

Solution processed lanthanum aluminate gate dielectrics for use in metal oxide-based thin film transistors

M. Esro, R. Mazzocco, G. Vourlias, O. Kolosov, A. Krier, W. I. Milne, and G. Adamopoulos

Citation: [Applied Physics Letters](#) **106**, 203507 (2015); doi: 10.1063/1.4921262

View online: <http://dx.doi.org/10.1063/1.4921262>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/106/20?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Physical properties of Cu₂ZnSnS₄ thin films deposited by spray pyrolysis technique](#)

[J. Renewable Sustainable Energy](#) **5**, 023113 (2013); 10.1063/1.4795399

[Fabrication of high quality nanocrystalline Cd \(1- x\) Zn x S thin films for optoelectronic applications](#)

[AIP Conf. Proc.](#) **1512**, 674 (2013); 10.1063/1.4791217

[Structural, optical, electrical and surface properties of Co-doped ZnO films prepared by spray pyrolysis](#)

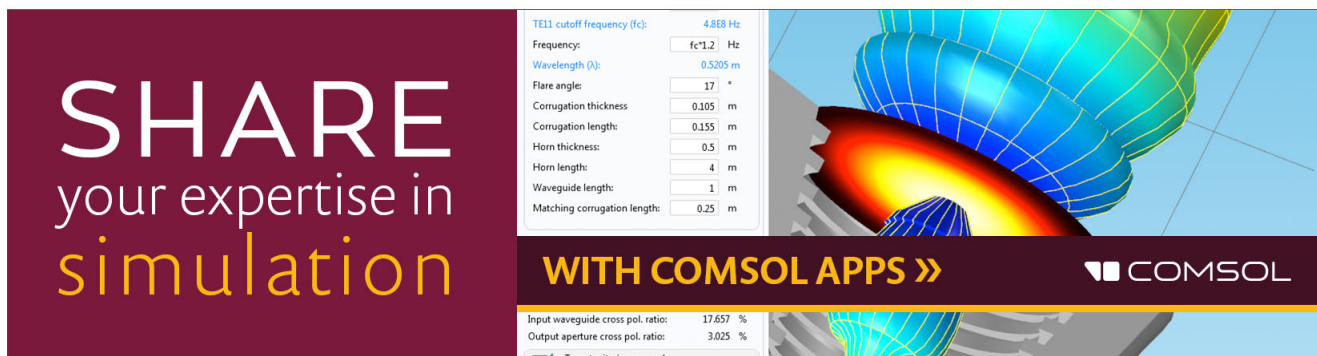
[AIP Conf. Proc.](#) **1476**, 221 (2012); 10.1063/1.4751599

[Low-voltage ZnO thin-film transistors based on Y₂O₃ and Al₂O₃ high- k dielectrics deposited by spray pyrolysis in air](#)

[Appl. Phys. Lett.](#) **98**, 123503 (2011); 10.1063/1.3568893

[Electronic properties of ZnO field-effect transistors fabricated by spray pyrolysis in ambient air](#)

[Appl. Phys. Lett.](#) **95**, 133507 (2009); 10.1063/1.3238466



SHARE
your expertise in
simulation

TE11 cutoff frequency (fc): 4.868 Hz
Frequency: fc*1.2 Hz
Wavelength (λ): 0.5205 m
Flare angle: 17 °
Corrugation thickness: 0.105 m
Corrugation length: 0.155 m
Horn thickness: 0.5 m
Horn length: 4 m
Waveguide length: 1 m
Matching corrugation length: 0.25 m

WITH COMSOL APPS »

COMSOL

Input waveguide cross pol. ratio: 17.657 %
Output aperture cross pol. ratio: 3.025 %
 Target criterion: passed.

Solution processed lanthanum aluminate gate dielectrics for use in metal oxide-based thin film transistors

M. Esro,¹ R. Mazzocco,² G. Vourlias,³ O. Kolosov,² A. Krier,² W. I. Milne,^{4,5} and G. Adamopoulos^{1,a)}

¹Engineering Department, Lancaster University, Lancaster LA1 4YR, United Kingdom

²Physics Department, Lancaster University, Lancaster, LA1 4YB, United Kingdom

³Physics Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

⁴Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge CB3 0FA, United Kingdom

⁵Department of Electrical and Computing Engineering, University of Canterbury, 4800 Christchurch, New Zealand

(Received 2 March 2015; accepted 6 May 2015; published online 22 May 2015)

We report on ZnO-based thin-film transistors (TFTs) employing lanthanum aluminate gate dielectrics ($\text{La}_x\text{Al}_{1-x}\text{O}_y$) grown by spray pyrolysis in ambient atmosphere at 440 °C. The structural, electronic, optical, morphological, and electrical properties of the $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films and devices as a function of the lanthanum to aluminium atomic ratio were investigated using a wide range of characterization techniques such as UV-visible absorption spectroscopy, impedance spectroscopy, spectroscopic ellipsometry, atomic force microscopy, x-ray diffraction, and field-effect measurements. As-deposited LaAlO_y dielectrics exhibit a wide band gap (~ 6.18 eV), high dielectric constant ($k \sim 16$), low roughness (~ 1.9 nm), and very low leakage currents (< 3 nA/cm²). TFTs employing solution processed LaAlO_y gate dielectrics and ZnO semiconducting channels exhibit excellent electron transport characteristics with hysteresis-free operation, low operation voltages (~ 10 V), high on/off current modulation ratio of $> 10^6$, subthreshold swing of ~ 650 mV dec⁻¹, and electron mobility of ~ 12 cm² V⁻¹ s⁻¹. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921262>]

