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High performance solution-deposited amorphous indium gallium zinc oxide thin film transistors by oxygen plasma treatment

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Solution-deposited amorphous indium gallium zinc oxide (a-IGZO) thin film transistors (TFTs) with high performance were fabricated using O₂-plasma treatment of the films prior to high temperature annealing. The O₂-plasma treatment resulted in a decrease in oxygen vacancy and residual hydrocarbon concentration in the a-IGZO films, as well as an improvement in the dielectric/channel interfacial roughness. As a result, the TFTs with O₂-plasma treated a-IGZO channel layers showed three times higher linear field-effect mobility compared to the untreated a-IGZO over a range of processing temperatures. The O₂-plasma treatment effectively reduces the required processing temperature of solution-deposited a-IGZO films to achieve the required performance. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4718022>]

Transparent amorphous indium gallium zinc oxide (a-IGZO) thin film transistors (TFTs) have been extensively studied over the past few years due to their potential application in flat-panel displays.¹ Amorphous IGZO TFTs offer several advantages over the low mobility ($\leq 1 \text{ cm}^2/\text{Vs}$) amorphous silicon TFTs, which are being widely used in flat panel displays. An attractive feature of a-IGZO thin films is that they can be deposited at very low temperature with large-area uniformity due to the absence of grain boundaries. Moreover, a-IGZO thin films are highly transparent in the whole visible range enabling the realization of transparent active-matrix flat-panel displays with high filling factors. Despite the amorphous structure, IGZO thin films exhibit relatively high mobility because the bottom of the conduction band in a-IGZO is believed to be composed of spatially spread metal ns orbitals which overlapped with the neighbor ns orbitals and the magnitude of this overlap is insensitive to distorted metal–oxygen–metal (M–O–M) chemical bonds.² Amorphous IGZO TFTs with high performance have been recently reported using vacuum deposition techniques.^{3,4} In comparison to the vacuum deposition techniques, the use of solution process techniques offers an inexpensive fabrication of active matrix backplanes for large-area display applications. Solution based deposition methods such as spin coating,^{5–9} ink-jet,^{10,11} and gravure printing¹² have been used in the past few years for the fabrication of a-IGZO TFTs. However, high processing temperature and low device performance restrict the solution-derived a-IGZO TFTs to be used for low cost and high performance electronic applications. Appropriate chemicals, composition, and annealing conditions are very crucial to get low-temperature processed a-IGZO TFTs with high performances.^{13–16} Further, the electrical conductivity in oxide semiconductors is mainly controlled by oxygen vacancies which act as donors, thus, it is

necessary to minimize the oxygen related defects to achieve TFTs with controlled and high performance characteristics.

In the present work, the solution-deposited precursor films were exposed to oxygen plasma prior to high temperature annealing. This was primarily performed with the aim of facilitating the oxidation of metal ions at lower temperature and decreasing the oxygen related defects and hence to enhance the performance of a-IGZO TFTs. Amorphous IGZO thin film transistors were prepared in the annealing temperature range 300 °C to 400 °C. In all cases, the devices with O₂-plasma treated a-IGZO channel layers showed higher performances compared to the devices with untreated a-IGZO channel layers.

Indium chloride (3M), gallium nitrate hydrate (1M), zinc chloride (1M), and ethanolamine were dissolved in 2-methoxyethanol to prepare the precursor solution. The molar ratio of ethanolamine to indium, gallium, and zinc was maintained as 5:1, 1:1, and 1:1, respectively. The mixed solution was stirred at 50 °C in air for 1 h and aged for about 24 h. Indium tin oxide (ITO) coated glass substrates with aluminum titanium oxide (ATO) deposited by atomic layer deposition¹⁷ were used as the gate electrode and dielectric, respectively. The ITO/ATO substrates were cleaned ultrasonically by acetone and isopropanol. The cleaned ITO/ATO substrates were exposed to oxygen plasma for 3 min to enhance the hydrophilicity of the ATO surface. The precursor solution was spun on ATO surfaces at a rotation speed of 6000 rpm for 30 s in air. After spin coating, the wet precursor films were placed on a hot plate at 80 °C in air for 5 min and then subjected to annealing at 300–400 °C in air for 10 min using a quick-insertion annealing method (the sample was quickly inserted into a tube furnace idling at the desired process temperature). These IGZO films hereafter will be called as untreated films. For O₂-plasma treatment, the precursor films after hot plate heating were exposed to O₂-plasma (30 W) for 45 s and then the films were subjected to quick-insertion annealing at 300–400 °C in air for 10 min. These IGZO films will hereafter be called as O₂-plasma treated films. A second

