Low Temperature Solution-Processed Zinc Tin Oxide Thin Film Transistor with $O_2$ Plasma Treatment

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We fabricated solution-processed ZTO TFTs at annealing temperature of 350 °C with employing $O_2$ plasma treatment on active layer in order to improve the electrical characteristics of ZTO TFTs fabricated at low temperature. Threshold voltage of solution-processed ZTO TFTs without plasma treatment was larger than 35 V but reduced to 20.74 V with 15 ml/min and 300 W of $O_2$ plasma treatment since oxygen vacancies in $ZnO\cdotSnO_2$ and $SnO_2$ would increase and then electron concentration are also increased by ion bombardment from $O_2$ plasma treatment. Saturation mobility and Subthreshold Swing (S.S) of TFTs without plasma treatment was 0.09 cm$^2$/V·sec and 1.65 V/decade respectively, but saturation mobility increased to 0.58 cm$^2$/V·sec and S.S decreased to 1.20 V/decade, respectively, with 15 ml/min and 300 W of $O_2$ plasma treatment, since $ZnO\cdotSnO_2$ is produced which could work as semiconducting material, rather $Zn(OH)Cl$ is vanished which could work as impurity by $O_2$ plasma treatment.

**Introduction**

Recently, oxide semiconductors such as zinc oxide ($ZnO$), indium gallium zinc oxide (IGZO) and zinc tin oxide (ZTO) have attracted considerable attention for flat-panel displays (FPDs) as active channel materials for TFTs. Amorphous oxide-based thin film transistors (TFT) attract considerable attention for the driving elements of active matrix display. It is reported that oxide TFTs exhibits high mobility, visible light transparency, good uniformity and excellent environment stability (1-3).

However, indium (In) is a rare and expensive material, and thus In-free oxide semiconductors are needed for low cost and industrial applications. Therefore, zinc tin oxide (ZTO) which employing Sn instead of In addition has another advantage of low cost among oxide semiconductors.

Solution-processed oxide semiconductor TFTs have attracted considerable attention and various solution-processes such as spin-coating, dipping and ink-jet printing are investigated for low cost display applications because vacuum-deposition process such as rf magnetron sputtering and pulsed laser deposition require expensive manufacturing cost. The solution-processes are suitable for large area, high throughput and direct patterning so that, solution-processed oxide TFTs such as ZTO TFTs exhibit high mobility as well as high throughput (4, 5).

In solution-processed ZTO TFTs, high annealing temperature exceeding 500 °C is widely required in order to obtain low threshold voltage and high mobility (5). The
decrease of annealing temperature under 500 °C of solution-processed ZTO TFTs would be a critical issue not to glass and flexible substrates damaged in ZTO TFTs.

The purpose of this paper is to report that annealing temperature could be considerably decreased by employing O₂ plasma treatment on ZTO active layer. O₂ plasma treatment accelerates ZTO layer to have high electron concentration and not to have impurities. Therefore we could improve the electrical characteristics of ZTO TFTs to decrease threshold voltage and enhancing mobility at low annealing temperature of 350 °C for ZTO active layer by employing O₂ plasma treatment.

**Experimental**

We fabricated solution-processed ZTO TFTs with 350 °C of annealing temperature for ZTO active layer which is quite lower temperature than required temperature of 500 °C to make the characteristics of TFT be sufficient for industrial devices (6). ZTO TFTs with inverted staggered structure were fabricated on wafer substrates as Figure 1. About 760 μm heavily boron doped p-type silicon wafer substrate was used as the gate and gate insulator was fabricated with Silicon dioxide (SiO₂) of 2000 Å using thermal oxidation.

The precursor-based solution of ZTO for active layer was prepared by dissolving 0.07 M of Tin (II) chloride (SnCl₂, formulaire weight (FW) of 189.6, Aldrich) and 0.07 M of Zinc chloride (ZnCl₂, FW of 136.3, Aldrich) powders in Acetonitrile (CH₃CN) of 3mL at equal molar ratio. The mixed solution was stirred at room temperature for 15 min to promote the dissolving process.

