

**Effect of substrate temperature on vapour-phase self-assembly
of n-octylphosphonic acid monolayer
for low-voltage organic thin-film transistors**

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ABSTRACT

N-octylphosphonic acid (C₈PA) monolayer was self-assembled on aluminium oxide (AlO_x) from vapour in vacuum, while the substrate temperature was varied between 25 and 150°C. The capacitance, water contact angle measurement, Fourier transform infrared (FTIR) spectroscopy, and atomic force microscopy (AFM) confirmed the presence of C₈PA on AlO_x for all growth temperatures. However, the structural and electrical properties of such monolayers depend on their growth temperature. The minimum surface roughness of 0.36 nm, the maximum water contact angle of 113.5°±1.4°, the lowest leakage current density of ~ 10⁻⁷ A/cm² at 3 V, and the capacitance of 0.43 μF/cm² were obtained for AlO_x/C₈PA bi-layers with C₈PA deposited at 25°C. The elevated temperature led to increased surface roughness,

decreased water contact angle, increased leakage current, inferior molecular ordering, and lower molecular coverage; while the effect on the chemisorption of the phosphonate was minimal. Methyl and methylene FTIR vibrations associated with C₈PA aliphatic tails exhibited similar centre-peak wavenumbers to those observed for C₈PA monolayers assembled from solutions, presenting a viable ‘dry’ alternative to the existing solution process.

The substrate temperature applied during C₈PA self-assembly also affected the parameters of pentacene thin-film transistors with AlO_x/C₈PA gate dielectrics. The increase in the growth temperature from 25 to 150°C decreased the field-effect mobility from 0.060 to 0.026 cm²/Vs and increased the threshold voltage from -1.19 to -1.38 V, while maintaining the off-current at or below 10⁻¹² A and the subthreshold slope near 90 mV/decade.

Key words: Self-assembled monolayer, deposition temperature, vapour-phase, vacuum growth, organic thin-film transistor

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1. Introduction

Self-assembled monolayers of alkyl thiols [1–3], alkyl silanes [4–6], carboxylic acids [7], or alkyl phosphonic acids [8–15] are typically prepared in solutions. Monolayers based on alkyl phosphonic acids can be assembled on aluminium oxide [7–10], hafnium oxide [11], nitinol [12], gallium nitride [13], [14], and titanium oxide [15]. Vapour phase growth of octadecanethiol on gallium arsenide [1], (18-phenoxyoctadecyl) trichlorosilane on silicon dioxide [16], alkyl amines on chlorine-functionalized silicon surface [17], and octadecyltrimethoxysilane on silicon dioxide [18] was demonstrated as well. Recently, we demonstrated a vapour-phase self-assembly of n-octylphosphonic acid (C₈PA) on aluminium oxide (AlO_x) in vacuum [19]. Since vapour-phase self-assemblies are compatible with roll-to-roll processing and avoid using orthogonal solvents, they are of major interest for organic electronics.

During the solution self-assembly of alkyl thiols, alkyl silanes, carboxylic or alkyl phosphonic acids, the head group reacts with the metal/oxide, while the aliphatic chain orients away from the underlying surface. In such a case the monolayer assembly depends on the chemistry of the organic molecule and the underlying surface, the length of the aliphatic chain, concentration and temperature of the solution, and the adsorption time [7, 14, 20]. Vapour phase self-assembly of organic monolayers is much less explored. Previous research studied the exposure time [1], or used a special molecular design with different chemical properties of the head and tail groups of the organic molecule [16].

Our method of self-assembly of C₈PA monolayer is performed in vacuum. A layer corresponding to the thickness of several C₈PA monolayers is thermally evaporated on the surface of aluminium oxide to assure complete coverage. This is followed by the thermal desorption of all physisorbed molecules, leading to the monolayer formation [19]. This paper presents experimental evidence that such a monolayer is indeed chemically bonded to the

underlying AlO_x . In addition, we studied the effect of C_8PA growth temperature on the monolayer formation. Similar to the growth of inorganic materials, the substrate temperature is expected to affect the chemisorption of C_8PA to AlO_x as well as the overall growth kinetics, leading to different structural and electrical properties of the formed monolayer. Finally, the effect of C_8PA growth temperature was also studied in metal-insulator-metal (MIM) structures and organic thin-film transistors that implemented ultra-thin $\text{AlO}_x/\text{C}_8\text{PA}$ dielectric.

