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Effects of Ga Composition Ratio and Annealing Temperature on the Electrical Characteristics of Solution-processed IGZO Thin-film Transistors

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***Abstract*—Bottom gate thin-film transistors were fabricated using solution processed IGZO channel layers with various gallium composition ratios that were annealed on a hot plate. Increasing the gallium ratio from 0.1 to 0.6 induced a threshold voltage shift in the electrical characteristics, whereas the molar ratio of In:Zn was fixed to 1:1. Among the devices, the IGZO-TFTs with gallium ratios of 0.4 and 0.5 exhibited suitable switching characteristics with low off-current and low SS values. The IGZO-TFTs prepared from IGZO films with a gallium ratio of 0.4 showed a mobility, on/off current ratio, threshold voltage, and subthreshold swing value of 0.1135 cm^2/V•s, ~10^6, 0.8 V, and 0.69 V/dec, respectively. IGZO-TFTs annealed at 300℃, 350℃, and 400℃ were also fabricated. Annealing at lower temperatures induced a positive shift in the threshold voltage and produced inferior electrical properties.**

***Index Terms*—IGZO, Oxide TFT, Solution-processed, annealing, Ga**

I. INTRODUCTION

Amorphous oxide semiconductors (AOSs) have been studied extensively as an alternative to existing amorphous and polycrystalline silicon for the active-channel layer in thin-film transistors (TFTs) [1, 2]. These materials have considerable advantages, such as high field-effect mobility, good uniformity, low temperature device fabrication, and transparency [3, 4]. These amorphous oxide semiconductors can be applied to switching/driving devices in active matrix organic light-emitting diode (AMOLED) display, uniform film layers for large-scaled displays, and the next generation flexible displays for several years [5].

Among AOS materials available, indium-gallium-zinc-oxide (IGZO) has attracted considerable interest because of its stable electrical performance. Controlling the proper carrier density in the channel layer for highly stable TFTs is very important but difficult to accomplish [6]. Because Ga cations bind with oxygen and suppress the generation of oxygen defect sites, they perform the role as a carrier suppressor in the channel layer of devices [7, 8]. Therefore, the IGZO TFTs show a good outcome involving the carrier density, such as proper threshold voltage and low off-current.

IGZO layers are typically prepared using vacuum deposition techniques, such as RF-magnetron sputtering and pulsed laser deposition [9-11]. Recently, solution processes have been investigated because of their low cost, simplicity and high throughput [12]. This type of process can also be used to fabricate films with an accurate elemental composition. On the other hand, the oxygen content is difficult to control during the deposition process. Nevertheless, multi-component oxide semiconductor films with an innovative ratio can be achieved easily.

In this study, IGZO solutions were prepared with various Ga ratios, and TFTs with an IGZO channel layer were fabricated by spin-coating. The effect of the Ga

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ratios on the structure of films and electrical characteristics were examined. IGZO films were also annealed at different temperatures for TFTs, and the shift in the threshold voltage was investigated as one of the electrical characteristics.

II. EXPERIMENTAL DETAILS

The precursor solution for the IGZO active layer was prepared by dissolving 0.2 M of indium nitrate hydrate [$In(NO_3)_3$•xH_2O], gallium nitrate hydrate [$Ga(NO_3)_3$• xH_2O], and zinc acetate dihydrate [$Zn(OAc)_2$•$2H_2O$] in 2-methoxyethanol as a solvent. Monoethanolamine (MEA) was used as a stabilizer and the IGZO precursor solution was stirred at 70°C for 1h. The In and Zn precursors were mixed at a constant molar concentration of 1:1, and the relative molar ratio of Ga was varied from 0 to 0.6 for channel layers with accurate metal contents.

The IGZO thin films with a thickness of 50 nm were coated on n-type silicon wafers covered with a 200 nm SiO_2 dielectric layer. The spin-coated films were annealed at 400℃ and then annealed at lower temperatures (300-350℃) on a hot plate. A 100 nm thick Al layer as the source and drain was deposited on the top of the annealed IGZO layer by e-beam evaporation. The channel width (W) and length (L) through the shadow mask were 2000 and 150 µm, respectively.

X-ray diffraction (XRD) was used to examine the structural properties of the films. In addition, the composition of oxygen binding in the IGZO layer was analyzed by x-ray photoelectron spectroscopy (XPS). The TFT characteristics were measured using a semiconductor parameter analyzer at room temperature.

