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High performance In_2O_3 thin film transistors using chemically derived aluminum oxide dielectric

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We report high performance solution-deposited indium oxide thin film transistors with field-effect mobility of $127 \text{ cm}^2/\text{Vs}$ and an $I_{\text{on}}/I_{\text{off}}$ ratio of 10^6 . This excellent performance is achieved by controlling the hydroxyl group content in chemically derived aluminum oxide (AlO_x) thin-film dielectrics. The AlO_x films annealed in the temperature range of $250\text{--}350^\circ\text{C}$ showed higher amount of Al-OH groups compared to the films annealed at 500°C , and correspondingly higher mobility. It is proposed that the presence of Al-OH groups at the AlO_x surface facilitates unintentional Al-doping and efficient oxidation of the indium oxide channel layer, leading to improved device performance. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816060>]

Over the past 10 years, transparent oxide thin film transistors (TFTs) have been extensively studied due to their potential use in large area flat-panel display (FPD) applications. Oxide semiconductor based TFTs have been proven to be the alternative candidates to the low mobility silicon-based TFTs, which are currently being used for display applications.¹ High performance oxide TFTs have been reported using vacuum deposition techniques^{2–5} and have also been used for the demonstration of display devices.^{6,7} Solution deposition techniques have also been employed for the fabrication of oxide TFTs. During the last few years, zinc oxide,^{8,9} indium oxide,^{10,11} zinc tin oxide,^{12,13} indium zinc oxide,^{14,15} and indium gallium zinc oxide^{16–18} based thin film transistors with reasonable performance have been reported using spin coating technique. It is noted that, in most of the previously reports on solution processed TFTs, high annealing temperatures have been used to achieve better device performances and the TFTs are operated in very high operating voltage ranges. In practical, however, TFTs prepared at low processing temperatures with high field-effect mobility, high $I_{\text{on}}/I_{\text{off}}$ ratio, low turn-on voltage, and small sub-threshold swing values are needed for low-voltage operation and faster switching applications. The use of appropriate metal precursors, solvents, and appropriate gate dielectric are very crucial parameters to enable low process temperatures and good device performances. Low voltage operated TFTs with good performance have been reported using solution-processed gate dielectrics such as zirconium oxide¹³ and sodium beta-alumina.¹⁹ However, the processing temperature of typical dielectric layers is very high in these cases ($>500^\circ\text{C}$), which is not suitable to be used for practical display applications.

In the present work, we demonstrated the fabrication of high performance and low-voltage operated TFTs using solution processed In_2O_3 as the semiconducting layer and aluminum oxide (AlO_x) as the gate dielectrics at significantly lower temperature. We found that the aluminium hydroxide content

present in spin coated aluminium oxide dielectrics plays an important role to obtain high performance In_2O_3 TFTs.

The precursor solution for the preparation of AlO_x films was prepared by dissolving aluminum chloride (0.5 M) in a mixture of acetonitrile (AN) and ethylene glycol (EG) with AN to EG ratio of 3:7. The mixed solutions were stirred at room temperature in air for 4 h. Heavily doped p-type silicon wafers were used as the gate electrode and substrate. The Si substrates were cleaned ultrasonically by ethanol, acetone, and isopropanol and then exposed to oxygen plasma for 2 min to enhance the hydrophilicity. The AlO_x precursor solution was spun on the cleaned Si surfaces at a rotation speed of 3000 rpm in air. After spin coating, the wet films were placed on a hot plate at 90°C for 5 min and then subjected to rapid annealing at the temperature range of $250\text{--}500^\circ\text{C}$ in air for 10 min. The spin coating and annealing process was repeated for three times. Finally, the AlO_x films were annealed in the temperature range of $250\text{--}500^\circ\text{C}$ for 2 h in air. The AlO_x films prepared at 250°C , 350°C , and 500°C , hereafter will be called as $\text{AlO}_x\text{-}250^\circ\text{C}$, $\text{AlO}_x\text{-}350^\circ\text{C}$, and $\text{AlO}_x\text{-}500^\circ\text{C}$, respectively. The average thickness of the $\text{AlO}_x\text{-}250^\circ\text{C}$, $\text{AlO}_x\text{-}350^\circ\text{C}$, and $\text{AlO}_x\text{-}500^\circ\text{C}$ were found to be $\sim 120 \text{ nm}$, $\sim 115 \text{ nm}$, and $\sim 95 \text{ nm}$, respectively. Indium chloride (0.05 M) dissolved in acetonitrile and ethylene glycol (9:1 v/v) was used as the precursor solution for the preparation of In_2O_3 semiconductor channel layer. The mixed solution was stirred at $\sim 50^\circ\text{C}$ for 1 h. One layer of the indium oxide precursor solution was spun on AlO_x films at a rotation speed of 4000 rpm in air. The wet films were kept on a hot plate at 80°C for 5 min and then subjected to rapid annealing at 250°C for 1 h in air using a tube furnace. Circular shaped aluminum contacts (thickness $\sim 80 \text{ nm}$) with diameter of $100 \mu\text{m}$ were used for the capacitance and leakage current measurements of the AlO_x films. Aluminum source and drain electrodes with channel width to length ratio (W/L) of 10 ($W = 1000 \mu\text{m}$ and $L = 100 \mu\text{m}$) were used for the transistor characteristic measurements. The aluminum contacts were deposited using shadow mask and e-beam evaporation. Crystallinity of the AlO_x and In_2O_3 films were studied by x-ray diffraction (XRD) diffractometer (Bruker D8