Solution-processed film stacks constitute a promising alternative to conventional vapor deposition for large area applications as they could provide a breakthrough in manufacturing cost. In that respect and given the recent advances in metal oxide semiconductors deposited by vacuum-based techniques, solution processed devices offers an alternative approach by marrying fabrication simplicity with high-throughput manufacturing. Whilst progress on solution-processed oxide semiconductors has been rapidly advancing, research efforts towards the development of dielectric materials has been relatively slow, with most of the reported work performed using conventional dielectrics based on SiO_2 that usually results in high voltage transistor operation and hence increased power consumption. To tackle this problem, different approaches have been explored including the use of ultra-thin nanodielectrics,¹ electrolyte gate dielectrics,² and high- k dielectrics. Among these, the use of high- k dielectrics is arguably the most attractive option, since it can enable low leakage currents, through the use of physically thicker films, as well as low-voltage operation. There are already numerous candidate materials, such as transition metal oxides, i.e., TiO_2 ,³ ZrO_2 ,⁴ HfO_2 ,⁵ silicates,^{6,7} and phosphates,⁸ which could potentially replace SiO_2 . Additionally, rare earth metal oxides, such as La_2O_3 , Y_2O_3 , and Pr_2O_3 , have also been considered as potential high- k gate dielectrics alternatives to SiO_2 . Amongst them lanthanum oxide (La_2O_3), with a k of about 27 and a large band gap (~ 6 eV) is being considered as the most promising gate dielectric. However, there are still many issues with La_2O_3 that are

related to poor interface properties and chemical instability as it readily converts to $\text{La}_2(\text{CO}_3)_3$ and $\text{La}(\text{OH})_3$ during growth or upon annealing,^{9,10} or reacting with ambient water.¹¹

An obvious solution to this problem is the use of alloy forms or complex oxides where a combination of the desirable electrical and optical properties can be tailored by exploiting the properties of different component oxides.¹² To this end, LaAlO_3 , which is a compound of La_2O_3 and Al_2O_3 , shows high immunity against environmental moisture, thermal stability similar to that of La_2O_3 , high dielectric constant in the range between 25 and 27,¹³ and high optical band gap (5.6 eV for crystalline LaAlO_3 and 6.2 eV for amorphous LaAlO_3).^{14,15}

LaAlO_3 thin films have been deposited on a variety of substrates using a number of vacuum based techniques including atomic layer deposition (ALD),^{16–18} molecular beam epitaxy (MBE),^{19,20} pulsed laser deposition (PLD),^{21,22} RF sputtering,^{23,24} and metal organic chemical vapor deposition (MOCVD).^{25–27}

However, despite their attractive properties and extraordinary performance, vacuum-based deposition techniques still suffer from high manufacturing cost and incompatibility with large area deposition. In order to overcome this technology bottleneck, significant research has been focused on the development of alternative solution processing deposition methods such as spray pyrolysis^{28–31} and sol-gel.^{32–34}

Here, we study the structural, optical, electronic, and dielectric properties of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ gate dielectrics grown by spray pyrolysis in ambient air as a function of the lanthanum to aluminium atomic ratio. Lanthanum to aluminum atomic ratio was adjusted by the simple physical blending of the

^{a)} Author to whom correspondence should be addressed. Electronic mail: g.adamopoulos@lancaster.ac.uk

soluble precursors in alcohol and dimethylformamide-based solutions. We also demonstrate their implementation in high-mobility TFTs based on ZnO semiconducting channels similarly grown by spray pyrolysis.³⁵ The electronic and morphological properties of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ layers are investigated using a range of techniques including atomic force microscopy (AFM), UV-Vis absorption spectroscopy, admittance spectroscopy, spectroscopic ellipsometry, and x-ray diffraction (XRD). Finally, the electron mobility of the spray coated ZnO films employing $\text{La}_x\text{Al}_{1-x}\text{O}_y$ gate dielectrics was investigated using an optimized bottom gate–top contact (BG–TC) transistor architecture.

