Effects of Annealing Temperature on Electrical Characteristics of Solution-Processed Zinc Tin Oxide Thin-Film Transistors

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We investigated the effects of annealing temperature on the electrical characteristics of solution-processed zinc tin oxide (ZTO) thin-film transistors (TFTs). When the annealing temperature increased from 300 to 500 °C, the threshold voltage of solution-processed ZTO TFTs decreased from 16.89 to −0.23 V owing to the increase in electron concentration in the active layer. The increase in electron concentration is caused by the decrease in Cl atomic concentration. When the annealing temperature increased to 500 °C, the saturation mobility increased from 0.18 to 4.75 cm²/V·s and the threshold voltage shift for positive gate bias stress as a reliability characteristic decreased from 5.34 to 2.6 V, because of the decomposition of halide residues such as Cl and the nanocrystallization.

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1. Introduction

Oxide-based thin-film transistors (TFTs) employing oxide semiconductors such as indium gallium zinc oxide (IGZO) and zinc tin oxide (ZTO) are promising devices for active-matrix display applications because of their high mobility, visible light transparency, and good uniformity. Despite these excellent advantages of oxide TFTs, low-cost fabrication processes are desired in oxide TFTs for practical applications.

Sn-based oxide semiconductors may be suitable for low-cost and industrial applications because tin (Sn) is quite a low-cost material compared with indium (In). Therefore, ZTO TFTs employing Sn may be promising candidates among various oxide TFTs for achieving low-cost processes.

Non vacuum solution processes such as spin-coating, dipping, and ink-jet printing could be other methods for achieving low-cost fabrication because vacuum-deposition processes, such as rf magnetron sputtering and pulsed laser deposition, require a high manufacturing cost. Solution processes are also suitable for large-area, high-throughput, and direct patterning. Therefore, solution-processed ZTO TFTs are employed in this study for achieving low-cost fabrication as well as high mobility and high throughput.

For additional cost reduction and application extension to a flexible display, solution-processed ZTO TFTs need to be fabricated on inexpensive and flexible substrates such as glass and plastic. These substrates are easily damaged at high annealing temperatures, so low-temperature processes are essential for solution-processed ZTO TFT fabrication with flexible substrates. However, a high annealing temperature on an active layer exceeding 500 °C is required to obtain high device performance such as low threshold voltage and high mobility in solution-processed oxide TFTs from previous reports. To improve the device characteristics of solution-processed ZTO TFTs even at low annealing temperature on an active layer, a study of the effects of annealing temperature on the electrical characteristics of solution-processed ZTO TFTs is desired. There were some efforts to investigate the effects of annealingtemperature on solution-processed ZTO TFTs, but the electrical and chemical mechanisms of annealing temperature on solution-processed ZTO TFTs have been scarcely studied.

The purpose of this work is to fabricate ZTO TFTs using the spin-coating method for an active layer with various annealing temperatures on the ZTO active layer to investigate the effects of annealing temperature on the electrical characteristics of solution-processed ZTO TFTs such as threshold voltage and mobility, and to ultimately decrease the annealing temperature.

2. Experimental Methods

Solution-processed ZTO TFTs with inverted staggered structure were fabricated on silicon wafer substrates to observe the effect of annealing temperature effectively, as shown in Fig. 1. Heavily boron-doped p-type silicon wafer substrates and thermally oxidized silicon dioxide (SiO₂) of 2,000 Å were used as the gate and gate insulator, respectively.

The precursor-based solution of ZTO for the active layer was prepared with 0.07 M of zinc chloride (ZnCl₂) and 0.07 M of tin(II) chloride (SnCl₂) powders in acetonitrile (CH₃CN) of 3 mL at equal molar ratios. The mixed solution was stirred at room temperature for 15 min to promote the dissolving process. The ZTO active layer was deposited by spin-coating and isolated by the wet-etching process using diluted HF, and the ZTO active layers were annealed at 300–500 °C for 10 min by rapid thermal annealing (RTA) under ambient condition.

After the ZTO active layers were formed on the SiO₂, an indium zinc oxide (IZO) film was deposited by dc sputtering and then defined by a lift-off process to yield source and drain electrodes. Finally, a poly(methyl methacrylate) (PMMA) layer was employed for passivation to protect the active layer from water, oxygen, and hydrogen in the air.