2. Experimental details

AlO_x and $\text{AlO}_x/\text{C}_8\text{PA}$ samples for structural and surface characterization were prepared as follows. AlO_x was prepared by exposing aluminium deposited on Eagle 2000 glass to UV/ozone in ambient atmosphere [21]. To prevent the contamination of the oxidizing surface, UVOCS UV/ozone cleaner was enclosed under a Hepa filter. Approximately 10-nm-thick C_8PA layer was thermally evaporated on the surface of AlO_x at a pressure of $< 1 \times 10^{-6}$ mbar using the procedure described in [19]. Afterwards, the substrate temperature was raised to 160°C for 3 hours to remove all physisorbed molecules. C_8PA layer was thermally evaporated at substrate temperatures of 25, 75, 125, or 150°C . Fourier-transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM) and water contact angle (WCA) measurements were performed on such structures in ambient air. In addition, measurements of the AlO_x reference surface were performed for comparison. FTIR was measured with Nicolet 380 spectrometer. The surface topography of $1 \times 1 \mu\text{m}^2$ areas was studied using diInnova AFM in the tapping mode. Contact angles of $\sim 5\text{-}6 \mu\text{l}$ droplets of Millipore water were measured with Krüss DSA30B goniometer.

Metal-insulator-metal (MIM) or capacitor structures were fabricated to study the electrical properties of the above mentioned AlO_x and $\text{AlO}_x/\text{C}_8\text{PA}$ dielectrics. 20-nm-thick

aluminium lines were deposited on glass substrate. These lines were capped by a gold layer on one end to prevent their oxidation. UV/ozone oxidation of aluminium and C₈PA monolayer growth at temperatures of 25, 75, 125, and 150°C followed the same procedure described above. Finally, 50-nm-thick gold contacts were evaporated to complete the MIM structures. Several MIM structures were fabricated for each C₈PA growth temperature. In addition, AlO_x MIM structures with no C₈PA monolayer were prepared as reference.

Bottom-gate, top-contact organic thin-film transistors (OTFTs) based on thermally evaporated pentacene followed the same fabrication procedure up to and including the C₈PA monolayer. A 50-nm-thick pentacene layer was deposited at a pressure of $\sim 1 \times 10^{-7}$ mbar. The transistors were completed by evaporating gold source and drain contacts and their cross-section is shown in Figure 1. All fabrication steps were performed by using shadow masks. In addition, transistors with AlO_x dielectric (no C₈PA monolayer) were fabricated as a reference.

The fabricated transistors have channel lengths of 30, 50, 70, and 90 μm and a channel width of 1000 μm . The $W/L > 10$ to minimize the effect of the extending electric field lines that could lead to an overestimate of the field-effect mobility [22]. Transistors and capacitors were fabricated side by side and all evaporation steps were conducted in Minispectros (Kurt J. Lesker) high vacuum system ($< 10^{-7}$ mBar) enclosed in a N₂-filled glove box with O₂ and H₂O content less than 1 particle-per-million.

All reference samples (capacitors, transistors and samples for material characterization) with AlO_x dielectric only (no C₈PA monolayer) underwent a 3-hour anneal at 160°C. This anneal was applied to the Al/AlO_x structure before any subsequent steps were performed. This was to assure that if any changes in Al/AlO_x occur during the post-annealing of the C₈PA layer, these would be replicated in the reference samples. Consequently, any measured difference between the structure/device containing AlO_x/C₈PA and that containing AlO_x would result from the C₈PA monolayer.

The capacitor and transistor measurements were performed with Agilent B1500A semiconductor device analyzer under ambient environmental conditions. The dielectric capacitance of MIM structures was measured between 1 kHz and 1 MHz. The MIM current density was measured between -3 and 3 V. The transfer and output characteristics of the OTFTs were measured in a sweep mode. Transistor hysteresis was obtained by stepping the gate voltage from positive to negative values and back. Pentacene morphology of $2 \times 2 \mu\text{m}^2$ areas was studied by AFM.