$\text{La}_x\text{Al}_{1-x}\text{O}_y$ thin films were deposited by spray pyrolysis at a substrate temperature of 440 °C in air. Commercially available indium tin oxide (ITO) coated glass substrates acting as the gate electrode were placed onto a hotplate and (3:1) methanol and dimethylformamide solutions blends (0.1M) of lanthanum(III) 2,4-pentanedionate $\text{La}(\text{C}_5\text{H}_7\text{O}_2)_3$ and aluminum 2,4-pentanedionate $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ were sprayed onto them as aerosols using a conventional pneumatic airbrush. ZnO semiconducting channels thin films were sprayed subsequently from a methanol solutions of zinc acetate $\text{Zn}(\text{CH}_3\text{COO})_2$ at a substrate temperature of 400 °C. The dielectric properties of the as-processed $\text{La}_x\text{Al}_{1-x}\text{O}_y$ thin films were investigated using a standard metal-insulator metal (MIM) configuration with aluminum contacts evaporated through a shadow mask on top of glass/ITO/ $\text{La}_x\text{Al}_{1-x}\text{O}_y$ stacks. Similarly, aluminum metal source and drain electrodes were thermally evaporated under high vacuum (10^{-6}) through a shadow mask following ZnO deposition on the ITO/ $\text{La}_x\text{Al}_{1-x}\text{O}_y$ gate structures resulting in bottom-gate top-contact transistors with a channel width W of 1500 μm and channel length L in the range of 20–100 μm . Electrical measurements were performed under vacuum at 10^{-6} mbar.

Optical transmission spectra of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films on fused silica substrates were measured at wavelengths between 200 and 1000 nm using a Perkin Elmer lambda 35 UV-Vis

spectrophotometer. A set of Tauc plots of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films as a function of the $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ atomic ratio are shown in Figure 1(a). The optical band gap evolution as a function of the $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ ratio is illustrated in Figure 1(b) and is in good agreement with the values reported in the literature for solution processed La_2O_3 and Al_2O_3 dielectrics.

The optical band gap (direct) shows a monotonic decrease with increase in the $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ atomic ratio and varies between the 5.5 eV for La_2O_3 and the 6.4 eV for spray-deposited Al_2O_3 , respectively. The band gap value of the LaAlO_y ($[\text{La}^{3+}]/[\text{Al}^{3+}]:1$, stoichiometric thereafter) dielectric (~ 6.18 eV) complies with the band offset condition³⁶ which requires a dielectric of reasonably large band gap (potential barrier at each band >1 eV) for conduction into the dielectric's bands by the Schottky emission of electrons or holes of the ZnO semiconducting channel to be inhibited (ZnO band gap ~ 3.3 eV).

Additionally, the Urbach tail energy (E_u) of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films as illustrated in Figure 1(c) exhibits a monotonic decrease with increase in the $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ ratio. The latter can be attributed to a decrease of the dynamic disorder (exciton-phonon coupling) which is expected with increase in the lanthanum content and the formation of La_2O_3 nanocrystals. To note that the x-axis error bars correspond to the La:Al ratio obtained by Energy-dispersive X-ray spectroscopy (EDS) experiments on selected $\text{La}_x\text{Al}_{1-x}\text{O}_y$ thin films and they are in good agreement with the ratios calculated in the precursor solutions. Furthermore, EDS results confirmed LaAlO_3 structures for stoichiometric (in the solution) LaAlO_y .

The dielectric properties of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films sandwiched between ITO and Al electrodes were investigated using a Wayne Kerr 6550B Precision Impedance Analyzer at frequencies in the range between 100 Hz and 10 MHz applying a 60 mV AC voltage. Figure 2(a) illustrates the dielectric constant and Nyquist plots (inset Figure 2(a)) of Al_2O_3 , stoichiometric (in the solution) LaAlO_y and La_2O_3 . The geometric capacitances that were extracted from the Bode plots