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layer of IGZO was deposited on top of the first layer using the same conditions to achieve the desired thickness of ~ 20 nm. Finally, the samples were annealed at 300–400 °C for 1 h in air. Aluminum (70 nm) source and drain electrodes with channel width and length of 500 μm and 100 μm , respectively, were deposited using e-beam evaporation. Fourier transform infrared spectra (FT-IR) of the IGZO films were obtained by a Nicolet iS10 FT-IR (Thermo Scientific) Spectrometer. Crystallinity and cross-sectional images of IGZO films was studied by using a transmission electron microscope (Titan ST, FEI). The chemical composition of the IGZO films was analyzed by x-ray photoelectron spec-

troscopy (XPS) using an Axis Ultra DLD spectrometer (Kratos Analytical, UK). The current-voltage characteristics of the IGZO TFTs were performed using a semiconductor characterization system (Keithley 4200-SCS) and a Cascade Microtech (Summit-11600 AP) microprobe station.

Fig. 1 shows a schematic of the fabricated TFT devices, the output characteristics, and the transfer characteristics for both untreated and O_2 -plasma treated a-IGZO channel layers. The output curves were measured at a constant gate voltage (V_G) of 5 V and the transfer curves were measured at a constant drain voltage (V_D) of 3 V. The output characteristics of all the a-IGZO TFTs showed clear pinch-off and excellent saturation behavior with an enhanced mode operation. Both output and transfer characteristic curves clearly show an increase of drain current after O_2 -plasma treatment. The field-effect mobility (μ_{lin}) of the TFTs was estimated in the linear regime operation of the transfer curve (Fig. 2(b)) using the following equation:¹⁸

$$I_{D,\text{lin}} = \frac{W}{L} \mu_{\text{lin}} C (V_G - V_{\text{TH}}) V_D, \quad (1)$$

where I_D is the drain current, V_{TH} is the threshold voltage, W and L are the channel width and length, respectively, and C is the capacitance per unit area of the gate dielectric. The extracted TFT parameters are listed in Table I. The TFTs with untreated a-IGZO channel layer prepared at 300 °C showed a field-effect mobility, $I_{\text{on}}/I_{\text{off}}$ ratio, and threshold voltage of 0.8 cm^2/Vs , $\sim 1 \times 10^7$, and ~ 11.1 V, respectively. However, the device with plasma treated a-IGZO channel layer showed a field-effect mobility of 2.7 cm^2/Vs , which is more than three times higher than the value of mobility exhibited by the device with untreated a-IGZO as the channel layer. As can be seen from Table I, similar increase in mobility was obtained for the devices prepared at 350 °C. The TFTs prepared at 400 °C with untreated and O_2 -plasma treated a-IGZO channel layers exhibited the highest field-effect mobility of 4.3 cm^2/Vs and 11.2 cm^2/Vs , respectively. The subthreshold swing (S) of the a-IGZO TFTs calculated

FIG. 1. (a) Schematic device structure, (b) out-put characteristic curves measured at a constant V_G of 5 V, and (c) transfer characteristic curves measured at a constant V_D of 3 V for the TFTs with untreated and O_2 -plasma treated a-IGZO channel layers prepared at different annealing temperatures.