3. Results

3.1 Material characterization of C₈PA monolayer

The water contact angles of AlO_x and AlO_x/C₈PA surfaces as function of the C₈PA growth temperature are given in Table 1. The water contact angle of AlO_x is $30.8 \pm 0.7^\circ$ while AlO_x/C₈PA exhibits values larger than 107° for all deposition temperatures, showing that AlO_x is hydrophilic, while AlO_x/C₈PA is hydrophobic irrespective of the growth temperature. However, there is a slight decrease in the water contact angle with increasing C₈PA deposition temperature. The maximum value of $113.5^\circ \pm 1.4^\circ$ and the minimum value of $107.9^\circ \pm 0.8^\circ$ are obtained for n-octylphosphonic acid monolayer deposited at 25 and 150°C , respectively.

Table 1: Water contact angle of AlO_x/C₈PA surface as a function of C₈PA growth temperature. AlO_x is added as a reference.

Growth temperature ($^\circ\text{C}$)	Water contact angle ($^\circ$)
25	113.5 ± 1.4
75	112.1 ± 1.4
125	111.1 ± 0.7
150	107.9 ± 0.8
AlO _x reference	30.8 ± 0.7

The surface topography of $\text{AlO}_x/\text{C}_8\text{PA}$ deposited at temperature of 25, 125, and 150°C is shown in Figure 2(b)-(d), respectively. Figure 2(a) depicts the reference AlO_x surface. The root mean square (RMS) surface roughness of $\text{AlO}_x/\text{C}_8\text{PA}$ deposited at 25, 125 and 150°C is 0.36, 0.38 and 0.54 nm, respectively, while the surface roughness of AlO_x is 0.46 nm.

Figure 3 shows the results of FTIR measurements of C_8PA monolayer self-assembled on AlO_x at temperatures of 25, 75 and 150°C and the reference AlO_x layer. Although the spectrum was measured from 4000 to 600 cm^{-1} , only relevant sections of the spectrum are shown in Figures 3(a) and (b). Strong broad vibration around $\sim 930 \text{ cm}^{-1}$ was not used in the evaluation due to the major contribution from the Al-O stretch of AlO_x . Figure 3(a) shows the region from 2700 to 3100 cm^{-1} that corresponds to the symmetric and asymmetric CH_2 and CH_3 stretching modes. Figure 3(b) shows the region from 1025 to 1300 cm^{-1} that includes the absorption of the P=O groups of C_8PA and a broad peak around 1100 cm^{-1} that was previously interpreted as evidence of chemisorption of the phosphonate group to the surface of AlO_x [23]. The broad absorption peak in the reference AlO_x sample located near 1100 cm^{-1} overlaps with the band of the phosphonate salts and is associated with the surface Al-OH groups [24].

The symmetric and asymmetric CH_2 and CH_3 stretching modes observed in the reference sample are due to the presence of methane in the ambient atmosphere. These modes become stronger in the $\text{AlO}_x/\text{C}_8\text{PA}$ layers where the aliphatic chain of the phosphonic acid contributes to the absorbance. For C_8PA grown at 25°C their centre positions lay at $\nu_s(\text{CH}_2) = 2853 \text{ cm}^{-1}$, $\nu_a(\text{CH}_2) = 2925 \text{ cm}^{-1}$, $\nu_s(\text{CH}_3) = 2874 \text{ cm}^{-1}$, and $\nu_a(\text{CH}_3) = 2961 \text{ cm}^{-1}$. With the increasing C_8PA deposition temperature all maxima are marginally shifted to higher wavenumbers, indicating an increased molecular disorder with increasing growth temperature. For C_8PA grown at 150°C $\nu_s(\text{CH}_2) = 2854 \text{ cm}^{-1}$, $\nu_a(\text{CH}_2) = 2926 \text{ cm}^{-1}$, $\nu_s(\text{CH}_3) =$

2878 cm^{-1} , and $\nu_a(\text{CH}_3) = 2961 \text{ cm}^{-1}$. The full width at half maximum (FWHM) of the asymmetric CH_2 stretch does not change, while the FWHM of the symmetric CH_2 stretch is increased by 5 cm^{-1} when the C_8PA deposition temperature is raised from 25 to 150°C. While the amplitude and integral area of all vibration bands between 2700 and 3100 cm^{-1} are similar for C_8PA deposited at 25 and 75°C, they are visibly reduced for C_8PA deposited at 150°C.