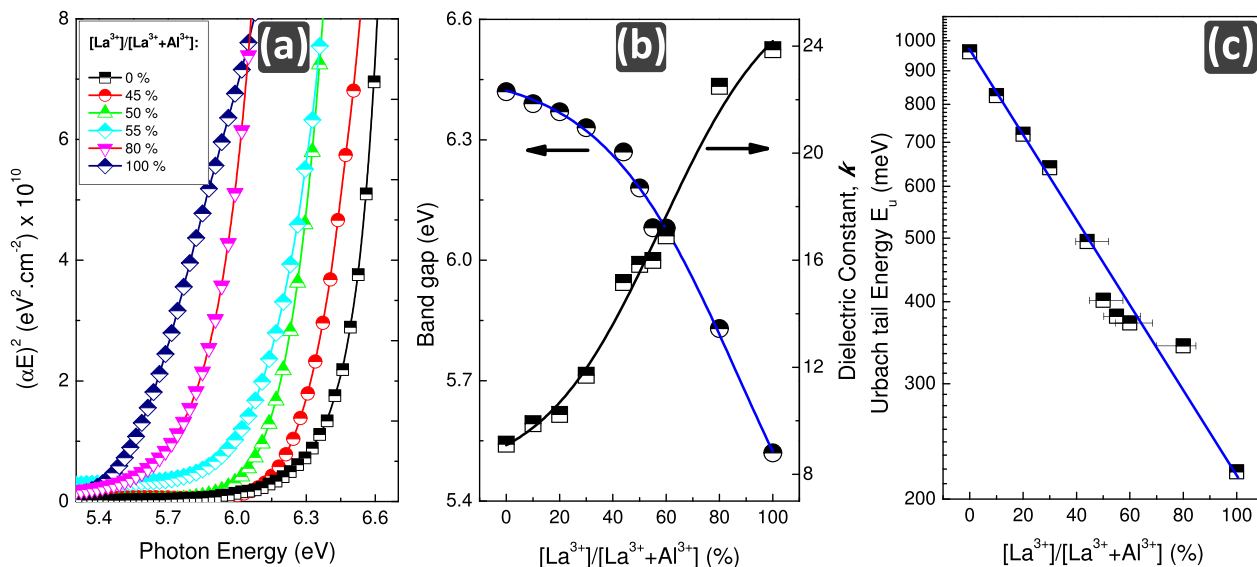


FIG. 1. (a) Tauc plots, (b) optical band gap and static dielectric constant, and (c) Urbach tail energy of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ dielectrics as a function of the $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ atomic ratio. The asymmetric error bars refer to $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ obtained from energy-dispersive X-ray spectroscopy measurements of selected samples. The solid lines are guide to the eye.

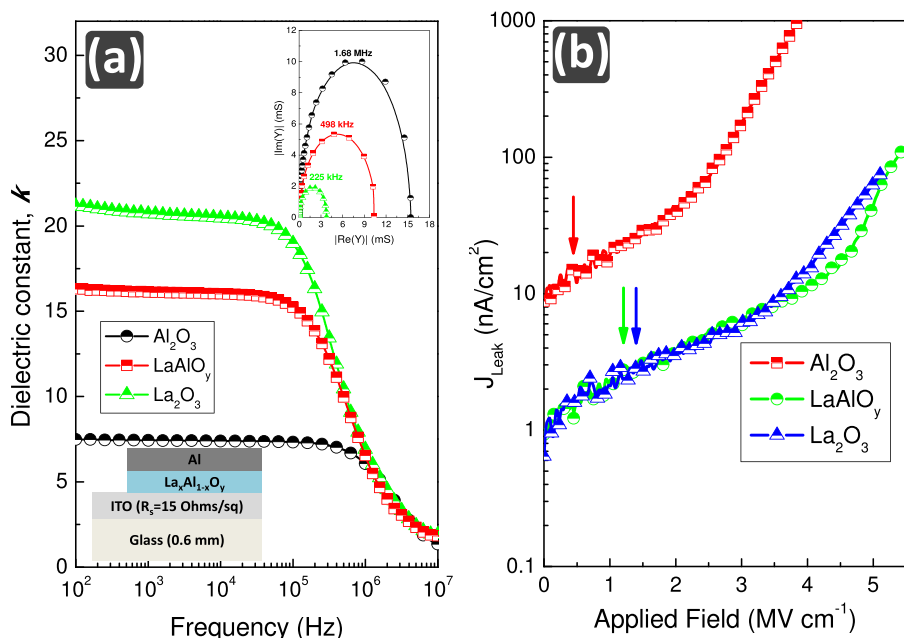


FIG. 2. (a) Dielectric constant dispersions in the frequency range between 100 Hz and 10 MHz and Nyquist plots (inset) of spray pyrolysis deposited Al_2O_3 , stoichiometric (in the solution) LaAlO_y and La_2O_3 layers sandwiched between ITO and Al electrodes. (b) Leakage current density versus applied electric field of Al_2O_3 , stoichiometric (in the solution) LaAlO_y and La_2O_3 layers film deposited by spray pyrolysis in air. The arrows indicate the applied field of the related ZnO-based TFTs operating at saturation.

(not shown) were 46 nF/cm^2 , 168 nF/cm^2 , and 147 nF/cm^2 for Al_2O_3 (175 nm), stoichiometric (in the solution) LaAlO_y (83 nm), and La_2O_3 (144 nm), respectively. The dielectric constant variation as a function of the $[\text{La}^{3+}]/[\text{La}^{3+} + \text{Al}^{3+}]$ ratio is also depicted in Figure 1(b).

The current-voltage density characteristics of MIM structures were also investigated. In the case of LaAlO_y and La_2O_3 dielectrics, the leakage current density was found to be very low (less than 3 nA/cm^2 at 1.5 MV cm^{-1} , typical field of the related TFTs operation at saturation) and no breakdown voltage occurred for electric fields up to 5 MV cm^{-1} .

One can immediately observe is the monotonic increase of the static dielectric constant with increase in the lanthanum content that reaches a value of about 16 for the LaAlO_y and 24 for La_2O_3 . The latter constitute the highest values for solution processed La_2O_3 and LaAlO_y ever reported.^{28,32} Additionally, Nyquist plots (inset Figure 1(a)) reveal stable stacks with excellent capacitive properties as evidenced from the equivalent circuit that consists of a large shunt and low series resistance.

The surface morphologies of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films were investigated by AFM. Atomic force microscopy images were taken in contact mode under ambient conditions using a MultiMode™ scanning probe microscope (MM-SPM) fitted to a Nanoscope IIIa controller unit employing a silicon tip of a radius $< 10 \text{ nm}$. Representative images of Al_2O_3 , stoichiometric LaAlO_y and La_2O_3 , respectively, are illustrated in Figure 3. The measured root-mean-square (RMS) roughness of the surface ($1 \mu\text{m} \times 1 \mu\text{m}$) was found to be $\sim 1.77 \text{ nm}$, $\sim 1.97 \text{ nm}$, and $\sim 2.52 \text{ nm}$ for Al_2O_3 , stoichiometric (in the solution) LaAlO_y and La_2O_3 , respectively.

