ZnO thin-film transistor grown by rf sputtering using Zn metal target and oxidizer pulsing

Dukyean YOO*, Wonjin JEON*, Junghwan KIM*,**, Jun MENG*, Youjung YANG*** and Jungyol JO*,**

*Department of Electrical and Computer Engineering, Ajou University, Suwon 16499, Korea
**Materials Research Center for Element Strategy, Tokyo Institute of Technology, Mailbox SE-6, 4259 Nagatsuta, Midori-ku, Yokohama, Japan
***Graduate School of IT Convergence, Ajou University, Suwon 16499, Korea

We studied ZnO films grown by rf sputtering using Zn metal targets. During the growth the metal target can be at a metal or at an oxide mode, depending on oxidation of the target surface. At a metal mode the target surface is free of oxide, and the sputtering yield is higher, but deposited ZnO films show poor TFT characteristics. ZnO films deposited at an oxide mode show better transistor characteristics, but the sputtering yield is lower. In order to solve these problems, we supplied oxidizer gas as pulses during the growth. We hoped that the target condition could be controlled by varying parameters of the pulses. Our ZnO was grown at 450°C using CO2 or O2 as an oxidizer. After sputtering growth ZnO films were annealed in mixture of CO2 and H2 at 400°C. With these methods, bottom-gate ZnO thin-film transistor showed 6.5 cm2/Vsec mobility, 5 x 106 on/off ratio, and ~5 V threshold voltage.

1. Introduction

Metal oxides such as ZnO have attracted much attention in recent years due to applications in display devices. High mobility in a thin-film transistor (TFT) is important for data transmission speed at flat panel displays. InGaZnO4 (IGZO) showed better TFT characteristics compared to ZnO. However, IGZO has a few problems for industry applications, because it requires complicated, three-component sputtering targets. Simpler fabrication process and lower production cost make ZnO a strong candidate in display applications. Various growth methods, such as radio-frequency (rf) sputtering,1-3) atomic layer deposition,4) metal-organic chemical vapor deposition (MOCVD),5) and spray deposition6) have been used to grow ZnO. Among these, rf sputtering is popular because it can deposit uniform films over a large area.

ZnO films can be grown using either ZnO ceramic targets or Zn metal targets. The ceramic target is more expensive than the metal target, and this is an important factor for industry applications. Another advantage of the metal target is related to the surface state of the target. Material composition at the surface of a ceramic target drifts due to selective sputtering. In our previous work we used a ZnO ceramic target for sputtering growth,7) and we observed that film qualities grown at the same conditions varied due to different target surfaces. For a metal target it is easier to control the surface, because Ar etching can reset the target surface whenever necessary.

Although there are advantages in using Zn metal targets, ZnO grown by the metal target does not show good TFT characteristics.5) It is well known that the metal target can be at a metal or at an oxide mode, depending on oxidation of the target surface.5) At a metal mode the target surface is free of oxide, and sputtering yield is higher, but ZnO TFT grown at this mode shows poor turn-off characteristics.10) ZnO films deposited at an oxide mode show better TFT quality, but the sputtering yield is lower. In order to solve these problems, we supplied oxidizer gas as pulses during the growth. We hoped that the target condition could be controlled by changing the pulse parameters. When ZnO is grown with a metal target, oxygen for ZnO formation can come from two sources. One is externally supplied oxidizer gas, and the other is oxide decomposition at the metal target.11) The presence of the second mechanism is confirmed from the fact that ZnO can be grown to a certain thickness without oxidizer gas.

Defect is important in determining current characteristics of ZnO TFT’s, and we wanted to analyze the effect under various conditions. We compared ZnO films grown with different oxidizers (O2 or CO2). There is a report that CO2 may suppress formation of O-related “dumbbell-like” defects.12) It is also possible that the carbon in CO2 may work as n-type dopants. Another method we used to control the defects is post-growth annealing. It was shown that TFT characteristics could be improved by annealing in various environments, such as oxygen plasma,13) H2O plasma,14) or water vapor.15) ZnO is polycrystalline containing high density of grain boundaries (GB).16) GB in ZnO decreases current flow at a given drain voltage, because extra voltage is required to cross the GB’s. In addition, gas adsorption at defects affects the TFT currents. We hoped that ZnO quality could be improved when the defects were removed by the annealing. Our annealing was performed in mixture of CO2 and H2 at 400°C.

