

## Chemical vapor deposition of highly resistive ZnO films using nonequilibrium N<sub>2</sub>/O<sub>2</sub> plasma generated near atmospheric pressure

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### Abstract

Zinc oxide (ZnO) films were fabricated by chemical vapor deposition using nonequilibrium N<sub>2</sub>/O<sub>2</sub> plasma generated near atmospheric pressure. Despite our ZnO were nominally undoped films, some films exhibited quite high specific resistivity exceeding 10<sup>6</sup> Ωcm at room temperature. Moreover, the specific resistivity of ZnO thin layer could be controlled over a wide range (10<sup>1</sup> – 10<sup>6</sup> Ωcm) by tuning the oxidizability of the plasma and the growth temperature. From the growth condition dependence of the specific resistivity, the impurities such as carbon, nitrogen or its complex seems to play important roles in the electronic state of highly resistive ZnO films.

### 1. Introduction

For decades, plasma processes were studied at a low pressure, which requires the use of vacuum equipment, decreases the throughput, increases the running cost and also has an issue regarding ion peening effect by ion bombardment. Therefore, the development of low temperature growth processes operated near atmospheric pressure (AP) has been strongly desired. [1] In general, AP plasma requires the use of expensive rare gas (He) as a dilution gas to maintain an arc-less, non-equilibrium and stable discharge. From an industrial viewpoint, He-less processes

must be realized. Therefore, we have developed chemical vapor deposition (CVD) system for oxide films using nonequilibrium AP N<sub>2</sub>/O<sub>2</sub> plasma and have reported the formation of ZnO films at the substrate temperature as low as 200 °C. [2] Additionally, we have succeeded in the control of (0001) preferred orientation for low temperature grown ZnO films. Although the recent researches regarding ZnO films go toward the application to transparent conductive films, ZnO also have attracted much attention as a piezoelectric material for the application to piezoelectric transducer, nanogenerator and energy harvester due to the excellent electromechanical coupling coefficient. Such devices require a highly resistive ZnO. Recently, we have found that AP plasma could produce a highly resistive ZnO layer without any intentional counter dopant such as group-I or group-V elements. In this paper, we will discuss the incorporation mechanism of unintentional dopant and the origin of high resistivity.

### 2. Experiment

Bis-[2,4]-octanedionato zinc [Zn(OD)<sub>2</sub>] was used as Zn source material. Vaporized Zn(OD)<sub>2</sub> was transported at the constant flow rate of 0.44 μmol/min by the carrier N<sub>2</sub> gas of 60 ml/min. The carrier gas was mixed with N<sub>2</sub> and O<sub>2</sub> gases controlled by the mass flow controller. The O<sub>2</sub> / (O<sub>2</sub> + N<sub>2</sub>) flow rate ratio was varied from 0 to 90% to change the rela-

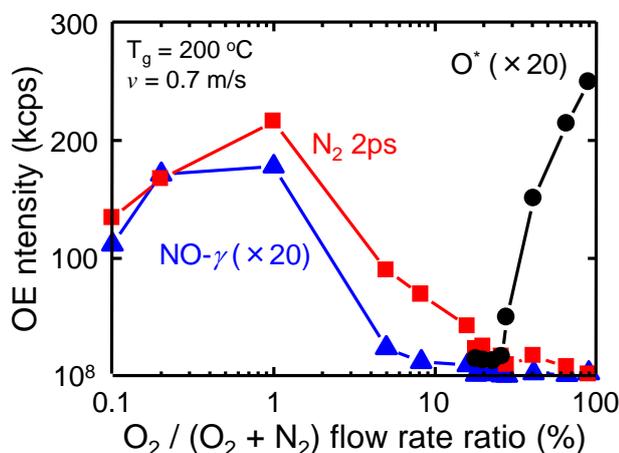


Fig. 1. Change in the OE intensity of N<sub>2</sub> 2ps (square), NO-γ (triangle) and O\* (circle) as a function of O<sub>2</sub> / (O<sub>2</sub> + N<sub>2</sub>) flow rate ratio.

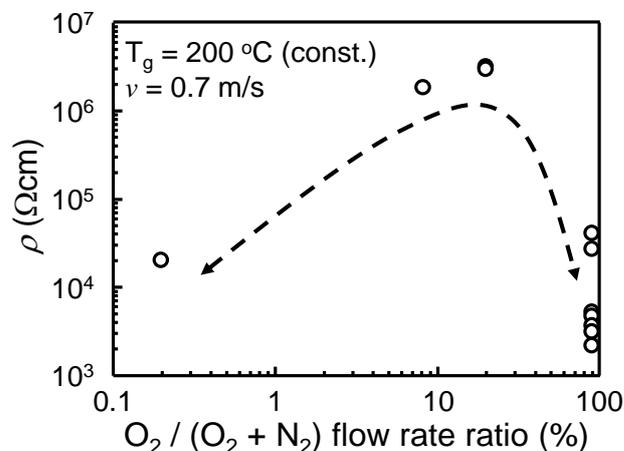


Fig. 2. O<sub>2</sub> / (O<sub>2</sub> + N<sub>2</sub>) flow rate ratio dependence of the specific resistivity of ZnO films deposited at the growth temperature of 200 °C.

tive density of the excited species. The total pressure of the chamber was maintained at 50 kPa. Deposition of ZnO films was performed on glass substrates or c-cut sapphire substrate heated at 200 - 400 °C mounted in the plasma. The excited species in the plasma were evaluated by optical emission spectroscopy (OES). After the deposition, the crystallographic structure of the films was investigated by X-ray diffraction (XRD) and the growth rate of the films was determined from the optical interference of the transmittance spectra and the cross-sectional SEM images. The specific resistivity of the films was measured by four probe method using van der Pauw's configuration.

