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Oxygen Plasma Functioning of Charge Carrier Density in Zinc Oxide Thin-Film Transistors

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A change in the charge carrier density of zinc oxide (ZnO) films for control the functioning of thin-film transistors (TFTs) has been studied by oxygen (O_2) plasma techniques. This effect was interpreted in terms of a threshold voltage shift and the variation in carrier mobility. The plasma-surface interaction on the molecular level and the behavioral characterization of ZnO films were investigated by X-ray photospectroscopy of the O 1s region. This process was highly sensitive at low level variations in defect and doping density. O_2 plasma treatment leads to a shift of turn-on voltage and a reduction of the off-current by more than two orders of magnitude in ZnO-TFTs. © 2013 The Japan Society of Applied Physics

Zinc oxide (ZnO) films have recently attracted great technical interest to be used as the channel layer in thin film transistor (TFT) applications because of their versatile properties including being transparent conducting oxide and a wide band gap (~3.37 eV) of the II–VI semiconductor group.[1,2] Oxygen is in a class of elements of the VIA group of the periodic table and zinc is a transition metal from a member of the IIB (now 12th) group. The considerable progress of low temperature ZnO thin film to be used in electronic device applications has been studied by several authors[3,4] using various deposition processes such as RF-magnetron sputtering[5] and laser ablation.[6] The reported interaction of O_2 ions with metal oxide surfaces[7,8] focused on the dependence of the oxide type, temperature, O_2 plasma power, pressure and process time. The thickness of the oxide layer obtained at low pressures (0.1 Pa) is approximately one monolayer. Over the past three decades, there have been a many studies on ZnO thin film, but there are still two major issues, which are very important to make it an ideal candidate to be used in the microelectronics industry. The first is that the high quality and high performance ZnO thin film deposition is carried out at low temperatures and the second is the difficulty in achieving ultra low thickness to shrink the size of electronics devices. Low deposition temperature and ultra low thickness are essential for deposition on inexpensive transparent substrates such as glass and plastic. ZnO is an ideal semiconductor material using in TFT device applications, which possess a higher mobility than amorphous silicon and lower deposition temperatures than polycrystalline silicon. Moreover, the wide band gap of ZnO leads to a desirable level of driving individual pixels in liquid crystal display (LCD) and organic light emitting diode (OLED).[9,10]

The purpose of the work reported here is to give a detailed account of the deposition of ultra thin ZnO films to be used in TFT applications using zinc-acetate sol–gel solution by spin coating techniques. The effect of O_2 plasma treatment on the surfaces and interfaces was characterized by a solution processed active channel layer from ultra thin ZnO films. The time induced ZnO oxidation processes occurred at room temperature on a silicon substrate when treated with O_2 plasma power and their effects on the as deposited film were studied in details by X-ray photospectroscopy (XPS) analysis and the changes in electrical performance of the ZnO-TFTs. The results suggest the chemical and ballistic effects are involved in this process to enhance the performance of ZnO ultra thin film transistors. The charge carrier density throughout ZnO films influenced by the O_2 plasma system showed a strong impact on the electrical measurements of TFTs, which was expected due to the enhanced surface and interface effects.