Such smooth dielectrics providing good interface properties between the dielectric and semiconducting channel are promising for the implementation of spray coated $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films into TFT devices.

The microstructure of the $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films were further characterized by x-ray diffraction. Grazing incidence XRD (GIXRD) experiments were performed using a Rigaku

Ultima⁺ diffractometer with $\text{CuK}\alpha$ radiation operating at 40 kV. The diffraction patterns of selected $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films on glass are depicted in Figure 4.

As evidenced from the diffraction patterns, only pure La_2O_3 shows crystalline features, whereas no obvious diffraction peaks related to Al_2O_3 or LaAlO_3 were detected for the rest of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films indicating amorphous films. Analysis of the (400) diffraction peak of the pure La_2O_3 pattern using the Debye–Scherrer formula yields an average crystallite size of 30 nm. Note that indexing of the La_2O_3 pattern is based on both the La_2O_3 cubic (ICDD 65-3185) and hexagonal (ICDD 05-0602) phases of La_2O_3 that seem to coexist in the film. As mentioned earlier, La_2O_3 is sensitive to environmental moisture and CO_2 . This is further evidenced by the diffraction pattern of La_2O_3 (Figure 4) where $\text{La}(\text{OH})_3$ (ICDD 06-0585), La_2CO_5 (ICDD 23-0320) and $\text{La}_2\text{O}_2\text{CO}_3$ (ICDD 48-1113) reflections also contribute to the pattern.

The performance of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films as gate dielectrics was investigated in TFTs employing spray coated ZnO as the semiconducting channel. ZnO semiconducting channels were spray coated onto the Al_2O_3 , a- LaAlO_y , and La_2O_3 -coated ITO substrates heated at 400°C from 25 mg/mL zinc acetate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$) solutions in methanol until films of typical thickness of $\sim 35 \text{ nm}$ were obtained. BG–TC transistors were fabricated by employing aluminum (Al) source and drain (S/D) electrodes (50 nm), which were thermally evaporated under high vacuum (10^{-6} mbar) through a shadow mask on the spray coated glass/ITO/composite/ZnO stacks. To prevent Al oxidation and exposure of the ZnO channel to air's water vapors, the device characterization was performed under high vacuum (10^{-6} mbar) at room temperature. Electrical measurements were carried out using an Agilent B1500A semiconductor parameter analyzer. The electron mobility was extracted from the transfer characteristics in both the linear and saturation regimes using the gradual channel approximation. A representative set of transfer characteristics obtained from ZnO-based TFTs ($L = 20 \mu\text{m}$ and $W = 1500 \mu\text{m}$) employing

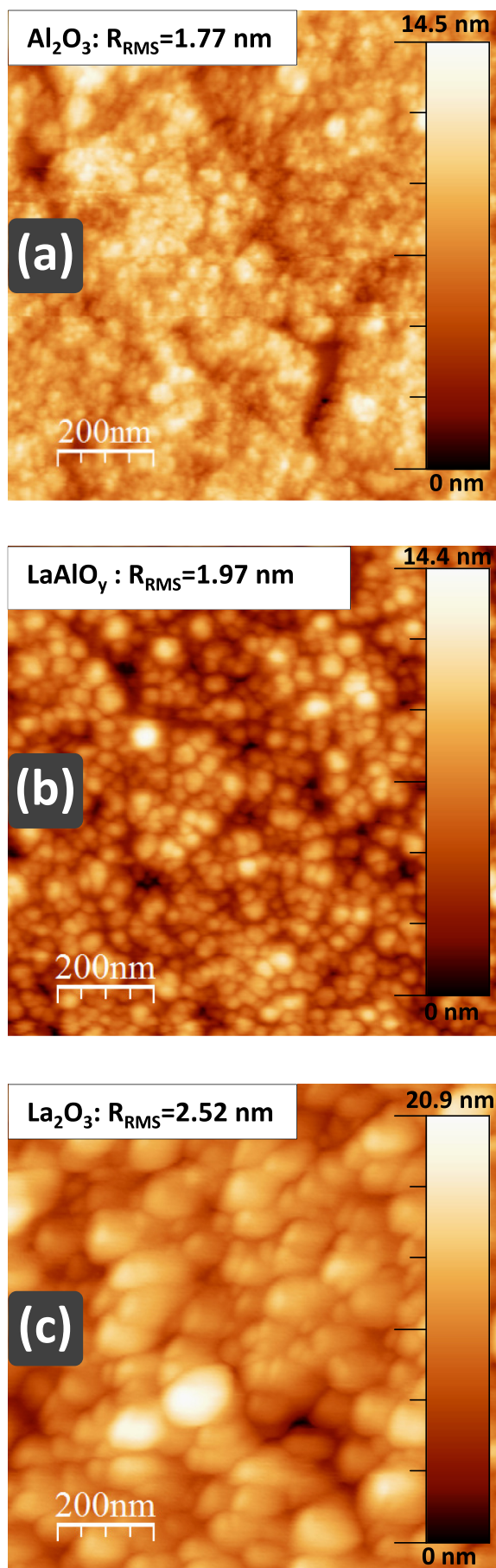


FIG. 3. AFM topography images (RMS roughness values are displayed in the inset) of solution processed of spray pyrolysis deposited (a) Al_2O_3 , (b) stoichiometric (in the solution) LaAlO_y , and (c) La_2O_3 layers on ITO coated glass.

