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Ultra-thin Anodized Aluminium Dielectric Films: The Effect of Citric Acid Concentration and Low-Voltage Electronic Applications

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Abstract

Anodically oxidized, ultra-thin ($d < 10$ nm) aluminium films emerge as the dielectric of choice for low-cost thin film capacitors (TFCs), thin film transistors (TFTs), and bio- and chemical sensors. In this work, the dielectric properties of ultra-thin aluminium oxide films grown by anodization in aqueous solutions of citric acid (CA) have been studied. It is observed that the electrolyte strength variation from 0.1 mM to 1000 mM has virtually no influence on the chemical composition, surface morphology and the dielectric properties of the fabricated alumina films. The anodized films are very smooth having RMS area roughness around ~ 5 Å. This was further improved after deposition of *n*-octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) to ~ 4 Å. Also, the elemental analysis using EDS and XPS unambiguously confirms that the obtained oxide films are amorphous, stoichiometric Al_2O_3 without any carbon contamination. The fabricated $\text{Al}/\text{Al}_2\text{O}_3/\text{Al}$ MIM capacitors show almost ideal capacitor characteristics from 10 Hz to 100 kHz. It has been found that the OTS coating does not only improve the capacitor frequency response further but also reduces the leakage current through the dielectric layer by passivating reactive dangling bonds on the oxide surface. As a result of the favourable properties of the anodized $\text{Al}_2\text{O}_3/\text{OTS}$ films, high-performance, low threshold voltage organic thin film transistors (OTFTs) operating below 1 V are demonstrated successfully.

Index Terms: Anodization; Ultra-thin aluminium oxide; Dielectrics; Impedance spectroscopy; Organic thin film transistor (OTFT).

1. INTRODUCTION

Solution-deposited metal oxide dielectrics have drawn a lot of attention in recent years because they can be used in the fabrication of high performance thin film capacitors (TFCs) (1, 2), low-voltage thin film transistors (TFTs) (3, 4), and bio- and chemical sensors (5, 6). However, the next generation of thin film electronic devices and systems will require reduced power consumption for which the development of dielectric materials that can be inexpensively deposited on large areas as ultra-thin films is urgently needed (7). Commonly, sophisticated deposition processes such as atomic layer deposition (ALD), pulsed laser deposition (PLD), chemical vapour deposition (CVD) and radio frequency (RF) magnetron sputtering are used to grow pinhole and defects free ultra-thin oxide layers but all of them depend on controlled environment and high temperature which significantly increases the processing costs. Recently, anodic oxidation (so-called anodization) has attracted a lot of attention because it is a low cost, solution-based deposition process that can be used to fabricate high quality, ultra-thin metal oxide films (8-10). Anodization is a self-limiting and self-healing process that gives pinhole-free, homogenous oxide layers that can be grown in ambient conditions using low cost set-ups and environmentally friendly chemicals (11).

Recently, high performance capacitors and TFTs (both organic and inorganic) operating at or below 1 V using ultra-thin, anodized metals as the gate dielectric have been demonstrated (3, 9, 12). However, the material properties including composition and surface morphology of these ultra-thin oxide films have not been sufficiently studied yet. Among the metals that can be anodized, Al has proved to be the most popular because it is cheap and readily available on a wide range of substrates (13, 14). It has been shown that when processed in neutral electrolyte solutions (e.g. ammonium pentaborate, ammonium adipate, tartaric acid, etc.) the resulting barrier-type Al_2O_3 has outstanding dielectric properties (15-17). To achieve high capacitance, high dielectric

breakdown strength aluminium oxide films for thin film electronic devices, dilute solutions of citric acid (CA) in deionized (DI) water are commonly used (18, 19). However, very little is known about the influence of citric acid concentration on the dielectric properties of anodized Al films. Also, the presence of dangling bonds on the surface of metal oxides often results in poor adhesion of active materials and metal electrodes. Accordingly, unsatisfactory device performance is often obtained. Salinization using organometallic molecules, such as *n*-octadecyltrichlorosilane (OTS), which results in a monolayer on top of metal oxide surfaces, remains the most ubiquitous technique to passivate the dangling bonds and reduce the material surface roughness. However, the effect of this thin layer of organometallic molecules on the overall dielectric properties of the anodically oxidized, ultra-thin Al₂O₃/OTS insulator stacks has not been studied yet properly.