Prior to the deposition process, a p-type silicon (p-Si) wafer was exposed to O_2 plasma for 1 min to enhance the hydrophilicity of a wafer. The 100-nm-thick SiO_2 as a gate dielectric layer was deposited on a wafer by using a horizontal furnace. The 0.05 M zinc-acetate solution was prepared by dissolving zinc-acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] into ethanol ($C_2H_5OH$, 10 mL). The formulated solution was rigorously stirred for at least 2 h at room temperature. The zinc-acetate sol–gel solution was then spin coated on a SiO_2/p-Si substrate at a speed of 500 rpm for 30 s and then 1000 rpm for 30 s. After the two-steps spin-coating process, as deposited samples were treated with O_2 plasma from 1 to 5 min, which supplied the plasma power of 18 W. These plasma treated films were also annealed at a temperature 300 °C for 1 h under normal environmental conditions. The surface morphology of the ZnO films on p-Si wafers was evaluated using atomic force microscopy (AFM), a Digital Instruments Nanoscope D-5000, at a scan size of 1 μm and a scan rate of 1 Hz. The thickness of ZnO ultrathin films was measured by transmission electron microscopy (TEM) image analysis. To fabricate the ZnO-TFT a shadow mask for source and drain contacts was used onto the deposited ZnO film over SiO_2/p-Si for TFT applications. The channel length (L) and width (W) between Al electrodes were 70 and 2000 μm, respectively. Similarly, the 300-nm-thick Al gate electrodes, on the backside of the substrate, were also deposited by a thermal evaporator system. Electrical measurements for ZnO-TFTs were performed using an Agilent 4156 probe station.

Figure 1(a) illustrates the expected three-step reaction of (i) hydrolysis, (ii) condensation, and (iii) O_2 plasma surface ion interaction to obtain an appropriate ZnO surface over the SiO_2/p-Si substrate. To clarify the mechanism of the improvement in this surface modification, the chemical structure of the as deposited and the plasma treated ZnO films were further investigated by XPS which appeared in details elsewhere in this text. This shows the successive removal of the hydroxide layer with the plasma treatment and is in good agreement with the results reported by Huang

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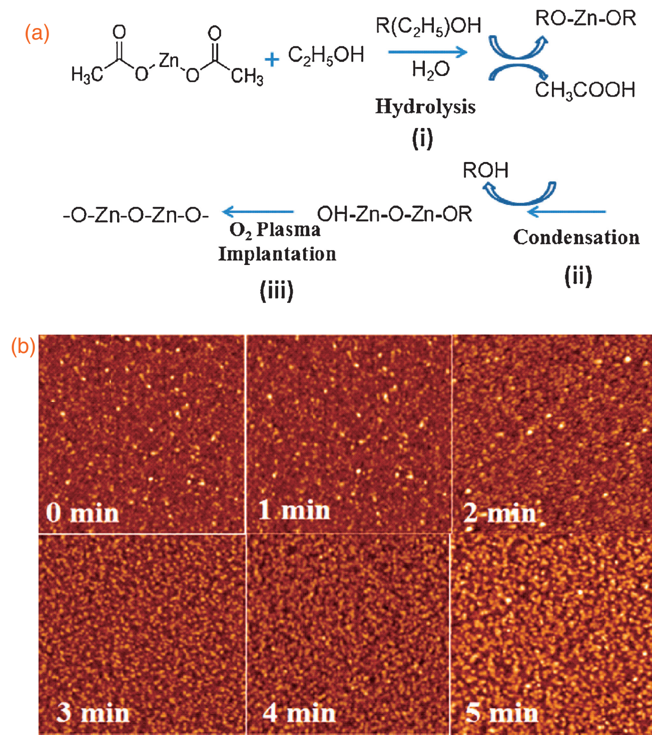

Fig. 1. (a) Schematic representation of the O_2 plasma growth mechanism for sol–gel-derived spin-coated as deposited ZnO film and (b) AFM images (scale: 1 μm) of the ZnO films with oxygen plasma treatment for 0–5 min.

et al.[11] The increase in the O–Zn bonding also shows the filling up of near surface oxygen vacancies, which are considered to be the main contributors to the shallow electron donor states. The root mean square (rms) surface roughness from AFM images for samples treated with O_2 plasma for 0–5 min shown in Fig. 1(b); which is between 1.0 and 1.8 nm. These AFM results revealed that the ZnO films treated with O_2 plasma from 0–3 min showed good quality with a large surface area, smooth, crack-free morphology, and a uniform ZnO film surface. It was pointed out from the results that the O_2 plasma treatment for 4 to 5 min or above time degrades the film quality and seriously affects the ZnO film surface, which degrades the performance while using it in TFT device application. The roughness and grain size of ZnO films slightly increased to about 1 nm but the post annealing ambient has no further significant effect on the morphology except the passivation of the film surface.