The reference AlO_x sample exhibits a weak vibration at 1263 cm^{-1} assigned to the methyl group of the ambient CH_4 . This is reproduced in all $\text{AlO}_x/\text{C}_8\text{PA}$ structures. In addition, C_8PA contributes 3 new vibration bands with centre positions at ~ 1204, 1226, and 1244 cm^{-1} assigned to the $\text{P}=\text{O}$ bond of the phosphonic acid [25]. While the amplitude and integral area of these three vibration bands are similar for C_8PA deposited at 25 and 75°C, they are visibly reduced for C_8PA deposited at 150°C. The centre position of the two stronger peaks located near 1204 and 1244 cm^{-1} and their FWHM do not change with C_8PA growth temperature. The broad absorption band centred near 1110 cm^{-1} is present in all samples. In the $\text{AlO}_x/\text{C}_8\text{PA}$ structures the main contribution to this vibration band is from $\text{Al}-\text{O}-\text{P}$ stretch mode [23] due to the phosphonate head group bonded to the surface of aluminium oxide. The integral intensity of this band is slightly smaller for C_8PA deposited at 25°C, if compared to that deposited at 75°C, and much larger than that of C_8PA deposited at 150°C.

Finally, molecules containing $\text{P}-\text{OH}$ groups exhibit two broad bands of the OH stretching vibration appearing near 2600 cm^{-1} and 2200 cm^{-1} [25]. Neither of these absorption bands is observed in the measured spectrum, indicating that the chemisorption of all C_8PA molecules proceeds via the $\text{P}-\text{OH}$ groups at all growth temperatures.

3.2 MIM electrical characterization

The total capacitance per unit area of AlO_x and $\text{AlO}_x/\text{C}_8\text{PA}$ MIM structures at 100 kHz is shown in Figure 4(a). The mean capacitance of AlO_x is $0.57 \mu\text{F}/\text{cm}^2$. The $\text{AlO}_x/\text{C}_8\text{PA}$ bi-layer has capacitance of $0.43 \mu\text{F}/\text{cm}^2$ for C_8PA deposited at 25°C . This value is slightly higher for C_8PA deposition temperatures of 75 and 125°C . When C_8PA is grown at 150°C , the capacitance value reaches $0.54 \mu\text{F}/\text{cm}^2$. In the case of bi-layer dielectric, the total capacitance consists of the oxide capacitance (C_{AlO_x}) and the capacitance of the phosphonic acid monolayer ($C_{\text{C}_8\text{PA}}$) connected in series and is given by $1/C_{\text{diel}} = 1/C_{\text{AlO}_x} + 1/C_{\text{C}_8\text{PA}}$. C_{AlO_x} is the reference oxide capacitance ($0.57 \mu\text{F}/\text{cm}^2$) that is identical in all MIM structures. C_8PA thickness shown in Figure 4(b) is calculated from the known values of C_{diel} and C_{AlO_x} using the relative permittivity of 2.1 [26].

The leakage current density of $\text{AlO}_x/\text{C}_8\text{PA}$ and the corresponding AlO_x are shown in Figure 5. The leakage current density of AlO_x is $\sim 3 \times 10^{-7} \text{ A}/\text{cm}^2$ at -3 V . This value is reduced to $\sim 1 \times 10^{-7} \text{ A}/\text{cm}^2$ when the AlO_x is functionalized with the vacuum-grown C_8PA monolayer. The deposition temperature of the organic monolayer has only minor effect on this value, leading to the lowest current when the layer is grown at 25°C .

3.3 OTFT properties

In this section, the properties of OTFTs with both AlO_x and $\text{AlO}_x/\text{C}_8\text{PA}$ gate dielectric are presented. The output characteristics of $\text{AlO}_x/\text{C}_8\text{PA}$ OTFTs with C_8PA deposited at 25°C are shown in Figure 6(a). Figure 6(c) shows the output characteristics of the reference AlO_x OTFT. The on-current increases by a factor of three when AlO_x is coated with C_8PA monolayer deposited at 25°C . The corresponding transfer characteristics measured for $V_{\text{DS}} =$

-0.1 and -2 V are shown in Figures 6(b) and (d). The transistor hystereses are shown in Figure 6(e).