In this work, the dielectric properties of ultra-thin ($d < 10$ nm) anodized, barrier-type aluminium films grown in different citric acid concentrations are reported. It is shown that the chemical structure, surface morphology and the dielectric properties of the Al₂O₃ layers are not affected by the variation of citric acid concentrations from 0.1 to 1000 mM. This finding is in a strong contrast with the recently reported anodized aluminium and tantalum films where it was shown that electrolyte byproducts are incorporated into barrier-type anodic coatings (20, 21). The chemical composition and stoichiometry of the anodized Al films are studied using EDS and XPS, respectively. Both of them reveals that the obtained oxide films consist of stoichiometric Al₂O₃ without any carbon contamination. XRD confirms the amorphous nature of the anodized aluminium films. The fabricated capacitors using pristine Al₂O₃ show almost ideal capacitor behaviour in 10 Hz to 100 kHz frequency range. When Al₂O₃ is passivated using OTS, a further improvement of the frequency response behaviour is observed between 100 mHz to 100 kHz. The optimized TFTs using poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5'-(2,5-di(thien-

2-yl) thieno [3,2-b] thiophene)] (DPP-TTT) as the active channel layer exhibit highly reproducible characteristics with no current-voltage hysteresis, a saturation field-effect mobility $\mu_{sat} \approx 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, threshold voltage of around $V_{TH} = -0.41 \text{ V}$, subthreshold swing $SS = 155 \text{ mV/dec}$, I_{on}/I_{off} ratio $> 10^3$, and leakage current (I_G) of approximately 100 pA at 750 mV. The fabricated DPP-TTT TFTs show typical p-channel transistor behaviour demonstrating a high potential to use the optimized Al anodization process for practical organic TFT fabrication.

2. EXPERIMENTAL DETAILS

2.1 Materials and chemicals

Citric acid (CA, 99.5%), *n*-octadecyltrichlorosilane (OTS), 2-propanol (IPA, 99.5%), acetone (99.5%), poly(methyl methacrylate) (PMMA, $M_w=97k$), 1,2-Dichlorobenzene (DCB, HPLC grade), and trichloroethylene (TCE, $\geq 99.5\%$) were purchased from Sigma Aldrich/Merck India and were used as received without further purification. Poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl) thieno [3,2-b] thiophene)] (DPP-TTT) and ultra-smooth quartz coated glass substrates were purchased from Ossila Ltd., UK. 99.999% pure Al and Au pellets were purchased from Kurt J. Lesker Company, UK. Cleaning of the substrates and preparation of the citric acid electrolyte solutions were done using high purity deionized (DI) water ($18.2 \text{ M}\Omega\cdot\text{cm}$, Milli-Q Direct 8).

2.2 Anodization and fabrication of devices

Metal-insulator-metal (MIM) capacitors and organic thin film transistors (OTFTs) were fabricated on ultra-smooth, quartz coated glass substrates (Ossila Ltd., UK). First, the substrates were cleaned by sonication in acetone and IPA for 15 minutes each. The cleaning was repeated two times and then the samples were dried using dry compressed air. Subsequently, the substrates were treated

with UV-Ozone for 10 mins with emissivity maintained at 95 % to remove any organic contaminants. Then, 100 nm thick Al electrodes were thermally deposited on the substrates through a metal shadow mask (Ossila Ltd., UK) using a PRO line PVD 75 system (Kurt J. Lesker Co, UK) at the working pressure $< 2 \times 10^{-6}$ Torr. Afterwards, the substrates with the deposited Al films were immediately anodized according to the anodization procedure reported previously (22, 23). To investigate the influence of the citric acid concentration on the dielectric properties of the anodized Al, the concentration of the citric acid in the electrolyte solution was varied ranging from 0.1 mM to 1000 mM. The MIM capacitor samples were anodised to 5.0 V which results in the oxide thickness (d) about 6.5 nm (24). Similarly, Al films for the OTFT devices were anodised to 2.3 V ($d \sim 3$ nm). After anodization, the substrates were washed using high purity deionized (DI) water and dried using dry air. The prepared Al/Al₂O₃ films were then annealed by keeping them on a hot plate at 120 °C for 5 minutes. To complete the devices fabrication for MIM capacitors, 50 nm thick Al was deposited through a metal shadow mask to serve as the top electrode over anodized aluminium films. For OTS-treated MIM capacitors, before the top electrode deposition, a solution of 4.5 μ l OTS in 4 ml of trichloroethylene (TCE) was spun at 3000 rpm on top of the anodized aluminium films and dried in a vacuum oven for 20 minutes at 120 °C. OTFTs with bottom-gate bottom-contact architecture were fabricated using Al₂O₃/OTS as the gate dielectric following similar ways reported earlier with changes as required (17, 18). Briefly, 50 nm thick Au contacts were deposited on the dielectric oxide layers through a metal shadow mask ($L = 20 \mu$ m, $W = 1000 \mu$ m) (Ossila Ltd., UK) using e-beam PRO Line PVD 75 system (Kurt J. Lesker, UK) as source (S) and drain (D) electrodes. Then, a blend solution of DPP-TTT and PMMA in 1,2-Dichlorobenzene (DCB) is prepared by dissolving 0.5 wt% of each separately and then blending them together with a 7:3 ratio under continuous stirring until completely mixed. Subsequently,