The ZTO film thicknesses were about 400 Å from the spin-coating process with 500 rpm for 5 sec and 4000 rpm for 30 sec and soft annealing of 200 °C for 10 min to solidify ZTO film was followed immediately. To avoid the fringing effect and a large leakage current, ZTO layers were isolated by the wet-etching process using diluted HF (HF : distilled water = 1 : 500) with AZ1512 channel passivation layer. After spin-coating, ZTO films were annealed at 350 °C for 10 min by rapid thermal annealing process and cooled down to room temperature. The final thicknesses of ZTO films all became about 250 Å by evaporation process during annealing.

O₂ plasma treatment was performed on ZTO active layer with flow rate of 15 ml/min and plasma powers of 100 W and 300 W for 10 min in order to improve the characteristics of ZTO TFT.

After ZTO films were forming on the SiO₂, poly(methyl methacrylate) (PMMA, MicroChem A4) and AZ1512, double layer were deposited for lift off process. After patterning the double layer, indium zinc oxide (IZO) film was deposited by dc sputtering with 1000 Å and then defined by a lift-off process to yield source and drain electrodes. And finally PMMA layer was employed for the passivation to protect active layer from water in the air.

![Figure 1. Cross-sectional view of the fabricated ZTO TFTs](image-url)
Characteristics of ZTO TFTs with O\textsubscript{2} plasma treatment

ZTO TFTs which treated by O\textsubscript{2} plasma with channel length of 10 μm and width of 100 μm were measured in the dark at room temperature. Drain current - gate voltage transfer characteristics are shown in Figure 2. Threshold voltage of solution-processed ZTO TFTs without plasma treatment was larger than 35 V but improved to 30.28 with 100 W and 20.74 V with 300 W of O\textsubscript{2} plasma treatment. Saturation mobility and Subthreshold Swing (S.S) of no plasma treated solution-processed ZTO TFTs was 0.09 cm\textsuperscript{2}/V·sec and 1.65 V/decade respectively, but saturation mobility increased gradually to 0.12 cm\textsuperscript{2}/V·sec and 0.58 cm\textsuperscript{2}/V·sec and S.S decreased gradually to 1.39 V/decade and 1.20 V/decade with 100 W and 300 W respectively. These results are demonstrated in Figure 3.

![Figure 2](image1.png)

Figure 2. Transfer characteristics of solution-processed ZTO TFTs with W = 100 μm and L = 10 μm according to O\textsubscript{2} plasma treatment

![Figure 3](image2.png)

Figure 3. Mobility & S.S of solution-processed ZTO TFTs with O\textsubscript{2} plasma treatment
Effects of O$_2$ plasma treatment on ZTO films

The ZTO films deposited on wafer with 200 ~ 550 °C of annealing temperature and ZTO solution are prepared to observe the chemical characteristics of ZTO active layer in TFTs (7). The Fourier transform-infrared spectroscopy (FTIR) transmittance spectra of the ZTO films are demonstrated in Figure 4 (a) and Thermogavimetry analysis (TGA), Differential Thermal Analysis (DTA) curves of the ZTO solution are shown in Figure 4 (b).

In Figure 4 (a), the broad peak in the range of 3000-3750 cm$^{-1}$ appears in ZTO films annealed with 200 °C and this peak is almost vanished above 300 °C. This peak is attributed to O-H stretching vibration so we can analyze that O-H bonding is almost desorbed under 300 °C. The peaks at 1087 and 1370 cm$^{-1}$, which is due to C-O stretching vibration and CH$_3$ deformation vibration respectively, are tend to appear above 500 °C remarkably (8). The peak of 500-800 cm$^{-1}$ is maintained without noticeable changes according to annealing temperature of 200 ~ 550 °C, so it is considered as stretching vibrations of Zn- and Sn- related inorganic materials.