3. Results and Discussion

The drain current-gate voltage transfer characteristics of solution-processed ZTO TFTs with a length (L) of 10 μm and width (W) of 100 μm in the dark at room temperature are investigated as shown in Fig. 2. When the annealing temperature increased from 300 to 500 °C, the on-currents were gradually increased, while the off-currents were scarcely altered, and the threshold voltages in particular
were drastically decreased in the negative direction. The threshold voltage of solution-processed ZTO TFTs decreased gradually from 16.89 to $-0.23\text{ V}$ with the increase in annealing temperature from 300 to 500 °C, as indicated in Fig. 3. The threshold voltages were derived by employing the widely used "constant current method" from the measured transfer characteristics in Fig. 2 at a drain–source current of 100 nA with forward swing. Furthermore, because the transfer characteristics of a solution-processed ZTO TFTs are usually slightly changed with each measurement, the threshold voltages of Fig. 3 are the averaged values of many measurements and are expressed with the error bars. In recent reports on sputter-processed oxide TFTs, the variation of threshold voltage has been analyzed by the change of electron concentration. The decrease in threshold voltage in solution-processed ZTO TFTs can be understood similarly to the increase in electron concentration of the ZTO active layer. Hall measurement result confirmed that when the annealing temperature increased from 200 to 500 °C, the electron concentration of the ZTO active layer increased from $1.9 \times 10^{16}$ to $5.6 \times 10^{17}$, and accordingly, the threshold voltage decreased, as shown in Fig. 3. The increase in electron concentration of the ZTO active layer with annealing temperature could be explained by the removal of impurities such as C and/or Cl, which come from precursors such as ZnCl$_2$ and SnCl$_2$ or CH$_3$CN. This reduction of impurities could be supported by the densification of the ZTO active layer after annealing. The thickness of the ZTO active layer was decreased from 420 to 300 Å when the annealing temperature increased from 300 to 500 °C, as measured by transmission electron microscopy (TEM), as shown in Fig. 4. The rutherford backscattering spectrometry (RBS) result also demonstrates the decrease in Cl atomic concentration from 14.39 to 3.83% in the ZTO active layer when the annealing temperature increased from 300 to 500 °C, as shown in Fig. 5. In contrast to the decrease in Cl atomic concentration, C atomic concentration was scarcely altered regardless of annealing temperature and was maintained at a considerably small quantity of about 2.7%. This shows that C impurities were sufficiently removed under 300 °C, so the removal of Cl would be dominant to the electrical characteristics of the ZTO active layer. On the other hand, O atomic concentration increased from 36.24 to 47.19% corresponding to the decrease in Cl atomic concentration, so consequently, Zn and Sn atoms
would be more tightly bound to O atoms when the annealing temperature increased. These findings could be confirmed with Raman spectroscopy result which shows the decrease in binding energy of the ZTO active layer from OH–Cl bonding to Zn–O and Sn–O bonding with the increase in annealing temperature.15) Furthermore, when the binding energy of oxygen decreases, the energy level of oxygen vacancies becomes close to the conduction energy minimum level so that oxygen vacancies working as donors generate electrons more easily, and consequently the electron concentration of the ZTO active layer increases.16,17) This increase in electron concentration is not a matter of the quantities of oxygen vacancies as many reports have mentioned because metal–oxide bondings are not sufficiently formed yet at low annealing temperature. Therefore, the decrease in Cl atomic concentration with annealing temperature resulted in the increase in electron concentration of the ZTO active layer, and accordingly the threshold voltage of ZTO TFTs decreased with the increase of annealing temperature from 300 to 500 °C.

The saturation mobility of solution-processed ZTO TFTs increased from 0.18 to 4.75 cm²/V·s with the increase in annealing temperature from 300 to 500 °C, and this result is also strongly related to the Cl atomic concentration as well as the microstructure of the ZTO active layer with annealing temperature, as shown in Fig. 6.

In Region I, below an annealing temperature of 450 °C in Fig. 6, the saturation mobility of ZTO TFTs was improved when the annealing temperature increased because halide residues such as Cl compounds in the ZTO active layer were decomposed, as confirmed by the RBS results in Fig. 5. Halide residues in the ZTO active layer could be considered as trap states, so they could act as obstacles for electron accumulation and transportation of electrons in the conduction band, and they consequently reduce mobility.10) Figure 7(a) shows a TEM diffraction pattern image of the ZTO active layer below 450 °C, and the ZTO active layer is amorphous in this region.

In Region II, above an annealing temperature of 450 °C in Fig. 6, the saturation mobility of ZTO TFTs was drastically improved, compared with Region I, because the ZTO active

Fig. 4. (Color online) (a) Cross-sectional image of ZTO active layer on SiO₂ gate insulator and wafer obtained by TEM and (b) thickness of the ZTO active layer.

Fig. 5. (Color online) Atomic concentration of O, Cl, Zn, Sn, and C atoms of ZTO active layer with the annealing temperature obtained by RBS analysis.

Fig. 6. (Color online) Saturation mobility of solution-processed ZTO TFTs and Cl atomic concentration with the annealing temperature.
layer was nanocrystallized in this region when the annealing temperature increased. Figure 7(b) shows a TEM diffraction pattern and dark field images of the crystallized ZTO active layer, of which the crystalline grains are about 1–2 nm, and the grain size was gradually increased above 450 °C. Nanocrystallization above the annealing temperature of 450 °C reduced the amount of trap states of the interface between the ZTO active layer and the SiO₂ gate insulator compared with those of the amorphous phase. Therefore, nanocrystallization as well as the decomposition of halide residues of the ZTO active layer improved the saturation mobility of solution-processed ZTO TFTs drastically because it decreased the amount of the defects of trap states in this region.

