

# Ozone oxidation methods for aluminum oxide formation: Application to low-voltage organic transistors



S. Gupta<sup>a,1</sup>, S. Hannah<sup>a</sup>, C.P. Watson<sup>b</sup>, P. Šutta<sup>c</sup>, R.H. Pedersen<sup>d</sup>, N. Gadegaard<sup>d</sup>, H. Gleskova<sup>a,\*</sup>

<sup>a</sup>Department of Electronic and Electrical Engineering, University of Strathclyde, Glasgow G1 1XW, United Kingdom

<sup>b</sup>School of Electronic Engineering, Bangor University, Dean Street, Bangor, Gwynedd LL57 1UT, United Kingdom

<sup>c</sup>New Technologies Research Centre, University of West Bohemia, Univerzitní 8, 306 14 Pilsen, Czech Republic

<sup>d</sup>School of Engineering, University of Glasgow, Glasgow G12 8QQ, United Kingdom

## ARTICLE INFO

### Article history:

Received 27 January 2015

Received in revised form 26 February 2015

Accepted 5 March 2015

Available online 9 March 2015

### Keywords:

Aluminum oxide

Ozone oxidation

FTIR

XPS

Organic thin-film transistors

## ABSTRACT

Four atmospheric pressure ozone oxidation methods were used to produce ultra-thin layers of aluminum oxide for organic thin-film transistors. They are UV/ozone oxidation in ambient (UV-AA) and dry (UV-DA) air, UV/ozone oxidation combined with high-voltage discharge-generated ozone in dry air (UV+O<sub>3</sub>-DA), and discharge-generated ozone in dry air (O<sub>3</sub>-DA). The lack of the high-energy UV photons during the O<sub>3</sub>-DA oxidation led to low relative permittivity and high leakage current density of the AlO<sub>x</sub> layer that rendered this method unsuitable for transistor dielectrics. Although this oxidation method led to the incorporation of oxygen into the film, the FTIR confirmed an increased concentration of the subsurface oxygen while the XPS showed the highest portion of the unoxidized Al among all four methods. The remaining three oxidation methods produced AlO<sub>x</sub> films with thicknesses in excess of 7 nm (2-h oxidation time), relative permittivity between 6.61 and 7.25, and leakage current density of  $(1-7) \times 10^{-7}$  A/cm<sup>2</sup> at 2 MV/cm, and were successfully implemented into organic thin-film transistors based on pentacene and DNNT. The presence of –OH groups in all oxides is below the detection limit, while some carbon impurities appear to be incorporated.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

The ultra-thin and high-*k* dielectrics lead to field-effect transistors with low operating voltages. However, to achieve good transistor operation such dielectrics must also exhibit very low leakage current. HfLaO (*k* ~ 15.3) [1,2], Ba<sub>1.2</sub>Ti<sub>0.8</sub>O<sub>3</sub> (*k* ~ 15.57) [3], SrTiO<sub>3</sub> (*k* ~ 12.1) [4], and high-*k* polymers dielectrics (*k* ~ 12.6) [5] have been explored for low-voltage organic thin-film transistors (OTFTs). OTFTs with medium-*k* gate dielectrics such as aluminum oxide (*k* ~ 6.2) [6] have achieved low operating voltages through reduction in their thickness [7]. The aluminum oxide is often further functionalized by organic monolayers to provide reduction in the leakage current and the surface energy [8].

Standard deposition methods for aluminum oxide include sputtering and atomic layer deposition. However, ultra-thin layers of aluminum oxide can also be prepared by oxidation of aluminum deposited in high-vacuum by thermal evaporation [9,10],

sputtering, or e-beam. Oxidation of aluminum has been performed by low-frequency pulsed discharge plasma [11], oxygen plasma [10], or anodic oxidation [12]. For the growth of thicker oxide layers the oxygen plasma method is preferred, but such process leads to an increase in substrate temperature (~300 °C) that is not compatible with many plastic substrates.

The reactive atomic oxygen required for the oxidation of aluminum can also be produced by dissociation of ozone [13] and the oxidation can be performed at atmospheric pressure. UV/ozone oxidation was previously used in the preparation of high-*k* gate dielectrics for CMOS. Some examples include hafnium silicate [14], zirconia [15] and hafnium-aluminum oxynitride [13].