the blend solution is spin coated at 2000 rpm for 120 seconds on the substrates patterned with S-D electrodes on the anodized Al pre-heated at 100 °C. To complete the OTFT fabrication, the deposited films were annealed at 100 °C for 1 hour under N₂ environment.

2.3 Characterization of thin films

Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDS) data were obtained using Apollo X SDD system coupled with a Nova Nano SEM 450 system without the top Al coating. Atomic force microscope (AFM) (NanoWizard®4 NanoScience AFM, JPK, Germany) was used to record the surface topographic images of the samples. AFM imaging was performed in tapping mode at tip setpoint 788 mV using silicon probes with force constant 40 N/m and resonance frequency 327.9 kHz. JPK data processing software was utilized to analyze AFM data. X-ray photoelectron spectroscopy (XPS) data of glass and glass/Al/ Al₂O₃ films were recorded by versatile Omicron ESCA 2SR XPS system with Mg-Kα X-ray source of energy 1253.6 eV.

2.4 Electrical Characterizations of capacitors and TFTs

Electrochemical Impedance Spectroscopy (EIS) data for all fabricated MIM capacitors were measured using Zahner Zennium Pro electrochemical workstation by connecting the working electrode at the bottom electrode. Typically, the frequency was swept from 100 mHz to 100 kHz with an AC bias amplitude set to 50 mV. Transistor characteristics were measured with Keithley 4200 SCS Source-Measure Unit and Janis ST-500 probe station at room temperature and a pressure 10⁻⁴ Torr.

3. RESULTS AND DISCUSSION

Figure 1(a) shows anodization voltage (V_A) and current (I_A) vs. time (t) profiles during the growth of aluminium oxide layer in 1 mM aqueous solution of citric acid. As expected, the applied I_A remains constant until the desired V_A is reached and then it decreases exponentially (23). In order to see whether the concentration of CA influences the speed of aluminium oxide growth, anodization time (t) vs. electrolyte concentration (C_E) for $V_A = 5.0$ V was studied. As shown in Figure 1(b), it appears that t is almost independent on C_E for six different electrolyte concentrations, i.e. 0.1, 1, 10, 100, 500 and 1000 mM. Therefore, we conclude that increasing the concentration of the citric acid by four orders of magnitude does not significantly affect the anodization time to grow ultra-thin, barrier type aluminium oxide layers. However, the anodization process involves the direct motion of aluminium and oxygen ions through the oxide layer during growth depending on the established electric field. The initial constant current regime (galvanostatic anodization regime) indicates that the formation of every oxide layer requires an increase of the potential drop to maintain the internal electric field in it constant keeping the anodization current (I_A) in the cell constant as appeared in Figure 1(a). As a result, the potential drop across the oxide layer is reached to the set anodization voltage (V_A) regime (potentiostatic anodization regime) after a while and the anodization current (I_A) starts dropping immediately which indicates the reduction of ion motion further involved with the oxide layer growth. This indicates the oxide layer growth is stopped completely and thickness of this anodized oxide layer is solely depends on the set anodization voltage (25). Assuming that the growth rate (so-called anodization ratio) of aluminium oxide in aqueous solutions of citric acid is 1.3 nm/V, the thickness of the oxide layers for all CA concentrations is the same and it is estimated to be approximately 6.5 nm (including the native oxide) (22, 23). To avoid the effect of film thickness variation on the