The next step towards the determining the effect of O_2 plasma techniques on ZnO films by making a device configuration of the designed bottom-gate and top-contact ZnO-TFTs. For the investigation of the charge transport properties for our ZnO thin film, we chose the TFT device configuration shown in Fig. 2(a). This was also used to determine the effect on charge carrier mobility due to the variation in charge carrier density of ZnO films. Figure 2(b) shows a cross-sectional TEM image of the ZnO/SiO_2 structures. The average thickness of the ZnO film was estimated to be about 5.0 nm for the sample treated with O_2 plasma for 0–5 min. The TEM image indicates the solution-derived semiconductor layer consists of only a 4.5-nm-thick ZnO film, which acts as an active semiconductor layer in

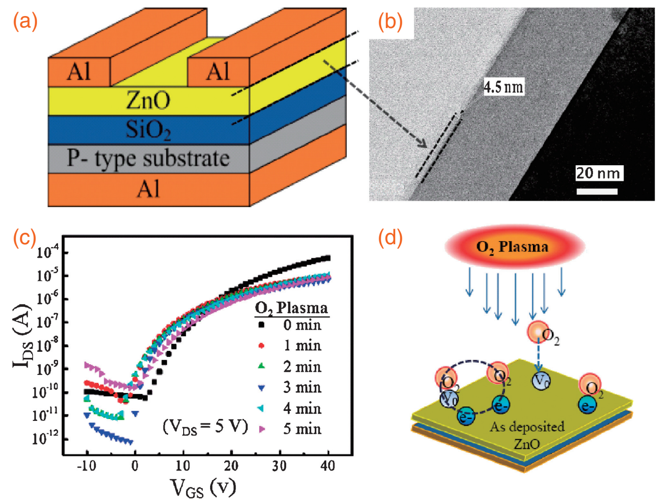

Fig. 2. (a) Schematic configuration of ZnO-based TFT structure, (b) cross-sectional TEM image of ZnO layer of 4.5 nm thickness, (c) transfer (I_{DS}–V_{GS}) characteristics measured at a constant $V_{DS} = 5$ V for O_2 plasma-treated ZnO films as channel layer at different times from 0–5 min, and (d) possible model of O_2 plasma for the threshold voltage shift depending on O_2 ratio.

Table I. Summary of various electrical parameters of ZnO-TFTs treated at different O_2 plasma processing times from 0 to 5 min.

Plasma-treatment time (min)	μ_{sat} ($cm^2 V^{-1} s^{-1}$)	Carrier concentration (cm^{-3})	V_{th} (V)	I_{on}/I_{off} ratio
0	0.06	4.2×10^{18}	12	1.1×10^6
1	0.045	3.9×10^{17}	8.2	3.6×10^5
2	0.032	1.2×10^{18}	9	2.1×10^6
3	0.022	4.3×10^{18}	9.3	1.2×10^7
4	0.027	5.1×10^{18}	9.5	1.4×10^6
5	0.032	6.8×10^{18}	11.8	1.4×10^4