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Discover) using Cu $K\alpha$ radiation. The chemical composition of the AlO_x and In_2O_3 films were analyzed by x-ray photoelectron spectroscopy (XPS) using an Axis Ultra DLD spectrometer (Kratos Analytical, UK). Capacitance of the AlO_x films was measured by a Precision LCR meter (Agilent E4980A). The current-voltage characteristics of the AlO_x capacitors and In_2O_3 TFTs were performed using a semiconductor characterization system (Keithley 4200-SCS).

The x-ray diffraction (XRD) patterns of the AlO_x films prepared at different annealing temperatures are shown in Fig. 1(a). No peak corresponding to the crystalline Al_2O_3 was observed, suggesting amorphous AlO_x films were obtained over the entire range of annealing temperatures. The AFM images of the corresponding AlO_x films are shown in Figs. 1(b)–1(d). The interface roughness of the gate dielectric is one of the crucial parameter to reduce carrier scattering and obtain high field-effect mobility. The root mean square surface roughness of the AlO_x -250°C, AlO_x -350°C, and AlO_x -500°C was measured to be 0.3 nm, 0.2 nm, and 0.2 nm, respectively, and the obtained low surface roughness values are ideal for obtaining good device performances.

The chemical composition of the AlO_x films was investigated by XPS measurements. The XPS O1s peaks of the AlO_x films prepared at different annealing temperatures are shown in Fig. 2(a). The open circles show the measured data and the solid lines represents the Gaussian peak fitting results. The deconvoluted results of O1s peaks exhibited a peak at ~ 531.0 eV, attributed to the O^{2-} in Al_2O_3 and another peak at ~ 532.3 eV, attributed to oxygen associated to the OH^- in aluminum hydroxide.²⁰ The intensity of the two peaks at ~ 531.0 eV and ~ 532.3 eV were comparable in case of AlO_x -250°C. Interestingly, the intensity of the peak at ~ 532.3 eV decreased and subsequently, the intensity of the peak at ~ 531.0 eV increased with increasing annealing temperature above 250°C. The decreased intensity of the peak at ~ 532.3 eV may be attributed to the conversion of more aluminum hydroxides to form Al_2O_3 at higher temperatures. It may be noted here that the associated OH groups are mainly

FIG. 1. (a) XRD patterns of AlO_x films prepared at different annealing temperatures and AFM images of AlO_x films prepared at (b) 250°C, (c) 350°C, and (d) 500°C.

FIG. 2. XPS (a) O1s and (b) Al2p spectra of AlO_x films prepared at different annealing temperatures. (c) Leakage current vs voltage and capacitance vs frequency curves (inset) of AlO_x films prepared at different annealing temperatures measured with $\text{p}^+\text{-Si}/\text{AlO}_x/\text{Al}$ structures.

due to the water absorbed from the environment in the AlO_x films after the final annealing. At low annealing temperatures, all the aluminum atoms are not completely oxidized and hence they absorb water molecules from the environment to form aluminum hydroxides. Fig. 2(b) shows the Al2p peaks of the AlO_x films prepared at different annealing temperatures. The XPS spectra show a singlet Al2p peak at ~ 74.3 eV in case of AlO_x -250°C and AlO_x -350°C, whereas, it was shifted to 74.2 eV in case of AlO_x -500°C. The shifting of the Al2p peak towards lower binding energy in case of AlO_x -500°C may be attributed to the decrease in the concentration of OH^- ions or coordination number of Al^{3+} ions in the film.²¹ Fig. 2(c) shows the leakage current of different AlO_x films measured with $\text{p}^+\text{-Si}/\text{AlO}_x/\text{Al}$ structures. It is clearly seen that the leakage current of the AlO_x films was decreased with increasing annealing temperature. The capacitance of the aforementioned $\text{p}^+\text{-Si}/\text{AlO}_x/\text{Al}$ structures were measured in the frequency range of 1 kHz to 1 MHz and the obtained curves are shown in the inset of Fig. 2(c). The measured capacitance at 1 MHz for AlO_x -250°C, AlO_x -350°C, and AlO_x -500°C were found to be 66 nF/cm², 75 nF/cm², and 58 nF/cm², respectively. The high value of capacitance in case of the low temperature annealed AlO_x films may attribute to the presence of OH-groups.²²

