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

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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 transistor 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 × 10⁶ on/off ratio, and −5 V threshold voltage.

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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 in 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.⁸⁾ 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.⁹⁾ 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 O₂-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

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Fig. 1. (a) A schematic diagram of rf sputtering system. Dc voltage was applied to the substrate, and dc current was measured. (b) Oxidizer pulsing during the growth.

was added to the Ar flow. When 1.5-sccm O_2 flow was added to the Ar flow, the pressure was 0.54 Pa. ZnO films for TFT's were grown on p+ Si substrates (10^{19} 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. Dc 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 (O_2 or CO_2) was turned off for 30 s, and remained on for 60 s. Five periods (8 min 30 s) were used to grow ZnO for TFT's, and 25 periods were used to grow ZnO for the optical measurements. We grew ZnO with negative voltage (-70 V) applied to the substrate. The negative voltage attracts positive ions (Zn^+ , CO_x^+ , O^+) to the substrate, and this is equivalent to an increased source supply. The negative voltage also prevents bombardment of negative ions (O^- , ZnO^- , CO_x^-) to the substrate.^{11),17)}

TFT's were fabricated by evaporating Al through a shadow mask (channel length = 25 μm , width = 500 μm). For TFT measurements two sets of samples (A and B) were compared. Sample A was grown with O_2 , and sample B grown with CO_2 as an oxidizer. ZnO film for the optical measurement was grown with O_2 as an oxidizer. TFT's before the anneal were designated as A1 and B1. Samples A2 and B2 were annealed for 20 min at 400°C in flows of 5-sccm H_2 and 5-sccm CO_2 , at 20-Pa pressure. A3 and B3 were grown without the oxidizer pulsing, and A4 and B4 represent those after the anneal. TFT's grown at slightly different conditions were designated as A2A, A2B, B2A, and B2B. Current-voltage characteristics were measured by Keithley 2400 sourcemeters. X-ray characteristics were measured by Rigaku Ultima III, using Cu K α line as a source. Optical absorptions were measured by an Agilent 8453 spectrophotometer.

3. Results and discussions

The effects of oxidizers and substrate voltages were investigated by studying dc currents measured at the substrate. **Figure 2** shows substrate currents measured between 30 and -70 V under different gas flows (Ar only, Ar+ O_2 , or Ar+ CO_2). Ar flows were

Fig. 2. Substrate currents measured at different gas flows (Ar only, Ar+ O_2 , or Ar+ CO_2).

Fig. 3. Substrate currents measured at increased oxidizer flows. Solid lines represent currents at 2-sccm oxidizer flows, while triangles and circles are currents for 2.5 sccm CO_2 and O_2 flows, respectively.

fixed at 4 sccm, and 2-sccm O_2 or CO_2 was added. The pressures for the three gas flows were 0.54, 0.54, and 0.68 Pa, respectively.

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 electron flows. Note that the currents are larger when Ar+ O_2 is used. The larger current in this case indicates that the plasma density is higher when O_2 is used as an oxidizer.

When CO_2 was added to the Ar flow, the pressure increased from 0.54 to 0.68 Pa. In contrast, addition of O_2 to Ar did not change the pressure (0.54 Pa). We explain that the increase of pressure for CO_2 is due to CO_2 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 O_2 suggests that the gas mole increase by O_2 dissociation is relatively small.

Figure 3 shows currents at different oxidizer flows. For Ar+ CO_2 , increase of CO_2 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 O_2 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 O_2 flow can be explained by the higher plasma density discussed above. It appears that the effect of CO_2 increase is different from that of O_2

Fig. 4. Substrate currents measured during the growth, at -70 V substrate voltage. Oxidizer flows were off during the regions denoted as Ar. In (a) O_2 was used as an oxidizer, and in (b) CO_2 was used as an oxidizer.

increase. We think that shorter mean free path at the higher pressure is the reason for the smaller currents at the CO_2 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 off for 30 s, and remained on for 60 s. During the growth the substrate voltage was maintained at -70 V. Figure 4(a) shows currents measured when O_2 is used as an oxidizer, and 4b shows currents for CO_2 oxidizer. When oxidizer flow is off (denoted as Ar in the figures), both figures show decreasing currents, and the two current values are similar. When oxidizer flow is on (denoted as O_2 or CO_2), both figures show increasing currents, although the starting points are different. The pressures during the growth were different from those of the steady states used in Fig. 2, due to the oxidizer pulsing. In the Ar regions, Ar flow was 3 sccm, and the pressure was 0.51 Pa. When 1.5 sccm O_2 flow was added to the Ar, the pressure increased from 0.51 to 0.54 Pa. When 1.5 sccm CO_2 flow was added to the Ar flow, the pressure increased from 0.51 to 0.61 Pa. CO_2 regions still showed higher pressure than O_2 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.¹⁸⁾ We think that this is the reason for the current increase in the O_2 and CO_2 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.

Fig. 5. (a) A schematic diagram of a ZnO TFT structure. (b) Drain currents measured in O_2 -grown TFT's (A1 and A2), and (c) CO_2 -grown TFT's (B1 and B2), as a function of gate voltages ($V_{DS} = 10$ V). (Drain current of 1 mA in our TFT is equivalent to 2 mA/mm current density, which is calculated from the channel width.) Solid lines (A1, B1) represent data before the anneal, and dotted lines (A2, B2) are data after the anneal. Square roots of drain currents are also shown.