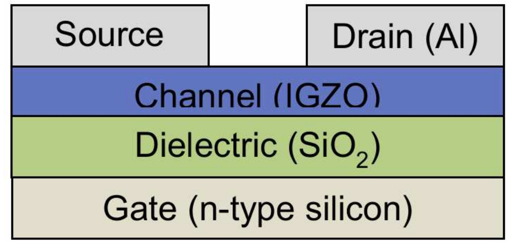

Fig. 1. Solution-processed IGZO-based TFT structure.

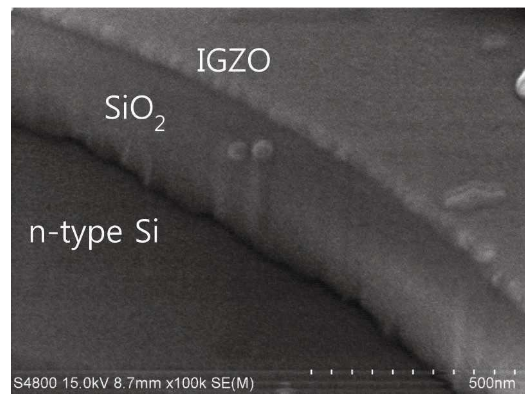

Fig. 2. SEM image of an IGZO film on a SiO2 dielectric.

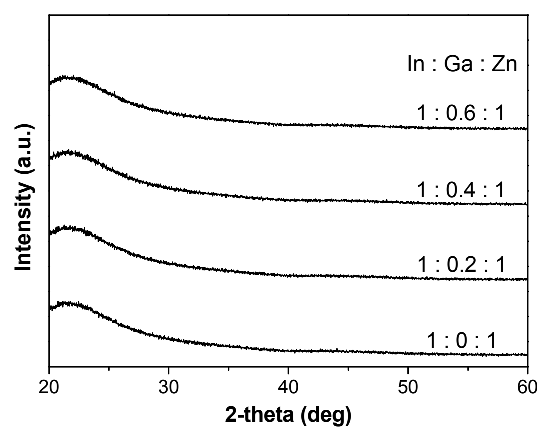

Fig. 3. XRD patterns of the IGZO thin films at various Ga ratios.

III. RESULTS AND DISCUSSION

Fig. 1 shows a schematic diagram of the structure of the inverted staggered IGZO-TFT. Fig. 2 shows a SEM image of the tilting angle with a spin-coated IGZO film on the SiO_2 dielectric. XRD was performed to observe the crystal orientation of IGZO films, with Ga ratios ranging from 0 to 0.6. Although the coated films on glass were heated steadily at 400°C, no distinct peaks were detected (Fig. 3). Solution-processed IGZO films crystallized with nanosized grains were reported because of the structure of InO_2 layers and GaO(ZnO)m blocks, which are similar to the c-axis orientation of ZnO under the influence of Ga addition [13]. On the other hand, the crystalline structure for appropriate stacking was not observed because the content of In ions that disturb matching is relatively higher than that reported elsewhere [12-14]. Hence, all the IGZO films had an amorphous structure without any peaks.

The oxygen binding energy of O_{1s} was measured by XPS. A Gaussian fit of these curves was conducted to observe detailed quantitative analysis, as shown in Fig. 4. Two peaks were observed at a lower O_L value of 530.5

