 Å/s is comparable to the best values reported previously for low-voltage OTFTs. In addition, it is similar to on/off current ratio obtained for alkyl phosphonic acids with intermediate alkyl chain length (10-14 carbon atoms) [6, 7, 19].

Finally, the higher-field effect mobility achieved with AlO_x/C_8PA dielectric results in higher transistor on-current, even though the dielectric capacitance is lower than that of AlO_x.

4. Conclusion
To date alkyl phosphonic acid monolayers were assembled from solutions only. Our developed process provides a ‘dry’ alternative to the existing solution deposition, while being compatible with large-area, roll-to-roll processing. The transistors allow low-voltage operation of less than 3 V. The drain current of AlO_x/C_8PA OTFTs is 10^4 times higher than the gate leakage current, showing good electrical insulation provided by AlO_x/C_8PA bi-layer. In addition, the performance of AlO_x/C_8PA OTFTs is superior to that of AlO_x OTFTs.

The higher C_8PA evaporation rate leads to higher field-effect mobility and on/off current ratio. The off-current and subthreshold slope are reduced with increasing C_8PA evaporation rate. At the highest C_8PA evaporation rate of 7 Å/s, the highest field-effect mobility of ~ 0.061 cm^2/Vs, the threshold voltage of -1.49 V, the lowest subthreshold slope of 89 mV/decade, the minimum off-current of 1.32 × 10^-12 A and the maximum on/off current ratio of ~10^6 are obtained. At present it is not clear how the evaporation rate affects the structural properties of the C_8PA monolayer, but relevant measurements are underway. Finally, we would like to mention that the developed gate dielectric is not limited to transistors based on pentacene and may be implemented in other transistor technologies.

Pentacene grain size is less than 100 nm (see Figure 6(a)) when it is deposited on AlO_x. This small grain size is correlated with lower field-effect mobility of AlO_x OTFTs. Pentacene deposited on AlO_x/C_8PA surface exhibits different morphology with grain size of about 150-200 nm (see Figure 6(b)). C_8PA deposition rate has only minor effect on pentacene morphology, even though the field-effect mobility in the corresponding OTFTs varies. This variation in the field-effect mobility could result from different C_8PA structural properties. Previously we observed that the C_8PA growth temperature affected the structural properties of the organic monolayer [15]. The effect of the C_8PA deposition rate on the structural properties of the self-assembled monolayer is under investigation.

Figure 4: OTFT field-effect mobility (a), threshold voltage (b), off-current (c), and subthreshold slope (d) as functions of C_8PA evaporation rate. The reference aluminium oxide is presented as dashed line.

Figure 5: On/off current ratio of OTFTs with AlO_x/C_8PA and AlO_x (dashed line) gate dielectric. The channel width and length are 1000 and 30 µm, respectively.

Figure 6: AFM images of pentacene deposited on AlO_x (a) and AlO_x/C_8PA (b) dielectrics. C_8PA was deposited at a rate of 7 Å/s.
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6. References