2. Experimental details

Our sputtering system (SCIEN Tech, Korea) has a 2-inch diameter Zn metal target, with a 13.56 MHz rf power source. Target-substrate distance was 6 cm, and rf power during growth was set at 30 W. High vacuum was achieved by a diffusion pump, and base pressure was 10-3 Pa. The pressures during growth were 0.51 Pa at 3-sccm Ar flow, and 0.61 Pa when 1.5-sccm CO2 flow
was added to the Ar flow. When 1.5-sccm O2 flow was added to the Ar flow, the pressure was 0.54 Pa. ZnO films for TFT’s were grown on p+ Si substrates (10¹⁹ cm⁻³ doping density) with a thermal oxide of 150 nm thickness. The growth temperature was 450°C. ZnO films for optical measurements were grown on glass substrates at the same temperature.

Figure 1(a) is a schematic diagram of our sputtering system. De currents between the substrate and the vacuum chamber were measured by a Keithley 2400 sourcemeter. Figure 1(b) shows the oxidizer pulses during the growth. Oxidizer (O2 or CO2) was pulsed during the growth. Oxidizer (O2 or CO2) was added to the Ar flows. The diode-like current behavior in Fig. 2 can be explained by the mass difference between electrons and ions. Lighter-mass electrons experience higher acceleration by the rf field, and therefore the larger currents at the positive voltages are mostly made of electrons.

At positive substrate voltages, negative ions and electrons in the plasma are attracted toward the substrate. At negative voltages, positive ions (Ar or oxidizer) are pulled to the substrate. The diode-like current behavior in Fig. 2 can be explained by the mass difference between electrons and ions. Lighter-mass electrons experience higher acceleration by the rf field, and therefore the larger currents at the positive voltages are mostly made of electrons. Note that the currents are larger when Ar+O2 is used. The larger current in this case indicates that the plasma density is higher when O2 is used as an oxidizer.

When CO2 was added to the Ar flow, the pressure increased from 0.54 to 0.68 Pa. In contrast, addition of O2 to Ar did not change the pressure (0.54 Pa). We explain that the increase of pressure for CO2 is due to CO2 dissociation in the plasma, because the dissociation would increase moles of gases in the chamber. The fact that the pressure remained at the same level for the O2 suggests that the gas mole increase by O2 dissociation is relatively small.

Figure 3 shows currents at different oxidizer flows. For Ar+CO2, increase of CO2 flow from 2.0 to 2.5 sccm caused the pressure to increase (from 0.68 to 0.72 Pa), and the current to decrease (from 7.37 to 7.34 mA at −70 V). Increase of O2 flow from 2.0 to 2.5 sccm caused smaller pressure increase (from 0.54 to 0.55 Pa), and larger current increase (from 8.88 to 9.56 mA at −70 V). The current increase at the higher O2 flow can be explained by the higher plasma density discussed above. It appears that the effect of CO2 increase is different from that of O2.
increase. We think that shorter mean free path at the higher pressure is the reason for the smaller currents at the CO2 flows. When Ar flow was increased from 4 to 4.5 sccm, the pressure increased from 0.54 to 0.55 Pa, and the current increased from 7.15 to 7.33 mA at −70 V. In this case, the current increase can be the result of higher sputtering by the increased Ar, while the pressure increase is small.

Figure 4 shows substrate currents measured during ZnO growth when oxidizer pulsing is used. The oxidizers were O2 or CO2, and the pressure increased from 0.51 to 0.54 Pa. When 1.5 sccm CO2 flow was added to the Ar, the pressure increased from 0.51 to 0.54 Pa. When 1.5 sccm CO2 flow was added to the Ar flow, the pressure increased from 0.51 to 0.61 Pa. CO2 regions still showed higher pressure than O2 regions.

We explain that the current behaviors are related to the change of oxidized portion on the target surface. The changes at the target surface will affect the plasma density, and substrate current will change as a result. The surface of a metal target is a mixture of metallic areas and oxidized areas. When oxidizer flow is on, the oxidized portion of the target will increase, and the plasma density will increase due to higher ionization rate of the oxide.15) We think that this is the reason for the current increase in the O2 and CO2 regions in Fig. 4. When oxidizer flow is off, the target oxide is etched away by Ar+ ions, and oxidized areas of the target will decrease. This can explain the current decrease in the Ar regions of Fig. 4. The reason for the stepwise current changes at the oxidizer transitions is not understood yet. It appears that the pressure changes discussed in Fig. 3 are related to the current steps.
and Sample A2B (dotted line) was grown with lower O2 flow (1.2 sccm), compared to sample A2 (1.5 sccm O2). They were annealed in the same conditions as used in A2. ZnO grown at higher O2 flow (A2A) shows larger drain current and more negative Vth. Sample with lower O2 flow (A2B) shows smaller current. The effect of O2 variations in these two samples could be related the ZnO layer thickness, where the thicker layer shows larger current.