The field-effect mobility and threshold voltage are extracted using the standard MOSFET equations. The on- and off-currents are the maximum and minimum drain currents at $V_{DS} = -2$ V. The mean and standard deviations are calculated for OTFTs with varying C₈PA growth temperature. Figure 7(a)-(d) depicts the field-effect mobility, threshold voltage, off-current, and the subthreshold slope as a function of C₈PA growth temperature, respectively. The corresponding parameters of AlO_x OTFTs are also included in the respective figures.

When the C₈PA deposition temperature is raised from 25 to 150°C, the field-effect mobility decreases from 0.060 to 0.026 cm²/Vs. Although the mean value of the threshold voltage slightly increases from -1.19 to -1.25 V when the growth temperature is raised from 25 to 75°C, the values are similar within the error of measurement. On the other hand, higher threshold voltage of -1.38 V is achieved for OTFTs implementing C₈PA deposited at 150°C. The field-effect mobility and the threshold voltage of the reference AlO_x OTFT are 0.023 cm²/Vs and -1.26 V, respectively. C₈PA growth at 25°C leads to the off-current of $\sim 10^{-12}$ A which is similar to the off-current of the reference OTFT. This value is slightly reduced for OTFTs implementing C₈PA grown at elevated temperature, reaching a minimum value of $\sim 5 \times 10^{-13}$ A at deposition temperature of 125°C. The subthreshold slope of AlO_x/C₈PA OTFTs is comparable to that of the reference AlO_x OTFTs. Mean values of ~ 90 mV/decade are observed and the variation in the C₈PA growth temperature leads to similar values of the subthreshold slope. The subthreshold slope of the reference AlO_x OTFTs is 93 mV/decade.

AFM surface images of pentacene grown on top of AlO_x and AlO_x/C₈PA are shown in Figure 8. Figures 8(a) and (b) show pentacene deposited on C₈PA grown at 25 and 125°C, respectively, while Figure 8(c) shows pentacene deposited on reference AlO_x. The grain

diameter is around 300 nm for C₈PA deposited at 25°C. Both AlO_x and C₈PA grown at 125°C lead to smaller pentacene grains.

4. Discussion

The stability and ordering of alkyl phosphonic acid SAMs in solution depends on the affinity toward metal oxide [27], used solvents [28], and the post-deposition annealing treatment [14]. After coating AlO_x with thermally evaporated C₈PA monolayer a large change in the water contact angle from ~30° to more than 107° is observed, confirming the change from hydrophilic to hydrophobic surface. This is a result of the attachment of the phosphonate group to the AlO_x surface, while the aliphatic tails are oriented away from the binding surface. With increasing C₈PA growth temperature from 25 to 150°C, the water contact angle decreases from 113.5°±1.4° to 107.9°±0.8°. This reduction in the contact angle correlates with increased surface roughness of C₈PA monolayer (see AFM results) and increased disorder in the molecular ordering (see FTIR results). Similar range of water contact angles was obtained for alkyl phosphonic acid monolayers self-assembled from solutions [8, 27]. The surface exposure of methylene groups in addition to the methyl groups previously resulted in lower water contact angle [29], which would explain the observed reduction in the water contact angle of C₈PA monolayers deposited at elevated temperature.

The minimum AFM surface roughness is achieved for C₈PA deposited at 25°C. This value is smaller than that achieved for the underlying AlO_x surface. The surface roughness of C₈PA is increasing with its increasing growth temperature. For C₈PA monolayer grown at 150°C, the surface roughness is ~ 0.54 nm which is higher than that of the underlying AlO_x. This is likely a consequence of reduced C₈PA molecular ordering and surface coverage (see capacitance data).

Phosphonic acids self-assembled from solutions strongly attach to aluminium oxide [8]. The attachment is facilitated by the head group. It was proposed that during the solution self-assembly of the phosphonic acid monolayer the head group reacts with the surface hydroxyl groups of the aluminium oxide [10]. This reaction proceeds via an acid-base condensation mechanisms in three stages and ultimately results in tridentate binding configuration of the phosphonic acids [30–32]. Initially the two P–OH groups of the C₈PA head group react with two Al–OH groups on the surface of aluminium oxide to produce two P–O–Al bonds of a bidentate complex. In the last step, the P=O group forms the third P–O–Al bond and converts the bidentate complex into a tridentate one. (P–O–Al stretch mode is located near 1100 cm⁻¹ [10].) Even though the mechanism of this reaction is not fully understood, three possible reaction paths have been proposed for the P=O group. In the first case the P=O groups react with the surface Al atoms, where the number of unsaturated Al atoms determines the maximum number of the tridentate complexes [33]. In the second case the –OH groups on the surface of aluminium oxide are protonated and released as water, allowing the formation of the P–O–Al bond [34]. In the third case, a hydrogen bond is formed between the P=O group and the surface hydroxyl group (P=O···H–O) [9]. Tridentate bonding was observed by Hotchkiss et al. [35] and Giza et al. [10] for n-octadecylphosphonic acid (C₁₈PA) on ZnO and AlO_x, respectively; but it was not observed for C₁₈PA deposited on ITO [23].