the TFT-device application for a sample treated with O_2 plasma for 3 min only. It was pointed out that the O_2 plasma affect the thickness of ZnO films for various times, when the thickness of ZnO is sufficiently thin, thus O_2 plasma showed the small change in thicknesses rather than a dramatic change. Definitely it is reduced toward lower side between 6.1 and 3.8 nm for ZnO film treated with O_2 plasma treatment time for 0 to 5 min. Figure 2(c) shows the transfer characteristics of the plasma-treated ZnO-TFTs. The I_{on}/I_{off} ratio is 10^6 in the case of the as deposited (0 min) sample. The I_{on}/I_{off} ratio increases continually as a function of plasma-treated time. In addition, the off-state leakage currents (I_{off}) of the plasma-treated ZnO-TFTs show significant improvement from 5.6×10^{-11} to 7.6×10^{-13} A. However, the degradation of I_{off} implies crucial changes in carrier concentration and distribution after oxygen plasma treatment for 3 min. The I_{off} was raised by more than two orders of magnitude during the treatment time from 3 to 5 min. To help understand the performance of ZnO-TFTs with various O_2 plasma-treatment times, the extracted TFT parameters are listed in Table I. The threshold voltage (V_{th}) is extracted from the $(I_{DS})^{1/2}$ versus V_{GS} plot. The saturation mobility (μ_{sat}) for ZnO-TFTs were calculated from the transfer curve [Fig. 2(c)] using the equation[12]

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$$I_{DS} = \frac{\mu_{sat} C_i W}{2L} (V_{GS} - V_{th})^2, \tag{1}$$

where C_i is the capacitance per unit area of the gate dielectric, W and L are the channel width and length, respectively, V_{GS} is the gate-source bias, and V_{th} is the threshold voltage. As shown in Table I, the as-deposited (0 min) ZnO-TFTs showed a saturation mobility, threshold voltage, and I_{on}/I_{off} ratio of 0.06 cm^2 V^{-1} s^{-1}, 12 V, and 1.1×10^6, respectively. However, the device with ZnO-TFTs treated by O_2 plasma for 3 min showed a saturation mobility of 0.022 cm^2 V^{-1} s^{-1}, which is almost three-times lower than the mobility of the device with as-deposited ZnO-TFTs. Similar decreases in I_{off} and V_{th} were obtained for the devices with plasma treatment for up to 3 min. Here, we have found some unusual differences in the electrical properties of ZnO-TFTs for low-plasma-powered devices. Thus, we design a possible model of O_2 plasma for the threshold voltage shift depending on O_2 ratio, as shown in Fig. 2(d), and further studied this effect by XPS analysis. The properties of ZnO-TFTs were highly influenced by oxygen ions in their O_2 plasma surface interaction, which may be because oxygen vacancies provide the necessary free carriers for electrical conduction. Oxygen vacancies could be easily generated inside the oxides.[13] The result in instance with the microstructural and electrical characterization, which indicates the plasma treatment efficiently, suppresses the chemisorptions (i.e., oxygen deficiency) on surface and the oxygen vacancies in ZnO. Therefore results in major reduction of the chemisorptions effects and the dark (leakage) current.

This effect can also be interpreted by the adsorption of active oxygen ions with a highly electronegative effect on the depletion layer in the ZnO film.[14] The carrier mobilities of ZnO-TFTs have been used to calculate the charge carrier density using the equation[15]

$$n = \frac{I_{DS} L}{q V_{DS} \mu_{sat} W d}, \tag{2}$$

where n is the carrier concentration, I_{DS} is the measured drain current at V_{DS}, L is the channel length, W is the channel width, d is the gate insulator thickness, q is the electron charge, and μ_{sat} is the carrier mobility. The carrier concentrations for ZnO thin films were calculated as follows 4.2×10^{18} cm^{-3} for the 0-min-treated sample, 3.9×10^{17} cm^{-3} for the 1-min-treated sample, 1.2×10^{18} cm^{-3} for the 2-min-treated sample, 4.3×10^{18} cm^{-3} for the 3-min-treated sample, 5.1×10^{18} cm^{-3} for the 4-min-treated sample, and 6.8×10^{18} cm^{-3} for the 5-min-treated sample. The resulting charge carrier concentration is decreased after 0 min plasma treatment and further increased slightly for longer plasma treatment times. This increment in carrier concentration may be expected due to desorption of negatively charged oxygen species, which increases oxygen vacancies or interstitial zinc atoms. The magnitude of the variation of V_{th} gradually decreased as the standing period increased until it finally reached a steady state value. The resulting carrier concentrations decreased with increasing O_2 ratio. This is because the oxygen vacancies compensated by O_2 make the channel layer less conductive in supplying free electron carriers to the conduction band. In other words, a higher O_2 ratio induces a lower density of oxygen vacancies that usually act as shallow donors. The remaining donor electrons after compensating for the acceptors contribute to channel mobile carriers in the ZnO channel layer. Thus, the density of the remaining electrons of the deposited ZnO film should be lower in a high O_2 ratio for longer O_2 plasma treatment time (3–5 min) than in a low O_2 ratio (i.e., short O_2 plasma treatment time).[16] Moreover, the interaction among the O_2 plasma surface ions and oxygen vacancies influences the carrier concentration in a positive way. The ZnO-based TFTs with a higher O_2 ratio showed the decrease of oxygen deficiencies, which can be clearly explained by observing the binding energy change of the O 1s peak.