dielectric behaviour of samples, maintaining the same oxide film thickness for all samples is crucial. Significantly, a sharp crossover between the galvanostatic and potentiostatic anodization regime confirms that the citric acid (CA) as electrolyte doesn't dissolve the native as well as anodized oxide layer during anodization process (25). As a control experiment, anodization of aluminium was also performed in high purity deionized water relying on the autoprotolysis of water. All other process parameters were identical including electrode separation of 20 mm as in the case of anodization in CA. It is observed that the set anodization voltage ($V_A = 5.0$ V) was reached instantaneously and that the anodization current (I_A) started to decrease slowly from about $I_A = 6.5$ μ A at the beginning of the anodization process to about $I_A = 4.0$ μ A after 15 minutes of anodization as shown in the Supplementary Material Figure S1(a). Importantly, I_A started decreasing from much lower value than the set value $I_A = 15$ μ A. This clearly indicates that the applied V_A has entirely dropped across the high purity DI water medium due to its large resistance ($>$ tens of M Ω). Therefore, we conclude that in order to grow oxide on aluminium films with native oxide layer using high purity DI water as the electrolyte either the anodization voltage has to be significantly increased (e.g. $V_A \geq 100$ V) or the distance between the electrodes significantly decreased ($d \leq$ mm). Also, since the thickness of the resulting films is controlled by the duration of anodization, the anodization in high purity DI water becomes difficult for thicker insulator films as anodization times increase considerably (23). In addition, the breakdown voltage of the fabricated Al/Al₂O₃/Al MIM capacitors occurred with V_B between 1.5 V to 3.0 V, as shown in the Supplementary Material Figure S1 (b). Again, this demonstrates that the anodization of Al in water strongly depends on anodization distance (i.e. conductivity/resistivity of the anodization solution) and is much more difficult to control/reproduce than the anodization of Al in aqueous solutions of CA.

Figure 1. (a) Anodization current (I_A) and voltage (V_A) profile as a function of anodization time (t). (b) Anodization time vs. molar concentration of citric acid (CA) used for $V_A=5$ V anodization process. Inset of Fig. 1(b), chemical formula of citric acid ($\text{C}_6\text{H}_8\text{O}_7$).

To study the effect of the electrolyte concentration on the aluminium oxide surface morphology, field-emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) have been utilized. Figure 2 (a) and (b) show FE-SEM and AFM images of oxide dielectric films anodized in 1 and 1000 mM CA after annealing at 120 °C, respectively. The films appear to be very smooth and no pronounced features can be seen. AFM topography reveals that the RMS area roughness (S_q) of both aluminium oxide film surfaces are about 5 Å which confirms that the surface of the anodized Al is relatively smooth (cf. insets of Figure 2 (a) and (b), respectively). As a result, we conclude that the influence of CA concentration on the surface roughness of anodized aluminium is negligible. Intriguingly, AFM images displayed in the insets of Figure 2 (a) and (b) suggest that the obtained oxide surface has a nanograin like structure. Since it is known that anodically oxidized aluminium is amorphous (26), to understand the origin of this phenomenon, AFM topography measurements of Al films before and after anodization were also performed. As

evidenced by the AFM topography images shown in the Supplementary Material Figure S2(a), it appears that the observed nanograin like structure is due to the initial morphology of the Al films. Indeed, as supported by the XRD study shown in the Supplementary Material Figure S3, the imaged nanodomains are amorphous. Whereas the S_q of the pristine Al films is about 10 Å, the S_q of the aluminium oxide films is only 5 Å. This result shows that the anodization of Al films results in much smoother surfaces and suggests that the aluminium oxide follows the original structure of the “seed” Al. Interestingly, as shown in the the Supplementary Material Figure S2(b), the RMS area roughness of anodically oxidized aluminium oxide can be reduced further from 5 to 4 Å by the application of OTS SAM.

To study the elemental composition of the prepared oxide films, energy-dispersive X-ray spectroscopy (EDS) has been performed. Figure 2 (c) and (d) show EDS spectra of aluminium oxide prepared in 1 and 1000 mM electrolyte concentrations, respectively. The EDS data has been compiled in Table 1. The analysis of the recorded spectra confirms that there is virtually no difference in the composition of both types of films. No traces of carbon in the anodized films of aluminium presented here is in strong contrast to the citric acid anodized tantalum films reported previously where incorporation of citric acid anion was observed (20). It is also crucial to note here that the peaks appeared on EDS spectra for the elements sodium (Na), calcium (Ca), and silicon (Si) originates from the used glass substrates.