The centre positions of the symmetric and asymmetric CH₂ and CH₃ vibration bands indicate less ordered molecular structure, as a result of the weak interaction between short aliphatic tails. These values are however similar to C₈PA monolayers self-assembled from solutions [36]. The broad band of AlO_x/C₈PA near 1100 cm⁻¹ indicates condensation reaction of Al–OH and C₈PA head group. The absence of P–OH absorption bands means that both P–OH sites of the C₈PA head group are consumed in the chemisorption process regardless of

the C₈PA growth temperature. The integral area of the band near 1100 cm⁻¹ is similar for C₈PA grown at 25 and 75°C. However, when C₈PA is grown at 150°C, the area is substantially smaller. For all C₈PA growth temperatures, small P=O vibrations are observed between 1200 and 1250 cm⁻¹, suggesting that some C₈PA molecules exhibit bidentate bonding. Finally, the reduction in the integral intensity of all vibration peaks for C₈PA deposited at 150°C is associated with fewer chemisorbed molecules. In summary, the FTIR measurements confirm that the increasing C₈PA growth temperature leads to increased molecular disorder, while the chemisorption process of the phosphonate is not visibly affected.

From Figure 4, it can be observed that the increase in C₈PA growth temperature from 25 to 125°C leads to a minor increase in the capacitance value. This minor increase is correlated with negligible increase in the C₈PA surface roughness and a decrease in the water contact angle. Even though the change in the C₈PA growth temperature from 25 to 125°C leads to gradual minor deterioration of the C₈PA material properties, best parameters are obtained at the lowest growth temperature of 25°C. Large increase in the capacitance occurs for C₈PA grown at 150°C, accompanied by a larger increase in the C₈PA surface roughness and a decrease in the water contact angle. This is an indication of a much reduced coverage of AlO_x with C₈PA molecules. This is supported by the overall reduction in the integral intensity of all vibration bands associated with C₈PA. According to Hauffman et al. [9], low monolayer coverage is related to “lying down” phase, while high coverage leads to a “standing up” phase. The high capacitance value of C₈PA monolayer grown at 150°C supports the fact that C₈PA molecules are lying down while they are standing up for monolayer grown at 25°C. The monolayer thickness calculated from the capacitance value is ~ 1 nm for C₈PA grown at 25°C, while it is reduced to ~ 0.2 nm for C₈PA grown at 150°C.

C₈PA monolayer grown at 25°C also leads to the lowest leakage current as shown in Figure 5. The higher growth temperature results in slightly larger leakage current density. This is most likely the consequence of a more disordered and/or thinner C₈PA monolayer.

In summary, the highest water contact angle, lowest surface roughness, best molecular ordering, lowest capacitance, and lowest leakage current density are achieved for AlO_x/C₈PA with C₈PA deposited at 25°C.

Figures 6(a) and (c) compare output characteristics of transistors with the same contact geometries. The on-current is three times higher for transistors implementing AlO_x/C₈PA if compared to the reference transistors with AlO_x only. Along with better insulating properties of AlO_x/C₈PA dielectric, the increase in the on-current is related to pentacene growth on AlO_x/C₈PA when compared to AlO_x surface. The same pentacene deposition conditions resulted in different pentacene morphology on AlO_x/C₈PA and AlO_x as shown in Figure 8(a) and (c), respectively. Previously Ashall et al. [37] reported that AlO_x, AlO_x/C₁₈PA, and AlO_x/PMMA dielectrics exhibit different pentacene morphology irrespective of the same pentacene growth parameters. Their observation is consistent with our findings.