Figure 9 shows current changes in CO2-grown samples. Sample B2 was grown with 30 s Ar time and 60 s Ar+CO2 time. Sample B2A (dotted line) was grown with longer CO2 time (75 s), and Sample B2B (solid line) was grown with longer Ar time (35 s). Sample grown with longer oxidation time (B2A) shows smaller current, while the off-current is larger. Similar behavior was observed when O2 time was longer (not shown here). We think that the larger off-current in B2A is due to excess
Table 1. Parameters obtained by fitting of X-ray reflectivity (XRR) data.

| Sample Name | Oxidizer | Thermal Treatment | t1 (µm) | t2 (µm) | t3 (µm) |
|-------------|----------|------------------|---------|---------|---------|
| A1          | O2       | as-deposited     | 2.28    | 12.82   | 5.80    |
| A2          | O2       | annealed         | 1.50    | 11.76   | 5.68    |
| B1          | CO2      | as-deposited     | 0.60    | 13.47   | 2.12    |
| B2          | CO2      | annealed         | 0.49    | 13.79   | 2.16    |

ZnO grown by O2 (A1, A2) showed thicker t1 layers, and their densities (t1) were smaller than those of the main layers (t2). The main layer densities were close to the bulk density of ZnO (5.606 g/cm³). The third layers (t3) in B1 and B2 were relatively thin, with lower densities. The presence of the low-density surface layers indicates that CO2-grown ZnO has a rough surface. In a bottom-gate TFT structure, current would flow through the t1 region, and electrical properties of the t1 layer would be important in determining TFT characteristics. We note that O2-grown samples have thicker t1 layers with lower densities, and this can make a difference in the TFT performance.

Figure 10 shows the effect of the H2–CO2 annealing in optical absorption. Absorption coefficient (α) was converted from transmittance (T) and reflectance (R) data using the relation

\[ T = (1 - R)^2 \exp(-\alpha d), \]

where d denotes the film thickness. The absorption characteristics below the bandgap energy (3.4 eV) were changed by the annealing, while the characteristics above the bandgap remained almost the same. It appears that defects responsible for the absorption were removed by the annealing. Similar behaviors were observed in the off-currents shown in Fig. 5.

In Fig. 11 we show X-ray reflectivity (XRR) data. Dots are measured data, and solid lines are fitting results. Table 1 shows parameters obtained from the XRR fitting, and a two-layer model shows as an inset in Fig. 11. O2-grown samples (A1 and A2) could be fitted with two layers, but CO2-grown samples (B1, B2) required three layers for a good fitting. Thickness of ZnO films obtained by the XRR fittings were between 13 and 15 nm. All samples showed thin initial layers (t1) before the main layers (t2), with lower densities. The third layers (t3) in B1 and B2 were relatively thin, with lower densities. The presence of the low-density surface layers indicates that CO2-grown ZnO has a rough surface. In a bottom-gate TFT structure, current would flow through the t1 region, and electrical properties of the t1 layer would be important in determining TFT characteristics. We note that O2-grown samples have thicker t1 layers with lower densities, and this can make a difference in the TFT performance.

Our results showed that the oxidizer pulsing was an effective tool to control surface condition of a metallic target. Our results also showed that CO2 can be a good oxidizer for sputtering growth of ZnO. ZnO grown by CO2 showed larger TFT currents, compared to the O2-grown ZnO. The larger TFT currents could be the result of increased n-type doping by the carbon, or elimination of the O2-related defects. O2 annealing usually removes all dopants in ZnO, resulting in lower TFT currents. We think that the effect of our H2–CO2 annealing is removal of defects without sacrificing the useful dopants. We also observed that using only one kind of gas (H2 or CO2) during the annealing was less effective in improving the turn-off characteristics. It is expected that co-existence of C and H during annealing would help to remove excess Zn by forming volatile CHxZn compounds.