Figure 2. (a) and (b) SEM topographic images of anodized aluminium films prepared using 1 mM and 1000 mM citric acid concentrations, respectively. Scale bar for both SEM images is 300 nm. Inset of (a) and (b) shows the topographic images using AFM for both films mentioned in (a) and (b), respectively. Scale bar for both AFM images is 50 nm. (c) and (d) EDS data recorded for both above-mentioned films used to identify their elemental composition.

Table 1: EDS elemental analysis of anodized Al films for 1 and 1000 mM concentrations of citric acid.

EDS	Concentration (mM)	Na	Ca	Si	Al	O	Total
Weight%	1	7.6	6.5	34.3	13.5	38.0	100
	1000	7.5	5.0	34.7	15.4	37.4	100
Atom%	1	7.2	3.5	26.6	10.9	51.7	100
	1000	7.1	2.7	26.9	12.4	50.9	100

To determine the influence of the CA concentration on the chemical stoichiometry of the anodized Al films XPS technique was employed. The survey spectrum scan of two aluminium oxide films

anodized with CA concentration of 1 and 1000 mM are shown in the Figure 3 (a) and (d), respectively. The charging effect was adjusted for both films by considering the BE position of C1s peak at 284.8 eV of carbon-carbon bond (C-C). It has been reported that the C1s peak appears due to carbon contamination if film is exposed to a moist environment (27). As can be seen on the survey scan for both the films, the binding energy (BE) position of Al2p and O1s appeared at 74.8 and 535.8 eV, respectively, which indicates that the major components of these films are aluminium and oxygen in some composite form due to the shifting from the pristine Al2p peak. Actually, the BE position of Al2p peak for pure Al metal is located at 72.5 ± 0.3 eV. To confirm the exact composition of the films further, high-resolution spectrum of O1s have been recorded as shown in the Figure 3 (b) and (e), respectively. Here, the photoelectron peaks at 535.7 and 527.2 eV of BE positions are actually generated from the used glass substrates as shown in the inset of Figure 3(e). Therefore, the peak at BE of 531.5 eV is the characteristic spectral line from the oxygen of anodized Al films as supported by the NIST XPS database (28). Further, the high-resolution spectrum of Al2p is also recorded for BE peak at ~ 74.9 eV without any energy splitting for both films as shown in the Figure 3 (c) and (f), respectively. Deconvolution results in two peaks inside the each Al2p envelop with the BE position at ~ 74.9 eV and ~ 75.7 eV as shown in the Figure 3 (c) and (f) for the films grown using CA concentration of 1 mM and 1000 mM, respectively. These BE positions of Al2p are indicating the growth of aluminium oxide films using Al anodization in CA as a very strong evidence of Al₂O₃ composition from NIST XPS spectral line database (29, 30). Interestingly, the Al2p spectral line peak at BE ~ 75.7 eV can also indicate the presence of Al(OH)₃. However, the recorded Al2p peak here shows a FWHM value of 2.01 eV which strongly recommends that the composition of films is Al₂O₃ (31). As a result, the XPS

characterisations clearly indicate that the anodized aluminium films mostly consist of a stoichiometric Al_2O_3 .

Figure 3. (a) and (d) XPS survey scans of the anodized aluminium films grown on glass substrates using 1 mM and 1000mM concentrations, respectively. (b) and (e) high resolution spectra of O1s peak with deconvolution fittings for the same films, respectively. Inset of (e) is the high resolution spectrum of O1s peak recorded from blank glass substrate. (c) and (f) are high resolution spectra of Al2p peak with deconvolution fittings for both samples as described above.

To investigate the effect of CA concentration on the dielectric properties of ultra-thin Al_2O_3 films anodized at $V_A = 5.0$ V, electrochemical impedance spectroscopy (EIS) techniques were employed. For all EIS characterizations, the devices having meal-insulator-metal (MIM) capacitor structure as shown in Figure 4(a) as schematics were used. Since penetration of ionic species into the prepared Al_2O_3 films could have large influence on their dielectric behaviour, EIS studies of the Al_2O_3 films grown using six different CA concentrations starting from 0.1 to 1000 mM were