The reliability characteristics according to annealing temperature for the active layer of solution-processed ZTO TFTs are demonstrated in Fig. 8. With positive gate bias stress of 10 V during 10,000 s, the threshold voltage of ZTO TFTs increased from 7.5 to 12.84 V with an annealing temperature of 350 °C and from −0.3 to 2.3 V with an annealing temperature of 500 °C, as shown in Fig. 8(a), with parallel shift without change of slope. In particular, the amount of threshold voltage shift for 10,000 s with various annealing temperatures is demonstrated in Fig. 8(b), showing that the threshold voltage shift for 10,000 s decreased from 5.34 V with an annealing temperature of 350 °C to 2.6 V with an annealing temperature of 500 °C.

The decrease in the threshold voltage shift for 10,000 s could also be explained with the decrease in Cl concentration and nanocrystallization of the ZTO active layer with the increase in annealing temperature from 300 to 500 °C. The reduction of halide residues such as Cl acting as trap states makes the number of trapped electrons at the ZTO active layer decreases and the nanocrystallization above the annealing temperature of 450 °C also makes the number of trapped electrons decreases at the trap states of the interface between the ZTO active layer and the SiO₂ gate insulator, so eventually the threshold voltage shift for 10,000 s decreases.

According to the above analyses, which indicate that the Cl atomic concentration decreases and the ZTO active layer are nanocrystallized with increasing annealing temperature, the details of chemical formation equations could be established with the chemical characteristics of spin-coated ZTO solution with the annealing temperature using thermogavimetry analysis (TGA) and differential thermal analysis (DTA). The TGA and DTA curves of Fig. 9 could be divided into three regions.

An endothermic reaction in Region ① below 200 °C represents the evaporation of residual solvent and hydroxylation of metal chloride compounds with H₂O coming from air, and it can be expressed by eq. (1). In this region, ZnCl₂ and SnCl₂ were transformed to Zn(OH)Cl and Sn(OH)Cl, respectively, so that Cl atomic concentration decreased with the increase in annealing temperature, but a considerable amount of Cl still remained below 200 °C. Therefore, Fig. 5 shows a high Cl atomic concentration at low annealing temperature, and it is well-matched with the low carrier concentration of the ZTO active layer at 200 °C, as the Hall measurement result in Fig. 3 shows.
ZnCl₂ + SnCl₂ + 3H₂O
→ Zn(OH)Cl + Sn(OH)Cl + 2HCl(↑) + H₂O(↑) (1)

Two exothermic reactions, occurred at 230–320 °C and 320–450 °C in Region 2, indicate the dehydroxylation of Sn(OH)Cl and Zn(OH)Cl with regard to the melting point of Sn of 232 °C and Zn of 420 °C, respectively. The dehydroxylated Sn(OH)Cl and Zn(OH)Cl would form the alloy of ZnO·SnO₂ (ZTO), and this can be expressed by eq. (2). Therefore, Cl atoms are gradually evaporated with HCl in this region, and the decrease in Cl atomic concentration in the RBS results of Fig. 5 with the increase in annealing temperature could be well understood. As a result, the electron concentration of the ZTO active layer increases and the threshold voltage of solution-processed ZTO TFTs decreases gradually, as shown in Fig. 3, and the saturation mobility increases gradually, as shown in Fig. 6, with the increase in annealing temperature from 300 to 500 °C owing to the decrease in Cl atomic concentration in this region.

2Zn(OH)Cl + 2Sn(OH)Cl + 2H₂O
→ ZnO·SnO₂ + Zn(OH)Cl + SnO₂ + 3HCl(↑) + 2H₂(↑)
ZnO·SnO₂ + Zn(OH)Cl + SnO₂
→ 2ZnO·SnO₂ + HCl(↑) (2)

Another exothermic reaction in Region 3 above 450 °C is associated with the crystallization of the solution-processed ZTO active layer. This could be further supporting data for the nanocrystallization of the solution-processed ZTO active layer with regard to the TEM results and the dramatic increase in saturation mobility of solution-processed ZTO TFTs above 450 °C, as shown in Fig. 6.

4. Conclusions

In summary, we fabricated solution-processed ZTO TFTs with various annealing temperatures, and the electrical characteristics of ZTO TFTs were improved with the increase in annealing temperature. The threshold voltage of solution-processed ZTO TFTs decreased from 16.89 to −0.23 V with the increase in annealing temperature from 300 to 500 °C owing to the increase in electron concentration in the active layer. Hall measurement showed that the electron concentration increased because the oxygen vacancies generate electrons more easily as the binding energy of ZTO active layer decreased with the removal of Cl. The saturation mobility of solution-processed ZTO TFTs increased gradually from 0.18 to 4.75 cm²·V⁻¹·s⁻¹ with the increase in annealing temperature from 300 to 500 °C because of the decomposition of halide residues such as Cl and nanocrystallization. In regard to the reliability characteristics with increasing annealing temperature of solution-processed ZTO TFTs with a positive gate bias stress of 10 V, the threshold voltage shift for 10,000 s decreased from 5.34 to 2.6 V when the annealing temperature increases from 350 to 500 °C because of the reduction of trap states by the decrease in Cl and nanocrystallization.

We successfully investigated the effects of annealing temperature on the active layer of solution-processed ZTO TFTs and established the chemical formation equation of the ZTO active layer with regard to the annealing temperature.