FIG. 2. Cross-sectional TEM images and Fourier transform of the (a) and (b) untreated and (c) and (d) plasma treated a-IGZO films prepared at 400 °C.

TABLE I. Electrical parameters of a-IGZO TFTs prepared at different annealing temperatures.

Annealing temperature	O ₂ -plasma treatment	μ_{lin} (cm ² /Vs)	$I_{\text{on}}/I_{\text{off}}$	V_{TH} (V)	S (V/dec)
300	No	0.8	$\sim 1 \times 10^7$	11.1	0.356
300	Yes	2.7	$\sim 2 \times 10^6$	9.3	0.398
350	No	2.8	$\sim 3 \times 10^6$	7.6	0.225
350	Yes	7.2	$\sim 4 \times 10^6$	6.2	0.254
400	No	4.3	$\sim 6 \times 10^6$	7.5	0.178
400	Yes	11.2	$\sim 2 \times 10^7$	3.3	0.180

by using the formula $S = \partial V_G / \partial \log I_D$ was found to be lowest (0.178-0.180 V/dec) in case of the devices prepared at 400 °C.

A series of materials analysis studies were conducted to understand the reason for the improved TFT performance exhibited by the O₂-plasma treated a-IGZO films. The TEM cross-sectional images and Fourier transform of the untreated and O₂-plasma treated a-IGZO films prepared at 400 °C are shown in Fig. 2. The Fourier transform of the IGZO layer showed a very diffused electron diffraction pattern for both the films (Figs. 2(b) and 2(d)), indicating the amorphous nature of the a-IGZO films. The amorphous nature of the a-IGZO films is consistent with the previous reports.¹³ Similar results were obtained for the a-IGZO films prepared at 300 °C and 350 °C. From the cross-sectional images shown in Figs. 2(a) and 2(c), it is seen that untreated films have a relatively rough a-IGZO/ATO interface compared to the O₂-plasma treated films. O₂-plasma treatment has been reported to be an effective method for removal of organics and residual chemicals from films.¹⁹ In fact, we observe a similar effect as shown in the FTIR spectra in Fig. 3, which shows the FTIR spectra of the untreated and 45 s O₂-plasma treated IGZO precursor films prior to high temperature annealing. The FTIR spectra of the untreated film exhibited an intense peak at 3422 cm⁻¹ due to the OH-stretching vibration of absorbed water in the film. The peaks at 1617 cm⁻¹ and 3172 cm⁻¹ are attributed to NH₂-bending and overtone of NH₂-bending vibrations, respectively.²⁰ The FTIR spectra also exhibited an intense broad peak consisting of two peaks

FIG. 3. FTIR spectra of untreated and 45s O₂-plasma treated IGZO films before high temperature annealing.

at ~ 1382 cm⁻¹ and 1338 cm⁻¹, corresponding to CH₂-wagging and C-O-H bending vibrations, respectively.²¹ The intensity of all the peaks decreased after O₂-plasma treatment indicating the removal of hydrocarbons and solvents from the IGZO film. The decrease in intensity of the peak corresponding to the OH-stretching vibration suggests the partial transformation of metal-hydroxide-metal (M-OH-M) to M-O-M groups by O₂-plasma treatment. The removal of organic moieties using O₂-plasma prior to annealing reduces the amount of residual gases that will be released from the films during thermal annealing thereby leading to a smoother interface. Thus, we believe that this difference in interface roughness is related to the evolution of residual chemical species during film crystallization which is more pronounced in the untreated films as shown by FTIR. Non-uniform removal of chemical species from different parts of the a-IGZO film can occur during film crystallization at high temperature, especially if large concentrations of such residual chemicals are present in the film prior to thermal annealing. This effect is the likely reason for the enhanced interfacial roughness of the untreated films.