performed in the 100 mHz to 100 kHz frequency range as depicted in Figure 4 (b) and (c). The analysis of the EIS results enables precise quantification of the probability of carbon contamination in the form of citrate anion ($C_6H_5O_7^{3-}$) penetration. Frequency dependence of impedance (Z) and phase (ϕ) of all Al_2O_3 films are shown in Figure 4 (b) which are commonly known as Bode plots. The low frequency region for both Z and ϕ shows a plateau and a dip, respectively, due to the slow formation of space charge resulting from electrical double layer (EDL) at both metal-insulator interfaces. After the formation of the stable EDL at the interfaces, devices show almost ideal capacitive nature with phase lag of nearly $\phi \approx -90^\circ$ between 10 Hz to 100 kHz. Inset of Figure 2(b) shows the almost similar phase lag ($\phi \approx -90^\circ$) at 1.0 kHz for all six samples prepared using different CA concentrations. This strongly indicates the invariance of dielectric properties among all Al_2O_3 films. However, OTS coating on top of the Al_2O_3 films improves overall frequency response between 100 mHz to 100 kHz with slight decrease in phase lag as shown in Figure 2(b). Specific capacitances ($C_i = \epsilon_0 \epsilon' / d$) for all samples are calculated from the measured impedance data and shown in Figure 4(c) in the same frequency range (i.e. from 100 mHz to 100 kHz). Here, the OTS coating on Al_2O_3 films again improves the frequency response as steep region at the lower frequency side of the spectrum is significantly minimized with a small sacrifice of the C_i value. It is also important to note that the specific capacitances for all devices show the same value of approximately 600 nF/cm² at 1.0 kHz as depicted in the inset of Figure 4(c). C_i is reduced to slightly below 400 nF/cm² by incorporating OTS SAM. Importantly, the ideal capacitor characteristics for all investigated ultra-thin, anodized Al films with negligible variation strongly suggests the absence of any ionic species in the Al_2O_3 films.

Figure 4. (a) Crossbar structure device schematic of the fabricated MIM capacitors. (b) Bode plot (Impedance Z (Ohm) and Phase angle ϕ (degrees) vs. frequency) of the measured impedance data for all devices. Inset shows the variation of phase lag at 1 kHz for all CA concentrations including OTS coated sample (for 10 mM). (c) Variation of the specific capacitances as a function of frequency (C_i - f) for all fabricated MIM capacitors. Inset shows the variation of specific capacitance at 1 kHz for all CA concentrations including OTS coated sample (for 10 mM).

Frequency dependence of the dielectric constant (ϵ') and dielectric loss $\tan(\delta)$ were calculated for all devices from the EIS measurement data and plotted as the function of frequency as shown in Figure 5(a). The results show that the dielectric constant is high in the low frequency region ($f < 1$ Hz) for all devices. However, ϵ' starts to decrease rapidly when the frequency starts to increase above 1 Hz because the electric dipoles in Al₂O₃ are unable to follow the variation of the applied

AC electric field at higher frequencies. Here, it can be observed that the magnitude of the dielectric constant remains almost independent of the molar concentrations of CA from 1 Hz to 100 kHz as shown in the inset of Figure 5 (a). All devices show the dielectric constant value around 6.0 for the oxide layer thickness of approximately 6.5 nm (excluding the native oxide) as depicted in the inset of Figure 5(a). It is reasonable to assume that the dielectric constant is significantly reduced from the oxide bulk values when the thickness of the dielectric layer is ≤ 10 nm. This could be due to non-stoichiometry of thin oxide films but also because of the dominant nature of the interfacial layers between the oxide and electrodes that reduce the bulk phase property as observed in the previous report (32). The OTS passivation of the Al_2O_3 surface reduces the effective dielectric constant to 3.0. However, the capacitor behaviour in terms of the frequency response range somewhat improves as can be seen in Figure 5(a). The quantity $\tan(\delta)$ is referred to as dielectric loss. Normally, the dielectric loss occurs due to the absorption of electrical energy which is used to rotate the dipoles in dielectric films (33). In nanomaterials, the lack of film homogeneity can induce an absorption current due to the formation of space charge which also contributes to the dielectric loss (34). In addition, the presence of the highly reactive dangling bonds on top of oxide thin film surfaces can give rise to absorption of gases like oxygen or nitrogen which may also result in an increase of the dielectric loss. The variation of $\tan(\delta)$ with frequency is shown in Figure 5(a) without and with OTS coating for 10 mM CA oxide films. As can be seen in the inset of Figure 5(b), the dielectric loss was found to be below 0.1 at 1 kHz for all investigated samples. The variation of the AC conductivity (σ_{AC}) with the frequency for all fabricated capacitors is shown in the Figure 5(b). σ_{AC} is found to be almost invariant at lower frequencies for all cases except the OTS one. As expected, the AC conductivity increases due to dispersion and charge carrier hopping in the films when the frequency exceeds 100 Hz. It can be noticed in Figure 5(b)