Figure 5 shows drain currents measured in ZnO TFT's. Figure 5(a) is a schematic diagram of a TFT structure. Figures 5(b) and 5(c) show drain currents of TFT's as a function of gate voltages, measured at 10-V drain-source voltage. Solid lines represent data measured before the anneal (A1 and B1), and dotted lines after the anneal (A2 and B2). Square root of drain currents are also shown in the figures, where the threshold voltage (V_{th}) was obtained from extrapolation. As shown in the figures, the annealing in H_2 and CO_2 at $400^\circ C$ improved turn-off characteristics of TFT's. This result is also consistent with the optical absorption change, which will be shown later. TFT B2 in Fig. 5 shows $6.5 \text{ cm}^2/\text{Vsec}$ mobility, 5×10^6 on/off ratio, and -5 V threshold voltage.

Figure 6 shows drain currents as a function of drain-source voltage, before [Figs. 6(a) and 6(c)], and after the anneal [Figs. 6(b) and 6(d)]. Although the currents before the anneal are larger, the current behavior is different from that of ideal TFT's, due to high defect density. Currents in B1 show step-like jumps, which could be related to the multi-layer nature of our ZnO. After the H_2 - CO_2 anneal, the irregular behavior of the currents is removed.

When ZnO films were grown without the oxidizer pulsing, turn-off characteristics of the TFT's were not good. ZnO films used in Fig. 7 were grown without oxidizer pulsing. Sample A3 was grown with O_2 oxidizer, and sample B3 was grown with CO_2 oxidizer. TFT's after the anneal were denoted as A4 and B4. The oxidizer gases (O_2 or CO_2) were supplied continuously during the same growth time as used in A1 and B1, while the oxidizer flow rate was reduced to 2/3 of those used in A1 or B1. It is obvious that the oxidizer pulsing is effective in controlling the turn-off characteristics.

Figure 8 shows current changes by O_2 flow variations, while other parameters are the same as those used in A2. Sample A2A (solid line) was grown with higher O_2 flow (1.8 sccm),

Fig. 6. Drain currents measured as a function of drain voltages, before [(a) and (c)], and after the anneal [(b) and (d)]. Gate voltages were changed in 10-V steps.

Fig. 7. Current characteristics of ZnO TFT's grown without the oxidizer pulsing. Solid lines (A3, B3) represent data before the anneal, and dotted lines (A4, B4) are data after the anneal. (a) Drain currents as a function of gate voltages. (b) Drain currents measured in O_2 -grown TFT's, as a function of drain voltages. (c) Drain currents measured in CO_2 -grown TFT's. Gate voltages in (b) and (c) were changed in 10-V steps.

and Sample A2B (dotted line) was grown with lower O_2 flow (1.2 sccm), compared to sample A2 (1.5 sccm O_2). They were annealed in the same conditions as used in A2. ZnO grown at higher O_2 flow (A2A) shows larger drain current and more negative V_{th} . Sample with lower O_2 flow (A2B) shows smaller current. The effect of O_2 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 CO_2 -grown samples. Sample B2 was grown with 30 s Ar time and 60 s Ar + CO_2

Fig. 8. Drain currents measured in TFT's grown with different O_2 parameters, as a function of (a) gate-source voltages, and (b) drain-source voltages. Solid lines are currents in A2A (higher O_2 flow), and dotted lines are currents in A2B (lower O_2 flow).

Fig. 9. Drain currents measured in TFT's grown with different CO_2 parameters, as a function of (a) gate-source voltages, and (b) drain-source voltages. Dotted lines are currents in B2A (longer CO_2 time), and solid lines are currents in B2B (longer Ar time).

time. Sample B2A (dotted line) was grown with longer CO_2 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 O_2 time was longer (not shown here). We think that the larger off-current in B2A is due to excess

Fig. 10. Absorption characteristics measured in 400-nm thick ZnO film, before and after the H₂-CO₂ annealing. Absorption characteristics below the bandgap energy were changed by the annealing.

Fig. 11. X-ray reflection (XRR) data measured in (a) O₂-grown samples (A1 and A2), and (b) CO₂-grown samples (B1 and B2). Solid lines are fitting results, and dots are measured data. The inset in (a) is a two-layer model used for the fitting.

oxygen incorporated during the longer CO₂ time. When Ar time was longer (B2B), the drain current was larger, but V_{th} was shifted to a negative direction, compared to B2 in Fig. 5. Because enhancement-mode TFT is more favorable for device applications, the negative shift of V_{th} is considered not good. The increase of TFT current at the longer Ar time could be attributed to an increase of Zn interstitial or oxygen vacancy.

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 $T = (1 - R) \exp(-\alpha d)$, 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 is shown as an inset in Fig. 11. O₂-grown samples (A1, 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).

Table 1. Parameters obtained by fitting of X-ray reflectivity (XRR) data. t: layer thickness (nm), ρ : density (g/cm³)

Sample Name	Oxidizer Gas	Thermal Treatment	t1 (ρ 1)	t2 (ρ 2)	t3 (ρ 3)
A1	O ₂	as-deposited	2.28 (3.55)	12.82 (5.80)	
A2	O ₂	annealed	1.50 (2.99)	11.76 (5.68)	
B1	CO ₂	as-deposited	0.60 (6.18)	13.47 (5.42)	1.22 (0.64)
B2	CO ₂	annealed	0.49 (5.85)	13.79 (5.36)	1.16 (0.49)

ZnO grown by O₂ (A1, A2) showed thicker t1 layers, and their densities (ρ 1) were smaller than those of the main layers (ρ 2). 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.¹⁹⁾ 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 CH₃Zn compounds.²⁰⁾

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.²¹⁾ 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.

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