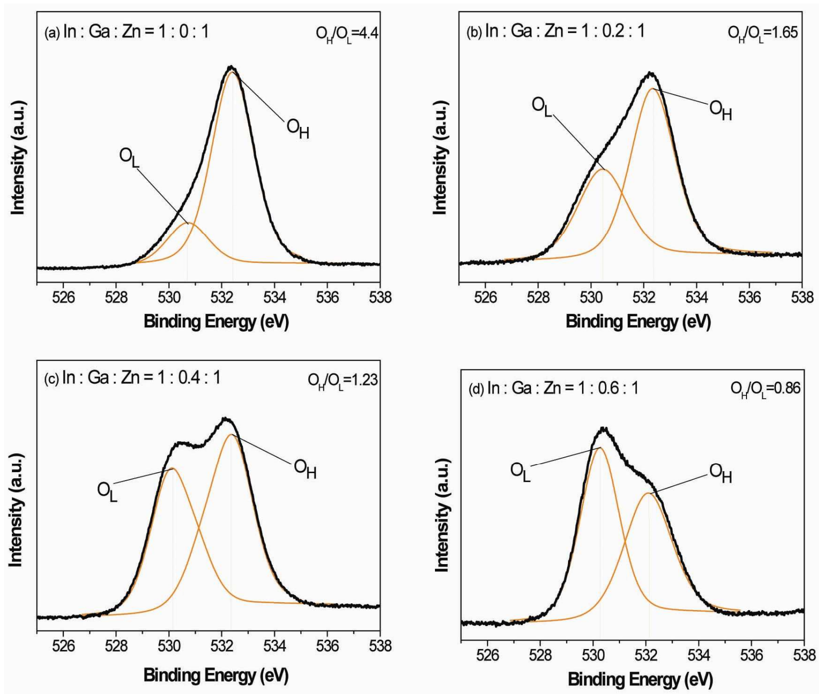

Fig. 4. XPS analysis results of the O1s region for a solution-processed IGZO film with In:Ga:Zn ratios of 1:x:1, where x = (a) 0, (b) 0.2, (c) 0.4, (d) 0.6.

eV and a higher O_H value of 532.3 eV. O_L was assigned to O_2- ions combining with In, Ga and Zn. O_H is associated with O_2- ions caused by oxygen defect regions and absorbed molecules on the IGZO surface, such as H_2O, CO_3 and O_2 [14, 15]. This peak might also include oxygen ions depending on O_H- residues from the precursors after heat treatment. Among them, the count from oxygen deficient regions has a considerable effect on the O_H peak. The others effects are marginal in that the annealing temperature and analysis conditions were identical.

The quantity of oxygen ions combining with heavy metals increases with increasing Ga content, which suppress the formation of oxygen defects in the IGZO films, but the O_H peak intensity decreases depending on the increased Ga content. Consequently, the O_H/O_L area ratios were calculated to be 4.40, 1.65, 1.23 and 0.86, where the Ga contents are 0, 0.2, 0.4 and 0.6, respectively. The intensity of oxygen ions combined with metals increased with decreasing O_H/O_L ratio(increasing Ga content), whereas the intensity of oxygen ions in the oxygen deficient regions decreased. Accordingly, the carrier concentration in IGZO films also decreased.

Fig. 5 shows the transfer curves of TFTs with the IGZO channel layers at the different Ga ratios. The drain-source voltage (V_{DS}) was fixed to 20 V and the gate voltage (V_G) was changed from -40 to 40 V. The devices were measured in the dark at room temperature. The IZO-TFT with no Ga content exhibited conducting characteristics, but at a weak Ga ratio of 0.1, the device showed semiconducting behavior. On the other hand, these TFTs were not stable as switching devices because of the higher off-current ($>10^9$) and extremely lower threshold voltage of < -20V. The off-current decreases and the threshold voltage shifts to a positive gate voltage with additional Ga. When the Ga content was more than 0.4, the TFTs with the IGZO channel layer showed an enhanced mode of operation near 0 V. The stable and identical switching curves were attributed to the suitable carrier concentration in the IGZO channel layer because the variation in the carrier concentration of IGZO film is attributed to a change in the oxygen vacancy, depending on the incorporation of Ga contents [14].

Table 1 lists the electrical characteristics of the IGZO-TFTs at various Ga ratios from Fig. 4. Although the mobility was low, the IGZO-TFTs with a Ga ratio of 0.4 and 0.5 showed an appropriate threshold voltage and lower maximum density of surface states (Nt) at the interface between the IGZO channel layer and gate dielectric layer. The device characteristics with the IGZO

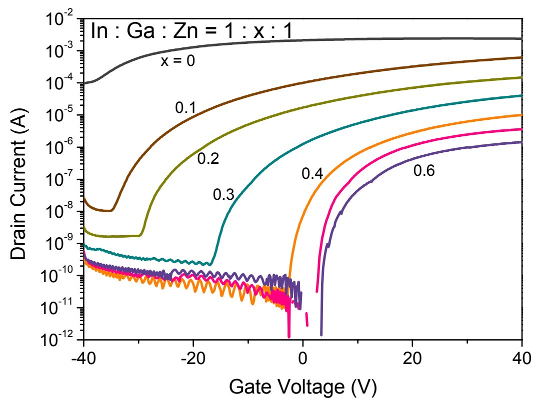

Fig. 5. I_{DS}-V_{GS} output curves of the TFTs with solution-processed IGZO channel layers with various Ga ratios.