The schematic of the TFT structure used in this work is shown in Fig. 3(a). Figs. 3(c)–3(e) show the out-put characteristics of the fabricated In_2O_3 TFTs using AlO_x -250°C, AlO_x -350°C, and AlO_x -500°C as the gate dielectrics. The

FIG. 3. (a) Schematic of the TFT structure, (b) transfer characteristic curves of the In_2O_3 TFTs fabricated using AlO_x films prepared at different temperatures as the gate dielectrics. Out-put characteristic curves of the In_2O_3 TFTs fabricated using (c) AlO_x -250 °C, (d) AlO_x -350 °C, and (e) AlO_x -500 °C as the gate dielectrics. The inset in (e) shows the I_D vs V_D curves measured at zero gate voltage for the TFTs fabricated using AlO_x dielectrics annealed at different temperatures.

out-put characteristics of the TFTs fabricated on AlO_x -250 °C and AlO_x -350 °C exhibited clear pinch-off and excellent hard saturation. Lower drain currents were obtained in case of the TFTs fabricated using AlO_x -500 °C as the gate dielectric and the TFTs were found to operate in the depletion mode operation with high negative turn-on voltage (V_{on}), which is the gate voltage at the onset of the initial sharp rise in drain current in a $\log(I_D)$ - V_G transfer characteristic curve. The transfer characteristic curves of all the TFTs obtained at a constant drain to source voltage (V_D) of 2 V are shown in Fig. 3(b). The field-effect mobility (μ_{sat}) of the TFTs was estimated in the saturation regime of the transfer curve (Fig. 3(b)) using the following equation:

$$I_{D,\text{sat}} = \frac{W}{2L} \mu_{\text{sat}} C_{\text{ox}} (V_G - V_{\text{TH}})^2, \quad (1)$$

where I_D is the drain to source current, V_G is the gate to source voltage, V_{TH} is the threshold voltage, W and L are the channel width and length, respectively, and C_{ox} is the capacitance per unit area of the gate dielectric. The values of μ_{sat} were found to be $82 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $127 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the In_2O_3 TFTs fabricated on AlO_x -250 °C and AlO_x -350 °C, respectively. The values of V_{on} for the TFTs fabricated on AlO_x -250 °C and AlO_x -350 °C were found to be -0.1 V and 0.1 V , respectively. The drain off-current to on-current ratio ($I_{\text{on}}/I_{\text{off}}$) for the TFTs fabricated on AlO_x -250 °C and AlO_x -350 °C were 3×10^4 and 1×10^6 , respectively. The low $I_{\text{on}}/I_{\text{off}}$ ratio in case of the TFTs fabricated on AlO_x -250 °C can be attributed to high leakage of

TABLE I. Electrical parameters of In_2O_3 TFTs fabricated using AlO_x films annealed at different temperatures as the gate dielectrics.

AlO_x annealing temperature	$\frac{O_V}{O_V + O_L}$	μ_{sat} (cm^2/Vs)	$I_{\text{on}}/I_{\text{off}}$	V_{on} (V)	SS (V/dec)
250 °C	24%	82	3×10^4	-0.1	0.271
350 °C	28%	127	1×10^6	0.1	0.137
500 °C	31%	5	2×10^3	-2.6	0.951

AlO_x -250 °C as evident from the I - V curve shown in Fig. 2(c). As seen from Table I, the TFTs fabricated using AlO_x -500 °C as the gate dielectric showed very inferior performance compared to the TFTs fabricated on AlO_x -250 °C and AlO_x -350 °C.