Prompted by our previous results achieved with UV/ozone oxidation of aluminum in the ambient air [16], this paper studies four different ozone oxidation methods that were applied to thermally evaporated aluminum layers. The produced oxide layers were implemented as gate dielectrics in OTFTs. Material characterization of the aluminum oxide (AlO<sub>x</sub>) was correlated with the performance of organic transistors aiming to identify the best procedure for the AlO<sub>x</sub> preparation.

The oxidation of aluminum was performed in UV/ozone cleaner system in ambient air, in which a high-pressure mercury lamp

\* Corresponding author.

E-mail address: [helena.gleskova@strath.ac.uk](mailto:helena.gleskova@strath.ac.uk) (H. Gleskova).

<sup>1</sup> Current address: Ecole Polytechnique Fédérale de Lausanne (EPFL), STII/IMT/IBI/LSBI, CH-1015 Lausanne, Switzerland.

emits UV light at 184.9 and 253.7 nm [16]. The higher energy photons are absorbed by the molecular oxygen, leading to ozone formation. The lower energy photons do not generate ozone. They illuminate the oxidizing surface, dissociate ozone, and assist in the removal of organic contaminants [17,18]. High-voltage discharge can also generate ozone [13]. Common commercial applications include water treatment and sanitation. Contrary to mercury lamps, the discharge produces ozone without the coexistence of high energy photons and the efficiency of the ozone generation depends on the relative humidity of the air. The results of this paper show for the first time that the ozone production method can have a profound effect on the properties of the produced  $\text{AlO}_x$ .

## 2. Experimental procedures

Four different methods of ozone generation have been implemented. The first one used UV/ozone cleaner (UVOCS) enclosed under a Hepa filter under ambient environmental conditions (21 °C, relative air humidity of ~45%). In the second case a flow of dry air (21 °C, relative air humidity  $\leq 0.1\%$ ) was supplied into the UV/ozone cleaner, while the remaining parameters were kept the same. In the third case, dry air passed through high-voltage ozone generator (A2Z Ozone) and the generated ozone was supplied into the running UV/ozone cleaner (mercury lamp was on). Finally, the fourth method was similar to the third one, except the mercury lamp was turned off. This condition aimed to investigate the role of UV photons illuminating the aluminum layers during their oxidation. These four methods are summarized in Table 1.

All samples were prepared on Eagle 2000 glass substrates. Samples for spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) started with ~30-nm-thick thermally evaporated Al layers. Samples were oxidized according to the conditions shown in Table 1 and the oxidation time was 2 h. The fifth sample was left to oxidize in dark ambient conditions to form a native oxide (Native AA). Finally, the UV-AA oxidation ranging from 5 min to 6 h was used to produce 6 samples. This allowed studying the thickness of the UV-AA  $\text{AlO}_x$  as a function of oxidation time.

Metal–insulator–metal (MIM) structures and organic thin-film transistors (OTFTs) were fabricated to study the effect of  $\text{AlO}_x$  oxidation process. Al/ $\text{AlO}_x$ /DNTT/Au and Al/ $\text{AlO}_x$ /C<sub>8</sub>PA/pentacene/Au transistors were fabricated for four  $\text{AlO}_x$  oxidation procedures listed in Table 1 (DNTT stands for dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene and C<sub>8</sub>PA for n-octylphosphonic acid monolayer). The fabricated transistors have channel lengths of 30, 50, 70, and 90  $\mu\text{m}$  and a channel width of 1000  $\mu\text{m}$ . The corresponding MIM structures were fabricated alongside. Each sample contained 12 transistors and 4 MIM structures.