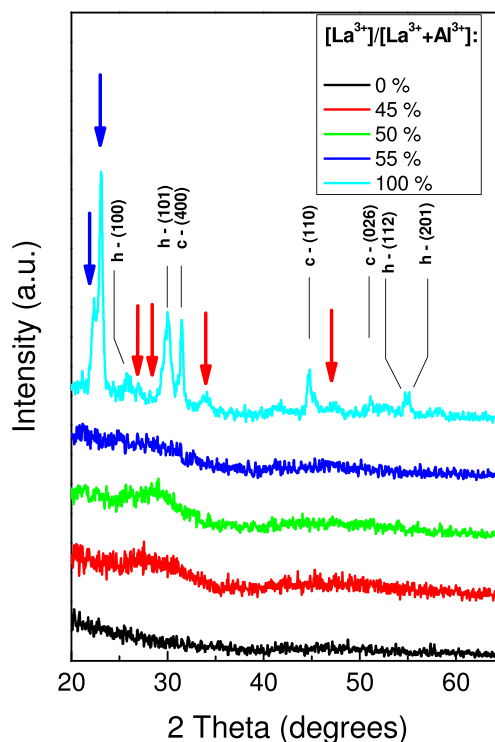


FIG. 4. GIXRD patterns of selected $\text{La}_x\text{Al}_{1-x}\text{O}_y$ dielectrics deposited by SP on glass substrates. Indexing of the patterns (when applicable) is based on both the La_2O_3 cubic and hexagonal phases of La_2O_3 . The red and blue arrows indicate contributions to the pattern due to $\text{La}(\text{OH})_3$ as well as La_2CO_5 and $\text{La}_2\text{O}_2\text{CO}_3$, respectively.

Al_2O_3 , stoichiometric a- LaAlO_y , and La_2O_3 gate dielectrics (with thickness of ~ 175 nm, ~ 83 nm, and ~ 144 nm, respectively) are illustrated in Figure 5(a). A set of output characteristics of the related ZnO TFT employing a- LaAlO_3 gate dielectric is also depicted in Figure 5(b).

In general, ZnO-based TFTs employing $\text{La}_x\text{Al}_{1-x}\text{O}_y$ gate dielectrics (Figure 5) exhibit excellent operating characteristics in terms of electron mobility of $\sim 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off current modulation ratios in the range between $\sim 10^6$ and $\sim 10^7$. One thing, however, that can be immediately observed is the upshift of the threshold/turn on voltage with increase of the lanthanum content. This upshift, in particular, for the TFT employing La_2O_3 as the gate dielectric, may be attributed to the presence of empty electronic traps at the $\text{La}_2\text{O}_3/\text{ZnO}$ interface. Similar behavior has already been reported for Indium Gallium Zinc Oxide (IGZO) semiconducting channels on LaAlO_3 gate dielectrics.³² Analyses also reveal improved operation characteristics for the TFTs that employ a- LaAlO_y gate dielectrics as evidenced by the hysteresis-free operation and decreased subthreshold swing (SS) of 650 mV dec^{-1} (compared with 1000 mV dec^{-1} and 800 mV dec^{-1} for TFTs employing Al_2O_3 and La_2O_3 gate dielectrics, respectively).

We have investigated the properties of $\text{La}_x\text{Al}_{1-x}\text{O}_y$ dielectrics as a function of the lanthanum to aluminum atomic ratio. The thin films were deposited by spray pyrolysis under ambient air at moderate substrate temperatures of $\sim 440^\circ\text{C}$ and were implemented as gate dielectrics in TFTs employing spray coated ZnO semiconducting channels. The $\text{La}_x\text{Al}_{1-x}\text{O}_y$ films were characterized using a wide range of techniques that revealed smooth $\text{La}_x\text{Al}_{1-x}\text{O}_y$ composites of