The O 1s XPS spectra of untreated and O₂-plasma treated a-IGZO films prepared at 400 °C are shown in Fig. 4. To avoid any contribution of oxygen and water molecules adsorbed at the surface of a-IGZO, the XPS spectra were obtained after etching ~ 4.5 nm of the a-IGZO films. The obtained O 1s peaks were deconvoluted using Gaussian profile which exhibited an intense peak at around 529.9 eV along with a broad shoulder peak at 531.3 eV. The peak at 529.9 eV is attributed to oxygen in a-IGZO having no oxygen deficiency whereas the peak at 531.3 eV is attributed to oxygen deficient regions in the a-IGZO system.^{9,15} The area under the peak at 531.3 eV in case of the untreated a-IGZO films was found to be higher than that of the O₂-plasma treated a-IGZO film indicating a presence of higher oxygen vacancy concentration in case of the untreated film compared to the O₂-plasma treated film. As the a-IGZO films were

FIG. 4. O 1s XPS spectra of the (a) untreated and (b) 45s O₂-plasma treated a-IGZO films prepared at 400 °C. The solid circles and lines represent the experimental data and Gaussian peak fitting results, respectively.

exposed to O₂-plasma before the high temperature annealing, we believe that the decrease in oxygen vacancies in this case may be attributed to the pre-oxidation of the metal ions and/or the formation of M-O-M groups that facilitated the oxide formation. Similar results were obtained for the untreated and O₂-plasma treated a-IGZO films annealed at 300 °C and 350 °C.

The field-effect mobility and the subthreshold swing of the semiconducting thin films are mainly affected by the presence of defect states that can cause electron trapping.^{22,23} Moreover, the performance of a TFT depends on the quality and roughness of the interface between the semiconductor and the dielectric because the conduction channel is formed mainly in a very thin layer close to the interface. Therefore, the increase in mobility of the TFTs achieved in the present work in case of TFTs with O₂-plasma treated a-IGZO channel layers can be attributed to the decrease in oxygen vacancies and hydrocarbon concentration as well as the formation a smoother interface between the a-IGZO channel layer and the ATO dielectric. Filling of oxygen vacancies has been reported to improve TFT mobility²⁴ as they can act as scattering centers. Similarly, residual trapped chemicals in the active layer and interfacial roughness can result in enhanced carrier scattering and hence reduced mobility. From Table I, it can be seen that the threshold voltage of the TFTs with plasma treated a-IGZO channel layers are lower than the TFTs with untreated a-IGZO. It may be noted that the subthreshold slope, which is a measure of interfacial trap density,²⁵ was not significantly affected by O₂-plasma treatment. It has been reported that the threshold voltage can be affected by charge trapping due to the interfacial roughness between the gate dielectric and the semiconductor channel layer.²⁶ From the FTIR and TEM results, it was found that the hydrocarbons were partially removed and comparatively smoother interfaces were formed after O₂-plasma treatment. Thus, the decrease in threshold voltage without significant change in subthreshold swing in the present work may be attributed to the reduction of charge trapping due to the formation of cleaner and smoother interface between ATO dielectric and O₂-plasma treated a-IGZO channel layer. The obtained high field-effect mobility with low subthreshold swing values in our solution-derived films is comparable to the previously reported results by vacuum deposition techniques. In addition, the obtained mobility of the a-IGZO TFTs prepared at 300 °C is higher than the previously reported sol-gel based a-IGZO TFTs prepared at this processing temperature using metal halides and nitrate based precursor materials.

In summary, thin film transistors were fabricated using solution processed a-IGZO channel layers annealed in the temperature range 300 °C to 400 °C. The wet-precursor films were exposed to O₂-plasma prior to the high temperature thermal annealing. In comparison to the untreated films, a smoother interface was obtained after O₂-plasma treatment.

In addition, the number of oxygen vacancies in case of the O₂-plasma treated a-IGZO films was lower than that of the untreated films. In all the cases, three times increase in linear field-effect mobility was obtained using O₂-plasma treated a-IGZO films as the channel layers. The O₂-plasma treatment prior to the high temperature annealing effectively reduced the processing temperature and improved device performance.

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