MIM structures were fabricated as follows. 30-nm-thick aluminum lines were deposited on glass substrate. One end of the lines was capped by gold layer to prevent their oxidation.  $\text{AlO}_x$  was prepared by using the four methods described above. In some samples, the  $\text{AlO}_x$  was functionalized with vapor-assembled monolayer of n-octylphosphonic acid (C<sub>8</sub>PA) using the procedure

described in [19]. The presence of monolayer on top of aluminum oxide reduces the leakage current and changes the hydrophilic surface into hydrophobic [8]. The vacuum vapor growth of C<sub>8</sub>PA monolayer was optimized with respect to the post-deposition annealing time [19,20], deposition temperature [21], and deposition rate [22]. All capacitors were completed by evaporating a 50-nm-thick gold layer [19]. The area of the capacitors was about 0.2 mm<sup>2</sup>.

Bottom-gate, top-contact organic thin-film transistors (OTFTs) based on thermally evaporated DNTT (Sigma–Aldrich) or pentacene (Tokyo Chemical Industry) followed the same fabrication procedure. A 15-nm-thick DNTT was deposited directly on  $\text{AlO}_x$ , while a 50-nm-thick pentacene layer was deposited on  $\text{AlO}_x$  functionalized with C<sub>8</sub>PA. Both transistor sets were completed by evaporating gold source and drain contacts. The cross-sections of pentacene and DNTT OTFTs are shown in Fig. 1. All fabrication steps were performed by using shadow masks. All thermal evaporation steps were conducted in Minispectros (Kurt J. Lesker) high vacuum system ( $\sim 10^{-7}$  mBar) enclosed in a N<sub>2</sub>-filled glove box.

The capacitor and transistor measurements were performed with Agilent B1500A semiconductor device analyzer under ambient environmental conditions. All fabricated devices were kept in oxygen and moisture-free environment until their measurement and they shared the same history. The gate dielectric capacitance of MIM structures was measured between 1 kHz and 1 MHz. The MIM current density was measured as a function of applied electric field. The transfer and output characteristics of the OTFTs were measured in a sweep mode. All fabricated MIM structures and transistors were measured for each  $\text{AlO}_x$  oxidation process. Mean values and standard deviations were calculated for all parameters.

The spectroscopic ellipsometry was performed with a J.A. Woollam M2000V in ambient air. Glass/Al/ $\text{AlO}_x$  samples were measured and fitted with a three-layer model using a B-spline fit. FTIR was measured with Ge detector in reflection mode with Nicolet 380 spectrometer in ambient air. The beam diameter was ~1.5 mm. PeakFit analysis provided the location of the peaks, their intensity, full width at half maximum (FWHM), and integral area. Polycrystalline white corundum was also measured for comparison. X-ray photoelectron spectroscopy was carried out in a SAGE 100 system (Specs GmbH) using a non-monochromatic MgK $\alpha$  source, with a beam diameter of 7 mm, operated at 10 kV (150 W). The base pressure during the analysis was around  $2 \times 10^{-7}$  mBar. Spectra were recorded at a take-off angle of 90 degrees with a pass energy of the hemispheric analyser of 50 eV for survey scans and 15 eV

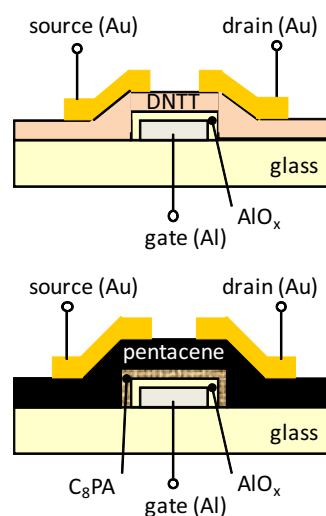


Fig. 1. OTFT cross-sections.

**Table 1**  
Conditions of investigated aluminum oxidations. AA stands for ambient air and DA for dry air.

Procedure	Mercury lamp	Ozone flow	Air conditions	Relative humidity (%)
UV-AA	On	No	Ambient air	~45
UV-DA	On	No	Dry air	$\leq 0.1$
UV+O <sub>3</sub> -DA	On	Yes	Dry air	$\leq 0.1$
O <sub>3</sub> -DA	Off	Yes	Dry air	$\leq 0.1$

Download English Version:

<https://daneshyari.com/en/article/7701720>

Download Persian Version:

<https://daneshyari.com/article/7701720>

[Daneshyari.com](https://daneshyari.com)