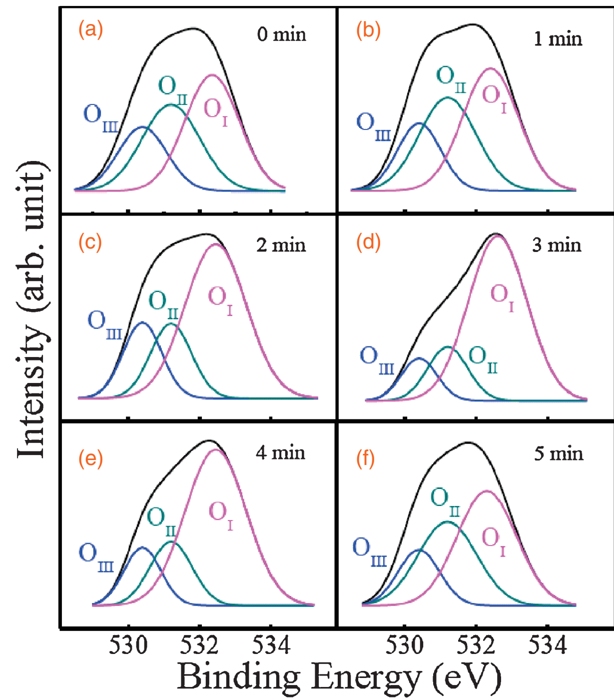

Fig. 3. XPS spectra from the O 1s region for ZnO films with O_2 plasma treatment for (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 min.

Figures 3(a)–3(f) reveal the XPS data that indicate that the O 1s peak in the ZnO surface can be consistently fitted by three Gaussians, centered at 532.4 (O_I), 531.2 (O_{II}), and 530.4 eV (O_{III}). The fitted peaks indicate that each resolved component has a full width at half maximum (FWHM) lower than 2.1 eV. The high binding energy component (O_I) located at 532.4 eV is usually attributed to the presence of loosely bound oxygen on the ZnO surface, such as $-CO_3$, adsorbed H_2O, and adsorbed O_2.[17] It was also observed that the O_I increased after the ZnO film was treated with O_2 plasma for 1 min. This result implied that the O_2 plasma treatment results in the accumulation of absorbed oxygen ions on the ZnO surface by increasing treatment time. The medium binding energy component (O_{II}), centered at 531.2 eV, is associated with the oxygen deficient regions within the matrix of ZnO.[18] The intensity changes of the component O_{II} can be connected with the variations in the concentration of oxygen vacancies. In addition, O_{II}-related oxygen vacancies provide free electrons in the active channel layers of ZnO TFTs. It was also mentioned that the intensity of O_{II} in part to the oxygen vacancies was reduced by O_2 plasma treatment for 3 min. The low binding