that the behaviour of σ_{AC} is similar for all devices independently of the used CA concentration. Surprisingly, as shown in the inset of Figure 5(b), $\text{Al}_2\text{O}_3/\text{OTS}$ devices show somewhat higher dielectric loss compared with Al_2O_3 only devices. This could be due to the contribution of SAM to the overall AC conductivity of the $\text{Al}_2\text{O}_3/\text{OTS}$ stack. Therefore, we conclude that the penetration of ionic species into the Al_2O_3 films is very unlikely.

The dielectric quality of the anodized Al films is further studied by measuring their breakdown voltage (V_B). As shown in the Supplementary Material Figure S4 (a) and (b), the devices show V_B about 5 V which is almost the same as the chosen anodization voltage. Therefore, we speculate that the anodization voltage is the most important parameter which decides the value of the breakdown voltage. Also, the obtained results clearly show that the annealing the Al_2O_3 films at 120 °C has no obvious influence on V_B .

Figure 5. (a) Variation of the dielectric constant (ϵ') and dielectric loss ($\tan(\delta)$) vs. frequency (f) of the studied MIM capacitors extracted from the measured impedance data. Inset shows the variation of dielectric constant at 1 kHz for all CA concentrations including OTS coated sample (10 mM). (b) variation of AC conductivity (σ_{AC}) with frequency (f) for all six devices prepared

with citric acid strength from 0.1 to 1000 mM. Inset shows the variation of dielectric loss at 1 kHz for all CA concentrations including OTS coated sample (10 mM).

Figure 6 (a) and (b) show the experimental Nyquist plots with fitted data of the Al_2O_3 films grown using CA concentrations for 10 and 1000 mM, respectively, for MIM capacitors with overlapping area 1.0 mm^2 in which negative value of imaginary impedance ($-Z''$) is plotted with real impedance (Z') (35). The semicircle diameter reflects the sum of the contact resistance (R_s) and the bulk resistance (R_{CT}) of the device which appear slightly different for two films prepared with CA concentration 10 and 1000 mM due to a minimal difference of the resistance value. To understand more precisely, the impedance data in Nyquist plot is fitted for both cases using an RC equivalent circuit containing different components as shown in Figure 6(c). This equivalent circuit contains a contact resistance (R_s) in series with a parallel combination of a constant phase element (Q) and a Warburg impedance (W) in series with bulk resistance (R_{CT}). The impedance of a constant phase element (Q) is expressed as $Z_Q = 1/[(j\omega)^\alpha \cdot Y]$ and this equation describes a capacitor with the constant $Y = C$ (the capacitance) when the exponent $\alpha = 1$. Usually, α is less than 1 for non-ideal capacitors. Interestingly, both studied capacitors show the value of $\alpha=1.0$ which strongly suggest that the ultra-thin films prepared by anodization in CA with varying concentrations are free of defects and ionic carbon contamination (36). On the other hand, capacitance-voltage (C - V) measurements at 1 kHz for a device fabricated using 10 mM CA concentration show that the capacitance is independent of applied voltage between -1.0 to $+1.0$ V as depicted in Figure 6 (d). Surprisingly, the measured value of $C = 7.25 \text{ nF}$ is also perfectly matching the evolved capacitance value from the fitting result of Nyquist data for both CA concentrations. Therefore, it can be concluded that all anodized aluminium films appear to be free of ionic species even by changing the strength of electrolyte by 4 orders of magnitude.

Figure 6. Nyquist plots with the fitting curve to model the anodized films grown using 10 mM (a) and 1000 mM (b) citric acid solutions. The insets show the list of the components with their corresponding values used for the fitting analysis. (c) An equivalent RC network circuit used to perform the fitting analysis for the experimental data in the Nyquist plots. (d) Capacitance vs. voltage (C-V) characteristic for the device prepared using 10 mM CA maintaining constant frequency at 1 kHz.

Figure 7. Representative (a) transfer (black line) with leakage current (red line) and (b) output characteristics of the fabricated bottom-gate bottom-contact DPP-TTT OTFTs. The inset in (a) shows $I_D^{1/2}$ vs. V_G plot used to find threshold voltage (V_{TH}). The inset in (b) shows the cross-sectional structure of the fabricated transistors using OTS-modified, anodized aluminium as the gate dielectric.