There were reports that thin-film growth shows transition from two-dimensional (2D) growth mode to three-dimensional (3D) growth mode as the film thickness increases. It is possible that the oxidizer pulsing in our case could interrupt the transition from the 2D growth mode into the 3D mode. More analysis is needed to clarify this point.

4. Conclusion

We demonstrated that oxidizer pulsing is a useful method when a metallic target is used for sputtering growth. Substrate currents measured during the growth were explained by the changes of oxidized portion on the metal target, induced by variations of the oxidizer flows. We compared currents of ZnO TFT’s grown with CO2 or O2, and CO2-grown ZnO showed larger currents. We also showed that annealing in mixture of H2–CO2 improved turn-off characteristics of ZnO TFT’s.

Acknowledgements We thank Seulki Kim of the Center for Material Characterization at Ajou University for X-ray measurements.

References
1) P. F. Carcia, R. S. McLean, M. H. Reilly and G. Nunes, Appl. Phys. Lett., 82, 1117–1119 (2003).
2) E. Fortunato, P. Barquinha, A. Pimentel, A. Gonçalves, A. Marques, R. Martins and L. Pereira, Appl. Phys. Lett., 85, 2541–2543 (2004).
3) A. Lu and H. Huang, Jap. J. Appl. Phys., 54, 106502 (2015).
4) P. K. Nayak, Z. Wang, D. H. Anjum, M. N. Hedhili and H. N. Alshareef, *Appl. Phys. Lett.*, 106, 103505 (2015).
5) J. Jo, H. Choi, O. Seo and B. Lee, *Thin Solid Films*, 517, 6337–6340 (2009).
6) G. Adamopoulos, A. Bashir, S. Thomas, W. P. Gillin, S. Georgakopoulos, M. Shkunov, M. A. Baklar, N. Stingelin, R. C. Maher, L. F. Cohen, D. D. C. Bradley and T. D. Anthopoulos, *Adv. Mater.*, 22, 4764–4769 (2010).
7) J. Kim, J. Meng, D. Lee, M. Yu, D. Yoo, D. W. Kang and J. Jo, *J. Nanomaterials*, 2014, 709018 (2014).
8) S. Li, Y. Cai, D. Han, Y. Wang, L. Sun, M. Chan and S. Zhang, *IEEE Trans. Electron Dev.*, 59, 2555–2558 (2012).
9) S. Takayanagi, T. Yanagitani and M. Matsukawa, *J. Cryst. Growth*, 363, 22–24 (2013).
10) K. Kumeta, H. Ono and S. Iizuka, *Thin Solid Films*, 518, 3522–3525 (2010).
11) K. Tominaga, T. Murayama, Y. Sato and I. Mori, *Thin Solid Films*, 343–344, 81–84 (1999).
12) P. Erhart, A. Klein and K. Albe, *Phys. Rev. B*, 72, 085213 (2005).
13) M. C. Chu, J. S. Meena, P. T. Liu, H. D. Shieh, H. C. You, Y. W. Tu, F. C. Chang and F. H. Ko, *Appl. Phys. Express*, 6, 076501 (2013).
14) Y. Kawamura, N. Hatton, N. Miyatake and Y. Uraoka, *J. Vac. Sci. and Technol. A*, 31, 01A142 (2013).
15) K. Nomura, T. Kamiya, H. Ohta, M. Hirano and H. Hosono, *Appl. Phys. Lett.*, 93, 192107 (2008).
16) F. M. Hossain, J. Nishii, S. Takagi, A. Ohtomo, T. Fukumura, H. Fujioka, H. Ohno, H. Koimura and M. Kawasaki, *J. Appl. Phys.*, 94, 7768–7777 (2003).
17) J. Jia, Y. Torigoshi and Y. Shigesato, *Appl. Phys. Lett.*, 103, 013501 (2013).
18) Y. Abe, K. Shinya, Y. Chiba, M. Kawamura and K. Sasaki, *Vacuum*, 84, 1365–1367 (2010).
19) O. Seo, J. Chung and J. Jo, *Eur. Phys. J. Appl. Phys.*, 54, 10302 (2011).
20) M. H. Shin, M. S. Park, S. H. Jung, J. H. Boo and N. E. Lee, *Thin Solid Films*, 515, 4950–4954 (2007).
21) S. I. Park, T. S. Cho, S. J. Doh, J. L. Lee and J. H. Je, *Appl. Phys. Lett.*, 77, 349–351 (2000).