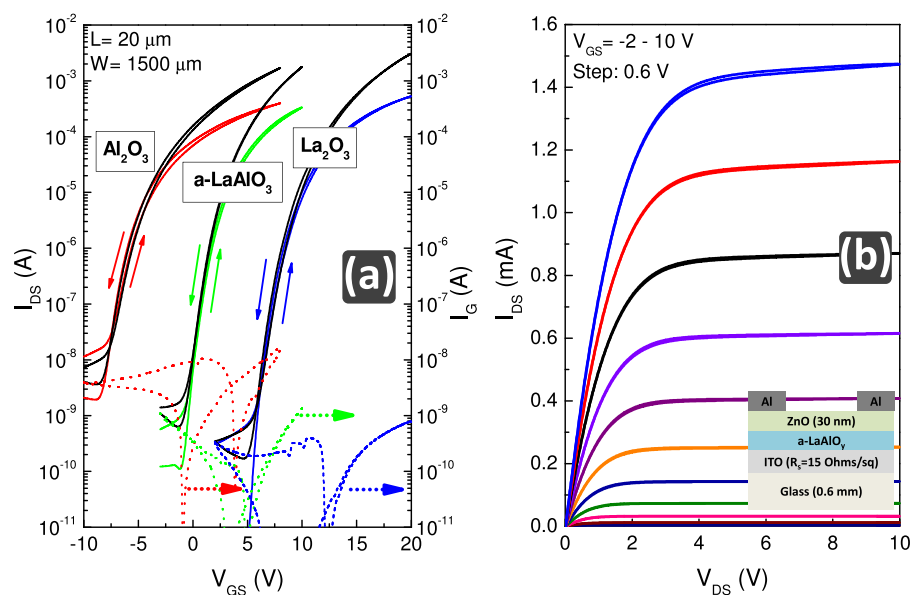


FIG. 5. (a) Transfer characteristics of bottom-gate, top-contact (inset: architecture employed) TFTs with channel width $W = 1500 \mu\text{m}$ and channel length $L = 20 \mu\text{m}$ employing spray coated Al_2O_3 ($V_{\text{DS,SAT}} = 8 \text{ V}$), stoichiometric a-LaAlO_y ($V_{\text{DS,SAT}} = 10 \text{ V}$), and La_2O_3 ($V_{\text{DS,SAT}} = 20 \text{ V}$) gate dielectrics (with capacitance of $\sim 46 \text{ nF/cm}^2$, $\sim 168 \text{ nF/cm}^2$, and $\sim 147 \text{ nF/cm}^2$, respectively). (b) Output characteristics of ZnO-based TFT employing spray coated stoichiometric a-LaAlO_3 gate dielectric.

amorphous phase, a wide band gap, and high dielectric constant. Stoichiometric a-LaAlO_y showed high dielectric constant, $k \sim 16$, wide band gap $E_g \sim 6.18 \text{ eV}$ and very low leakage currents ($< 6 \text{ nA/cm}^2$ at $\sim 3 \text{ MV cm}^{-1}$). ZnO-based TFTs employing stoichiometric a-LaAlO_y dielectrics showed excellent characteristics, i.e., hysteresis-free operation, electron mobilities of $\sim 12 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, slightly improved compared to those employing solution processed Al_2O_3 ($\sim 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and La_2O_3 ($\sim 11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) gate dielectrics, on/off current modulation ratio and subthreshold swing of 10^6 and 650 mV dec^{-1} , respectively. In addition, the excellent films uniformity and reproducibility over large areas combined with the TFTs stability under constant bias stress test (data not shown) indicates the potential for the rapid development of transparent oxide electronics at low manufacturing cost employing solution processing paradigms.

M.E. is grateful for support from the Ministry of Education Malaysia and Faculty of Electronic & Computer Engineering, Universiti Teknikal Melaka, Malaysia (UTeM).

- ¹M.-G. Kim, H. S. Kim, Y.-G. Ha, J. He, M. G. Kanatzidis, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **132**, 10352 (2010).
- ²H. Liu, J. Sun, Q. Tang, and Q. Wan, *J. Phys. Chem. C* **114**, 12316 (2010).
- ³S. A. Campbell, H. S. Kim, D. C. Gilmer, B. He, T. Ma, and W. L. Gladfelter, *IBM J. Res. Dev.* **43**, 383 (1999).
- ⁴R. Engel-Herbert, Y. Hwang, J. Cagnon, and S. Stemmer, *Appl. Phys. Lett.* **95**, 062908 (2009).
- ⁵M. Balog, M. Schieber, M. Michman, and S. Patai, *J. Electrochem. Soc.* **126**, 1203 (1979).
- ⁶G. D. Wilk and R. M. Wallace, *Appl. Phys. Lett.* **74**, 2854 (1999).
- ⁷G. D. Wilk and R. M. Wallace, *Appl. Phys. Lett.* **76**, 112 (2000).
- ⁸S. T. Meyers, J. T. Anderson, D. Hong, C. M. Hung, J. F. Wager, and D. A. Keszler, *Chem. Mater.* **19**, 4023 (2007).
- ⁹M. Nieminen, M. Putkonen, and L. Niinisto, *Appl. Surf. Sci.* **174**, 155 (2001).
- ¹⁰T. Gougousi, D. Niu, R. W. Ashcraft, and G. N. Parsons, *Appl. Phys. Lett.* **83**, 3543 (2003).
- ¹¹J. B. Cheng, A. D. Li, Q. Y. Shao, H. Q. Ling, D. Wu, Y. Wang, Y. J. Bao, M. Wang, Z. G. Liu, and N. B. Ming, *Appl. Surf. Sci.* **233**, 91 (2004).
- ¹²D. Afouxenidis, R. Mazzocco, G. Vourlias, P. J. Livesley, A. Krier, W. I. Milne, O. Kolosov, and G. Adamopoulos, *ACS Appl. Mater. Interfaces* **7**, 7334 (2015).