To test if the optimized Al_2O_3 films result in well working transistors, bottom-gate bottom-contact DPP-TTT:PMMA OTFTs with OTS-modified aluminium oxide (Al_2O_3) anodized at $V_A = 2.3$ V ($d \sim 3$ nm) have been fabricated (inset of Figure 7 (b)). Typical output and transfer characteristics of the fabricated OTFTs are shown in Figure 7 (a) and 7 (b), respectively. Threshold voltage (V_{TH}) is an important parameter which has influence on the operation mode as well as carrier mobility. Here, V_{TH} is estimated about -0.41 V from the $\sqrt{I_D}$ vs. V_G plot (inset of Figure 7 (a)). This negative value of V_{TH} indicates that the channel is p-type and it operates in the enhancement mode. The optimized devices operate below 1 V with virtually no hysteresis, the saturation field-effect mobility (μ_{sat}) is $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the threshold voltage -0.41 V, subthreshold swing 155 mV/dec, and the current on/off ratio is in excess of 10^3 . In addition, the leakage current measured at -700

mV is well below 0.1 nA and remains below that value for all applied biases. As can be seen, the achieved performance of the devices is comparable with the recently reported state-of-the-art 1 V OTFTs (37).

4. CONCLUSIONS

In conclusion, ultra-thin ($d < 10$ nm), barrier type aluminium oxide films were grown anodically in citric acid electrolyte solutions of various concentrations. The SEM and AFM data reveal that the surface of the anodized films is very smooth and pinhole free. The EDS scans and XPS spectra show that the films are free from carbon contamination which suggests that the citrate anions are not present in the anodized films. The XPS results further confirm that the obtained oxide films consist of a stoichiometric Al_2O_3 even when changing the electrolyte strength from 1 to 1000 mM. The analysis of impedance spectroscopy results strongly confirms that the CA concentration does not play any significant role in the control of the dielectric properties of such films. The effect of OTS SAM on the dielectric properties of the anodized Al films has also been studied. It is found that there is a noticeable improvement in terms of frequency bandwidth but all values related to the dielectric properties decrease as expected because of the increase in overall thickness. Finally, high capacitance Al_2O_3 films were used to fabricate organic TFTs. Low operational voltage devices were achieved by using extremely thin (3 nm) Al_2O_3 films that were modified by the application of an OTS SAM. The optimized DPP-TTT:PMMA transistors display threshold voltages around -0.41 V, low subthreshold slopes 155 mV/dec, they operate with negligible hysteresis and possess average saturated field-effect mobility (μ_{sat}) in excess of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 750 mV. This approach has a high potential to enable the fabrication of ultra-low voltage organic TFTs in a highly reproducible manner.

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Supplementary Material

Ultra-thin Anodized Aluminium Dielectric Films: The Effect of Citric Acid Concentration and Low-Voltage Electronic Applications

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Figure S1. (a) Profiles of anodization current (I_A) (black circles) and anodization voltage (V_A) (blue triangles) as the function of anodization time (t) using high purity DI water as the electrolyte. (b) Breakdown voltage (V_B) measurements of six randomly chosen Al/Al₂O₃/Al MIM capacitors (C 1 to C 6) fabricated on the same glass substrate using high purity DI water as the electrolyte. It can be noticed that the value of V_B substantially varies from device to device.

Figure S2. (a) AFM topography image of pristine Al film (100 nm thick) is recorded immediately after deposition on ultra-flat glass which shows RMS area roughness (S_q) about 9.2 $\text{\AA}$. (b) AFM topography image of annealed Al₂O₃/OTS film. Scale bar is 50 nm for both images.

Figure S3. XRD spectrum of the annealed, anodized Al₂O₃ film showing the amorphous nature.

Figure S4. Breakdown voltage (V_B) measurements of six randomly chosen Al/Al₂O₃/Al MIM capacitors (C 1 to C 6) fabricated on the same glass substrate using citric acid as the electrolyte, (a) before and (b) after annealing. The anodization voltage (V_A) and the anodization current (I_A) were 5 V and 15 μ A, respectively. The arrow in (a) indicates the estimated value of the breakdown voltage (V_B). Inset of (b) shows a schematic structure of the fabricated MIM capacitors used for the measurements.