Material characterizations of the In_2O_3 films were performed to understand the effect of annealing temperature of AlO_x thin film dielectrics on the performance of In_2O_3 TFTs. The crystallinity of the In_2O_3 films was investigated by XRD using grazing incidence geometry with an incident angle of 1° . The grazing incidence XRD patterns (Fig. 4(a)) of the In_2O_3 films deposited on different AlO_x films showed a broad peak at $\sim 30.5^\circ$ corresponding to the (222) plane of In_2O_3 . The Gaussian peak fitting of the observed peaks revealed that the full width at half maximum (FWHM) for the In_2O_3 films deposited on AlO_x -250 °C (FWHM = 2.5°) and AlO_x -350 °C (FWHM = 2.8°) are higher than that of the In_2O_3 film deposited on AlO_x -500 °C (FWHM = 2.1°). Furthermore, Fig. 4(b) shows the XPS O1s spectra of the In_2O_3 films deposited on AlO_x films annealed at different temperatures. The Gaussian fitting (solid lines) of the all the O1s peaks exhibited a strong peak at 529.8 eV along with two shoulder peaks at 531.1 eV and 532.3 eV. The peak at 529.8 eV is attributed to the oxygen in In_2O_3 lattice without oxygen vacancy (O_L).²³ The peaks at 531.1 eV and 532.3 eV are attributed to the oxygen in In_2O_3 lattice with oxygen vacancy (O_V) and the OH groups attached to indium ions, respectively.^{17,23} Interestingly, as shown in Table I, the ratio of $O_V/(O_L + O_V)$ is higher in case of the In_2O_3 film deposited on AlO_x -500 °C compared to the

FIG. 4. (a) XRD patterns and (b) O1s XPS spectra of the In_2O_3 films deposited on AlO_x films prepared at different annealing temperatures.

In_2O_3 films deposited on AlO_x -250 °C and AlO_x -350 °C, indicating the presence of smaller concentration of oxygen vacancies in the latter two cases.

It is interesting to discuss the origin of the observed broadness of the XRD peaks and lower oxygen vacancy concentration in In_2O_3 films deposited on the AlO_x -250 °C and AlO_x -350 °C dielectrics. First, the XRD peak broadening most likely comes from the development of a more amorphous-like structure, a trend which has been previously reported for Al-doped In_2O_3 films,¹¹ possibly owing to the big difference between the atomic radii of Al (1.43 Å) and In (1.66 Å).²⁴ Thus, we suggest that the XRD peak broadening in case of In_2O_3 films deposited on AlO_x -250 °C and AlO_x -350 °C films is likely due to Al diffusion into the In_2O_3 channel from the underlying AlO_x films that are rich Al-OH groups. Second, the OH-groups attached to the Al at the interface of AlO_x as seen from the XPS O1s spectra (Fig. 2(a)) can act as oxygen source and induce a more efficient oxidation of In_2O_3 after annealing at 250 °C. Both Al-doping and OH-assisted oxidation of In_2O_3 are expected to reduce the oxygen vacancy concentration in In_2O_3 films deposited on AlO_x -250 °C and AlO_x -350 °C films.^{11,25} In contrast, higher oxygen vacancy concentration is expected in the In_2O_3 deposited on AlO_x -500 °C due to the reduced OH group concentration in AlO_x -500 °C (see XPS in Fig. 2(a)). This is also expected to increase the carrier concentration and conductivity of In_2O_3 , which is believed to be controlled by oxygen vacancies.²⁶ The increased carrier concentration of In_2O_3 TFTs made on AlO_x -500 °C is indeed observed as can be seen from the plot of drain current vs drain voltage measured at zero gate bias, as shown in the inset of Fig. 3(e). Fig. 3(e) shows significantly higher drain current in In_2O_3 TFTs made on AlO_x -500 °C compared to the TFTs made on AlO_x -250 °C and AlO_x -350 °C dielectrics. The values of sub-threshold swing ($SS = \partial V_{\text{DS}} / \partial \log_{10} I_{\text{DS}}$) were found to be 0.271 V dec⁻¹, 0.137 V dec⁻¹, and 0.951 V dec⁻¹ for the TFTs fabricated on AlO_x -250 °C, AlO_x -350 °C, and AlO_x -500 °C, respectively. The high value of “SS” in case of the TFTs made on AlO_x -500 °C, further confirms the increased carrier concentration in In_2O_3 deposited on AlO_x -500 °C. Thus, the inferior performance in case of the In_2O_3 TFT fabricated using AlO_x -500 °C as the gate dielectric can be attributed to the scattering of carriers¹⁸ due to the high carrier concentration in the corresponding In_2O_3 semiconductor layer. Hence, we find that the presence of Al-OH groups in low temperature annealed AlO_x film plays a crucial role in In_2O_3 TFT performance. It is noted that the performance of our devices are superior to that of previously reported results for the solution processed In_2O_3 TFTs.^{10,11,27}

In summary, thin film transistors were fabricated using solution-processed In_2O_3 semiconductor as the channel layer and AlO_x films annealed at different temperatures as the gate

dielectrics. The TFTs were operated at very low voltage range and exhibited better performance than previously reported In_2O_3 TFTs processed at these temperatures. High performance In_2O_3 TFTs could be obtained at relatively low processing temperatures by controlling the Al-OH content in solution processed AlO_x gate dielectrics.

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