Table 1. Electrical characteristics of the solution-processed IGZO-TFTs at different Ga ratios

In:Ga:Zn molar ratios	V_{th} (V)	μ_{FE} (cm^2/Vs)	$I_{on/off}$ ratio	SS (V/dec)	N_t (cm^{-2})
1 : 0.1 : 1	-26.24	3.2198	6×10^4	2.53	4.47×10^{12}
1 : 0.2 : 1	-19.52	0.8889	9×10^4	1.86	3.26×10^{12}
1 : 0.3 : 1	-7.28	0.2959	2×10^5	1.64	2.86×10^{12}
1 : 0.4 : 1	0.8	0.1135	1×10^6	0.69	1.14×10^{12}
1 : 0.5 : 1	4.08	0.0722	2×10^7	0.48	7.61×10^{11}
1 : 0.6 : 1	5.92	0.0230	4×10^6	0.54	8.70×10^{11}

channel at a Ga ratio of 0.6 were similar to that of the TFTs with a Ga ratio of 0.5 but the reduction ratio of the mobility was large. Therefore, the optimal Ga ratio ranges from 0.4 to 0.5 at a fixed In to Zn ratio of 1:1. Nt values were obtained using following equation: [13]

$$Nt = \left(\frac{S\log(e)}{\frac{kT}{q}} - 1 \right) \frac{C_i}{q}$$

IGZO-TFTs with a Ga ratio of 0.5 were also measured after different annealing temperatures of 300°C and 350°C, which are lower than the previous temperature of 400°C, as shown in Fig. 5. The threshold voltage shifted severely toward a positive voltage, 20 V and 30 V at 350°C and 300°C, respectively. The large changes in the on-current and threshold voltage were attributed to the carrier quantity in the channel layer, suggesting a decrease in the carrier concentration in the IGZO layer depending on the relatively lower annealing temperature. When oxygen detaches from metal ions, two electrons are generated, which contribute to the current flow in the ns orbital of the metal. The oxygen defect sites arise through a chemical reaction, such as dehydroxylation and detachment of oxygen during annealing [16]. Thermal annealing over 400°C altered the TFT performances, including an increase in the off current and severe negative shift of threshold voltage. Therefore, the annealing temperature might have a significant effect on the carrier generation, regardless of the atomic ratio of metal.

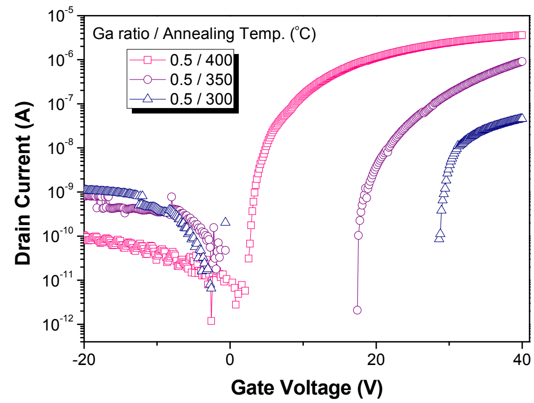

Fig. 6. I_{DS}-V_{GS} output curves of the TFTs with solution-processed IGZO channel layers with different annealing temperatures.

IV. Conclusions

In summary, solution-processed IGZO-TFTs with various Ga contents from 0 to 0.6 were fabricated and their electrical characteristics were measured. All the IGZO films had an amorphous structure after hot plate annealing at 400°C. A detailed investigation of oxygen quantity depending on Ga ratio was carried out. As the Ga ratio was increased at an identical In and Zn content, the O_H/O_L area ratio decreased gradually, which means that the carrier concentration in IGZO films decreases. An analysis of the electrical characteristics, the TFTs revealed an enhanced mode of operation when the Ga content was more than 0.4. The TFTs using an IGZO channel layer with a Ga ratio from 0.4 to 0.5 and an In to Zn ratio fixed to 1:1 showed an appropriate threshold voltage and a lower Nt value. The annealing temperatures were found to affect the electrical properties of the IGZO-TFTs. The threshold voltage shifted to a positive voltage with decreasing annealing temperature. Therefore, a lower annealing temperature suppresses the generation of carriers outside of the control of Ga cations.

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