Figure 4 (b) shows the TGA & DTA curves and these can be divided into three regions. First, most of weight loss is shown below 200 °C with endothermic reaction (Region $£$ in Figure 4 (b)). It represents the evaporation of residual solvent and decomposition of metal chloride compounds such as zinc chloride and tin chloride. Below 200 °C, decomposition of metal chloride compounds and metals, such as Zn and Sn, hydrolyzed to Zn(OH)Cl and Sn(OH)Cl were occurred (9). Therefore, O-H stretching vibration appears below 200 °C in FTIR results as shown above, and then these can be represented as equation [1]. H$_2$O comes from Air because RTA annealing is performed in environmental condition (10). HCl and H$_2$O which are produced by the reactions are vaporized.

$$ZnCl_2 + SnCl_2 + 3H_2O \rightarrow Zn(OH)Cl + Sn(OH)Cl + 2HCl (↑) + H_2O (↑) \quad [1]$$

At 300 ~ 450 °C (Region $¤$ in Figure 4 (b)), the exothermic reaction was observed with DTA peaks and small weight loss. It indicates the dehydroxylation of Zn(OH)Cl and Sn(OH)Cl occurred between 300 °C and 450 °C with forming the alloy reactions of ZnO-SnO$_2$ (ZTO). It is corresponded with the FTIR results of vanishment of O-H stretching vibration and can be expressed by equation [2].

$$2Zn(OH)Cl + 2Sn(OH)Cl + 2H_2O \rightarrow ZnO-SnO_2 + Zn(OH)Cl + SnO_2 + 3HCl (↑) + 2H_2 (↑) \quad [2]$$

With O$_2$ plasma treatment after annealing temperature of 350 °C , the bombardment by energetic O$_2$ ion perform physical momentum transfer so light atom such as H would be preferentially dissociated. Therefore, weak bonding such as hydrogen bonding would be broken so the reaction like equation [3] is expected by O$_2$ plasma treatment.

$$ZnO-SnO_2 + Zn(OH)Cl + SnO_2 \rightarrow 2ZnO-SnO_2 + HCl (↑) \quad [3]$$

Consequently, ZnO-SnO$_2$ is produced which could work as semiconducting material, rather Zn(OH)Cl is vanished which could work as impurity by ion bombardment from O$_2$ plasma treatment so that mobility and S.S could be improved in transfer characteristics.
Furthermore, oxygen vacancies in ZnO-SnO$_2$ and SnO$_2$ in equation [2] would increase and then electron concentration are also increased by ion bombardment from O$_2$ plasma treatment so that threshold voltage could be decreased in transfer characteristics (12). With plasma power increasing, the ion bombardment is accelerated so the electrical characteristics of TFTs are gradually improved.

![FTIR results of ZTO films](a)

![TGA & DTA results of ZTO solution](b)

Figure 4. (a) FTIR results of ZTO films, and (b) TGA & DTA results of ZTO solution according to annealing temperature
Conclusion

We successfully fabricated solution-processed ZTO TFTs at 350 °C of annealing temperature with O₂ plasma treatment of 15 ml/min flow rate and 100 W and 300 W powers in order to improve the electrical characteristics of ZTO TFTs fabricated at low temperature.

Threshold voltage of solution-processed ZTO TFTs without plasma treatment larger than 35 V but improved to 30.28 with 100 W and 20.74 V with 300 W of O₂ plasma treatment. Oxygen vacancies in ZnO·SnO₂ and SnO₂ would increase and then electron concentration are also increased by ion bombardment from O₂ plasma treatment so that threshold voltage could be decreased. Saturation mobility and S.S of ZTO TFTs without plasma treatment was 0.09 cm²/V·sec and 1.65 V/decade respectively, but saturation mobility increased gradually to 0.12 cm²/V·sec and 0.58 cm²/V·sec and S.S decreased gradually to 1.39 V/decade and 1.20 V/decade with 100 W and 300 W, respectively. ZnO·SnO₂ is produced which could work as semiconducting material, rather Zn(OH)Cl is vanished which could work as impurity by O₂ plasma treatment so that mobility and S.S could be improved.

With plasma power increasing, the ion bombardment is accelerated so the electrical characteristics of TFTs are gradually improved. Consequently, we confirmed that the electrical characteristics of solution-processed ZTO TFTs which is fabricated at low temperature of 350 °C could be improved by employing O₂ plasma treatment.

References