### 3. Result and Discussion

OES of the plasma was carried out to detect the electronically excited atomic and molecular species in the plasma. We systematically changed  $O_2 / (O_2 + N_2)$  flow rate ratio from 0.1 to 90%, and found that the predominantly observed OE lines were  $N_2$  2nd positive system ( $N_2$  2ps),  $NO-\gamma$  system ( $NO-\gamma$ ) and atomic O ( $O^*$ ). Fig. 1 shows the OE intensity of these transitions as a function of  $O_2 / (O_2 + N_2)$  flow rate ratio. OE intensity of  $N_2$  2ps and  $NO-\gamma$  rapidly decreases with increasing  $O_2 / (O_2 + N_2)$  flow rate ratio. On the other hand, that of  $O^*$  gradually increases with increasing the ratio. From  $2\theta-\omega$  scanned XRD analysis, all films showed (0001) preferred orientation with no hallow pattern from amorphous layer, and the FWHM of ZnO 0002 diffraction peaks were around  $0.4^\circ$ . Additionally, the growth rate of ZnO films was the most susceptible to the flow rate of  $Zn(OD)_2$  and independent on the growth temperature or  $O_2 / (O_2 + N_2)$  flow rate ratio, indicating that the growth of ZnO is performed in the supply rate limited region. Therefore it seems that the high resistivity is not due to the undecomposed residues.

Fig. 2 shows the effect of  $O_2 / (O_2 + N_2)$  flow rate ratio on the specific resistivity of ZnO films. All films show high resistivity above  $10^3 \Omega\text{cm}$ . Especially around 20%, where intense OE is not observed, ZnO film shows quite high resistivity exceeding  $10^6 \Omega\text{cm}$ . At low  $O_2 / (O_2 + N_2)$ ,

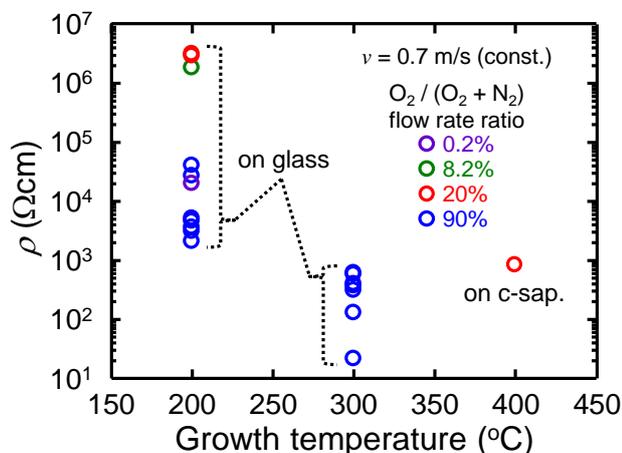


Fig. 3. Growth temperature dependence of the specific resistivity of ZnO films grown at various  $O_2 / (O_2 + N_2)$  flow rate ratio.

$O(^3P_2)$  which has very high oxidizability is produced from the photo-induced dissociation of  $O_3$ . [4] On the other hand, at high  $O_2 / (O_2 + N_2)$ , OE of  $O^*$  ( $\lambda = 777, 843$  and  $927$  nm) is observed and it is known as a strong oxidizer. Therefore the resistivity of ZnO films seems to be affected by the oxidizability of the plasma.

In our CVD process, ZnO films grows via the decomposition and the subsequent oxidation of the organic Zn source material [ $Zn(OD)_2$ ], which should be enhanced by the growth temperature. Fig. 3 shows the change of the specific resistivity against the change of growth temperature. With increasing the growth temperature, the resistivity of ZnO layer tends to decrease, probably due to the change of impurity concentration or its electronic state.

From above experimental facts, carbon and nitrogen from precursor seems to be the most possible impurities responsible for the high resistivity, because the incorporation efficiency of both carbon [5] and nitrogen [6] naturally decreases with increasing the growth temperature.

In the presentation, we will discuss the electronic state of our highly resistive ZnO films using an electrical measurement sensitive to the trap states in the deep levels.

### 4. Conclusions

In conclusion, we have successfully obtained highly resistive ZnO films by  $N_2/O_2$  plasma generated near atmospheric pressure without the degradation of crystal quality and deposition rate. The specific resistivity could be drastically changed by the growth condition. From the optical emission spectroscopy and electrical measurement, the specific resistivity of ZnO layer seems to be affected by the oxidizability of the plasma and the decomposition of the Zn source materials. This technique will be a useful method for the formation of highly resistive ZnO films without the use of unstable counter dopants such as group-I or group-V element. [7]

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