- ¹³X. B. Lu, Z. G. Liu, Y. P. Wang, Y. Yang, X. P. Wang, H. W. Zhou, and B. Y. Nguyen, *J. Appl. Phys.* **94**, 1229 (2003).
- ¹⁴S.-G. Lim, S. Kriventsov, T. N. Jackson, J. H. Haeni, D. G. Schlom, A. M. Balbashov, R. Uecker, P. Reiche, J. L. Freeouf, and G. Lucovsky, *J. Appl. Phys.* **91**, 4500 (2002).
- ¹⁵L. F. Edge, D. G. Schlom, S. A. Chambers, E. Cicerella, J. L. Freeouf, B. Holländer, and J. Schubert, *Appl. Phys. Lett.* **84**, 726 (2004).
- ¹⁶B. S. Lim, A. Rahtu, P. de Rouffignac, and R. G. Gordon, *Appl. Phys. Lett.* **84**, 3957 (2004).
- ¹⁷L. Niinisto, M. Nieminen, J. Paivasaari, J. Niinisto, M. Putkonen, and M. Nieminen, *Phys. Status Solidi A* **201**, 1443 (2004).
- ¹⁸D. H. Triyoso, H. Li, R. I. Hegde, Z. Yu, K. Moore, J. Grant, B. E. White, and P. J. Tobin, *J. Vac. Sci. Technol.*, **B 23**, 2480 (2005).
- ¹⁹C. Merckling, G. Delhay, M. El-Kazzi, S. Gaillard, Y. Rozier, L. Rapenne, B. Chenevier, O. Marty, G. Saint-Girons, M. Gendry, Y. Robach, and G. Hollinger, *Microelectron. Reliab.* **47**, 540 (2007).
- ²⁰S. Gaillard, Y. Rozier, C. Merckling, F. Ducroquet, M. Gendry, and G. Hollinger, *Microelectron. Eng.* **80**, 146 (2005).
- ²¹H. M. Christen and G. Eres, *J. Phys.: Condens. Matter* **20**, 264005 (2008).
- ²²C. M. Carlson, J. C. Price, P. A. Parilla, D. S. Ginley, D. Niles, R. D. Blaugher, A. Goyal, M. Paranthaman, D. M. Kroeger, and D. K. Christen, *Physica C* **304**, 82 (1998).
- ²³A. E. Lee, C. E. Platt, J. F. Burch, R. W. Simon, J. P. Goral, and M. M. Aljassim, *Appl. Phys. Lett.* **57**, 2019 (1990).
- ²⁴E. Sader, H. Schmid, K. Hradil, and W. Wersing, *Supercond. Sci. Technol.* **4**, 371 (1991).
- ²⁵A. D. Li, Q. Y. Shao, H. Q. Ling, J. B. Cheng, D. Wu, Z. G. Liu, N. B. Ming, C. Wang, H. W. Zhou, and B. Y. Nguyen, *Appl. Phys. Lett.* **83**, 3540 (2003).
- ²⁶A. C. Jones and P. R. Chalker, *J. Phys. D: Appl. Phys.* **36**, R80 (2003).
- ²⁷T. D. Manning, Y. F. Loo, A. C. Jones, H. C. Aspinall, P. R. Chalker, J. F. Bickley, L. M. Smith, and G. W. Critchlow, *J. Mater. Chem.* **15**, 3384 (2005).
- ²⁸A. N. Meza-Rocha, E. Zaleta-Alejandre, J. G. Cabanas-Moreno, S. Gallardo-Hernandez, Z. Rivera-Alvarez, M. Aguilar-Frutos, and C. Falcony, *ECS J. Solid State Sci. Technol.* **3**(2), N1 (2014).
- ²⁹M. Esro, G. Vourlias, C. Somerton, W. I. Milne, and G. Adamopoulos, *Adv. Funct. Mater.* **25**, 134 (2015).
- ³⁰G. Adamopoulos, S. Thomas, D. D. C. Bradley, M. A. McLachlan, and T. D. Anthopoulos, *Appl. Phys. Lett.* **98**, 123503 (2011).
- ³¹G. Adamopoulos, S. Thomas, P. H. Wöbkenberg, D. D. C. Bradley, M. A. McLachlan, and T. D. Anthopoulos, *Adv. Mater.* **23**, 1894 (2011).
- ³²P. N. Plassmeyer, K. Archila, J. F. Wager, and C. J. Page, *ACS Appl. Mater. Interfaces* **7**, 1678 (2015).
- ³³S. S. Shoup, M. Paranthaman, D. B. Beach, E. D. Specht, and R. K. Williams, *J. Mater. Res.* **12**, 1017 (1997).
- ³⁴M. F. Ng and M. J. Cima, *J. Mater. Res.* **12**, 1306 (1997).
- ³⁵G. Adamopoulos, A. Bashir, W. P. Gillin, S. Georgakopoulos, M. Shkunov, M. A. Baklar, N. Stingelin, D. D. C. Bradley, and T. D. Anthopoulos, *Adv. Funct. Mater.* **21**, 525 (2011).
- ³⁶J. Robertson, *Rep. Prog. Phys.* **69**, 327 (2006).