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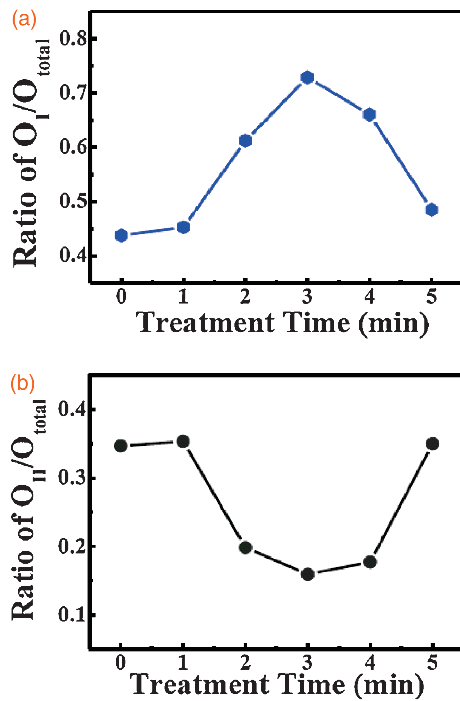

Fig. 4. Dependence of the intensity ratio of (a) high component (O_I) and (b) medium component (O_{II}) to total intensity (O_{total}) on treatment time for ZnO films.

energy component (O_{III}) of the O 1s spectrum at 530.4 eV is attributed to O^{2-} ions on the wurtzite structure of hexagonal Zn^{2+} ion array. The intensity of O_{III} is a measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding.

Figures 4(a) and 4(b) provide the significant evidence to present and explain how the plasma-induced active oxygen ions affect the electric properties of ZnO-TFTs. Figure 4(a) reveals that the relative intensity of O_I increases continuously with plasma-treated time from 0 to 3 min, which indicates the obvious collection of the oxygen chemical state on the ZnO surface. However, the relative intensity of O_I reverses after 3 min because the active oxygen ions reacted with residual hydrocarbon in the ZnO film.[19] Figure 4(b) shows that the relative intensity of O_{II} decreases obviously with increasing plasma-treatment time up to 3 min. The plasma treatment causes O_{II}-related oxygen vacancies to decrease, resulting in the suppression of the oxygen vacancies and improvement of carrier scattering in ZnO films. This phenomenon can also be explained by the effect of the reduction of the off-current on electric properties [as shown in Fig. 2(c)] attributed to a suppression of charge carriers by oxygen plasma treatment from 0 to 3 min. More likely, the reduction of charge carriers is caused by the adsorption of active oxygen ions on the surface of ZnO film.[20] Plasma-induced active oxygen ions are highly electronegative, which affect the depletion layer in the ZnO film and the free charge carrier density is thereby reduced. The relative intensity of O_{II} significantly increases after plasma treatment for 3 min. This effect implies that the active oxygen ions react with residual hydrocarbon. Therefore, the increase in the number of the oxygen vacancies can be explained mainly by the oxidation of residual hydrocarbon sites near the Zn atoms by the active oxygen ions during oxygen plasma treatment.

We have successfully used the solution-processed method and the effect of the O_2 plasma power to fabricate an ultrathin (4.5-nm-thick) ZnO-TFT device. The O_2 plasma showed the effect on these TFT devices, which have been exhibited the variation in carrier mobility with O_2 plasma treatment times ranging from 0 to 5 min. The transfer characteristics and XPS analysis confirmed that the solution-processed ZnO films are affected by various plasma-treatment times. The ZnO film was treated for 3 min; the transfer characteristics demonstrate very good electrical behavior in terms of threshold voltage, saturation mobility, and on/off current ratio. Moreover, the samples with a treatment time for 5 min or more time confirm the significant degradation caused by the active O_2 ions reacting with residual hydrocarbon and product excess oxygen vacancies near the Zn atoms. The effect of the threshold voltage shift on the ZnO-TFT device was expounded by the dynamic reaction equilibrium of O_2 plasma power in the ambient atmosphere as good for future low-process high-performance device applications.

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