Pentacene morphology is also dependent on the surface roughness and the ordering of SAM [38, 39]. We observed that C₈PA growth temperature affected the pentacene morphology. The average pentacene grain size on AlO_x/C₈PA is around 300 nm and it is larger than that reported in [19, 40], although not yet fully optimized. The largest grain size for C₈PA grown at 25°C is correlated with the lowest surface roughness, highest water contact angle and more ordered C₈PA SAM. This consequently results in the highest field-effect mobility of ~ 0.060 cm²/Vs and lowest threshold voltage of -1.19 V. The field-effect mobility is about one order of magnitude lower than the mobility of similar OTFTs with

pentacene dendrites of 2-3 μm in size [38]. The lower mobility in our OTFTs is likely a result of much smaller pentacene grains of ~ 300 nm in diameter.

Higher C₈PA deposition temperature also leads to an increase in the threshold voltage while the subthreshold slope is not affected. Comparing the threshold voltages of all OTFTs, one would infer that low C₈PA molecular coverage with laying down aliphatic tails leads to higher threshold voltage. This threshold voltage is even higher than that of the reference AlO_x OTFT.

5. Conclusion

We studied the effect of substrate temperature on C₈PA self-assembly using a vacuum, vapour deposition process. The material properties (water contact angle, FTIR, and AFM) of such C₈PA monolayers were correlated with their electrical properties. In addition, C₈PA-functionalized AlO_x dielectric was implemented into OTFTs and low operating voltage of ~ 2 V was achieved.

C₈PA coverage and molecular ordering on top of AlO_x depend on the C₈PA growth temperature. The properties of the AlO_x/C₈PA dielectric and the OTFT performance are also influenced by the C₈PA growth temperature. C₈PA monolayer grown at 25°C resulted in the smallest AlO_x/C₈PA surface roughness of 0.36 nm, the largest water contact angle of $113.5^\circ \pm 1.4^\circ$ and the best molecular ordering. At the same time, the AlO_x/C₈PA with C₈PA deposited at 25°C led to the lowest leakage current density of $\sim 7 \times 10^{-8}$ A/cm² at 2 V, the capacitance of 0.43 $\mu\text{F}/\text{cm}^2$, the highest OTFT mobility of ~ 0.060 cm²/Vs and the lowest threshold voltage of -1.19 V. The increase in C₈PA growth temperature led to higher AlO_x/C₈PA surface roughness, smaller water contact angle and lower molecular ordering. Also, the AlO_x/C₈PA dielectrics with C₈PA deposited at elevated temperature led to higher leakage current density, higher capacitance, lower OTFT mobility, and higher threshold

voltage. For C₈PA deposited at 150°C, low molecular coverage with laying down aliphatic tails is observed.

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Author contributions

H.G. proposed and supervised the project. P.Š. carried out FTIR measurements and ‘Peakfit’ analysis. D.A.L. performed the water contact angle measurements. S.G. prepared all samples and carried out the remaining measurements with the corresponding data processing. S.G. and H.G. analysed the data and wrote the manuscript.

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Figure captions:

Figure 1: OTFT cross-section.

Figure 2: AFM surface image of C₈PA grown at temperature of 25 (b), 125 (c), and 150°C (d). Reference AlO_x surface is shown in (a).

Figure 3: Sections of FTIR spectra of C₈PA grown at temperatures of 25, 75, and 150°C on the AlO_x. Reference AlO_x layer is shown in each spectrum.

Figure 4: Capacitance per unit area of AlO_x/C₈PA dielectric (a) and the extracted C₈PA thickness (b) as functions of C₈PA growth temperature. The dashed line corresponds to the reference AlO_x capacitance.

Figure 5: Leakage current density of AlO_x and AlO_x/C₈PA MIM structures.

Figure 6: Output (a,c) and transfer (b,d) characteristics of OTFTs with L = 50 μm. The solid and dashed lines correspond to OTFTs with AlO_x/C₈PA and AlO_x dielectric, respectively. The hysteresis for OTFTs with L = 70 μm is shown in (e).

Figure 7: OTFT field-effect mobility (a), threshold voltage (b), off-current (c), and subthreshold slope (d) as functions of the C₈PA deposition temperature. The dashed lines represent values of the reference AlO_x OTFTs.

Figure 8: AFM images of pentacene deposited on AlO_x/C₈PA where C₈PA is grown at 25 (a) and 125°C (b). Reference sample of pentacene grown on AlO_x is shown in (c).















