

P-8-3

## Optical and Electrical Characterizations of ZnMnO Thin Films on *c*-Al<sub>2</sub>O<sub>3</sub>

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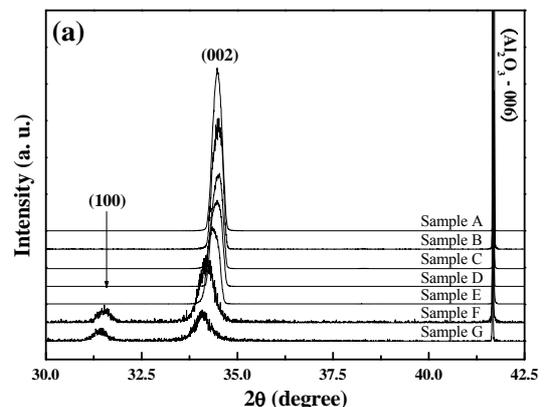
### 1. Introduction

Due to its wide band gap and its superior excitonic properties, ZnO has attracted considerable attentions for applications in room temperature optoelectronic devices such as ultraviolet (UV) lasers, light emitting diodes, transparent conductive films, and thin film transistors, etc. In particular, another application of ZnO is focused on the emerging field of spintronics. In this field, diluted magnetic semiconductors (DMSs) such as ZnMnO provide the possibility of manipulating both the charge and spin of electrons in semiconductors, so they are widely used as building materials for spintronic devices. In this study, the optical and electrical characterizations of ZnMnO thin films on *c*-Al<sub>2</sub>O<sub>3</sub> have been investigated by x-ray diffraction (XRD) spectra, Hall measurements, impedance spectroscopy (IS)[1], absorption and photoluminescence (PL) spectra. The effect of the Mn concentration on the material properties such as lattice constant, grain size, energy band gap, carrier concentration, and mobility, etc. were studied comprehensively.

### 2. Results and Discussion

The samples used in this study including one reference ZnO and six Zn<sub>1-x</sub>Mn<sub>x</sub>O thin films which were grown by plasma-assisted molecular beam epitaxy (PAMBE) on *c*-Al<sub>2</sub>O<sub>3</sub> at substrate temperature of 650 °C, and at various manganese cell temperatures  $T_{Mn}$ . These seven specimens are designated as A for the reference ZnO sample, and B to G for the rest six samples grown at  $T_{Mn}$  = 700 to 800 °C in steps of 20 °C, respectively, with a thickness of about 500 ~ 750 nm. As shown in Fig. 1, the typical (006) XRD peak of the sapphire substrate is found at 41.6°, and the (002) XRD peak of the ZnMnO films are clearly observed at lower angles. We can observe that when Mn concentration is increased, the lattice constant *c* decreases first due to the surfactant effect, and then increases due to the larger ionic radius of Mn<sup>2+</sup>. The grain size determined from the full width at half maximum of (002) diffraction peaks decreases with increasing the Mn concentration.[2] Figure 2 shows the mobility, carrier concentration, and resistivity of samples A to E at 300 K. The decrease in mobility and the increase in resistivity for the higher Mn content might be related with increasing of impurity scattering centers.

Besides, the decrease in the carrier concentration was exhibited. It has been explained that the energy level of Mn is about 2 eV below the conduction band, which significantly suppressed the concentration of the intrinsic donor.[3] The variations of the grain interior and grain boundary contributions on the electric conduction can be determined by using the IS. The results of IS measured by Agilent 4284A LCR meter are shown in Fig. 3. Two semicircles at high and low frequencies correspond to the signals from the bulk grain and grain boundary, respectively. The frequency corresponding to the peak of each semicircle is given by  $\omega\tau=1$ , where  $\tau$  is the relaxation time. The development of two separate arcs as Mn component increases is obvious, indicating that the relaxation time increased gradually. The fitting parameters are listed in Table I. The optical absorption and PL spectra of ZnMnO thin films at 10 K are shown in Fig. 4. When more Mn composition is incorporated into the ZnMnO thin films, a blue shift of the absorption edges and the PL emission peaks is observed. This result can be simply understood by the fact that the higher Mn flow rate the more Zn<sup>2+</sup> atoms are substituted by Mn<sup>2+</sup> atoms, and then a larger ZnMnO band gap is resulted. Furthermore, it is worth to note that a weak peak located at the energy near 3.35 eV for samples C, D and E. This transition energy is very close to that of reference ZnO film. We believe that this may due to the Mn cluster effect.



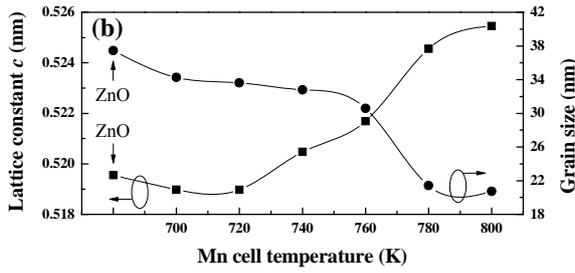


Fig. 1. (a) XRD spectra of ZnO and ZnMnO thin films; (b) lattice constant  $c$  and grain size as the function of  $T_{Mn}$ .

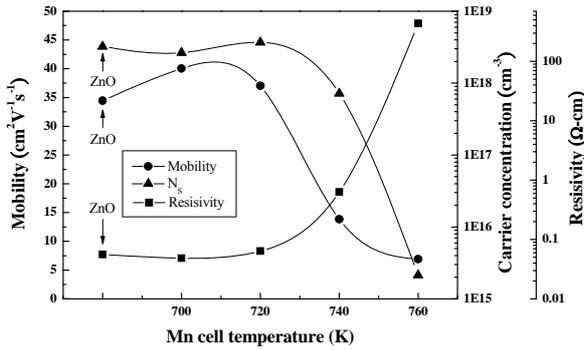


Fig. 2 Mobility, carrier concentration and resistivity of ZnMnO films at room temperature.

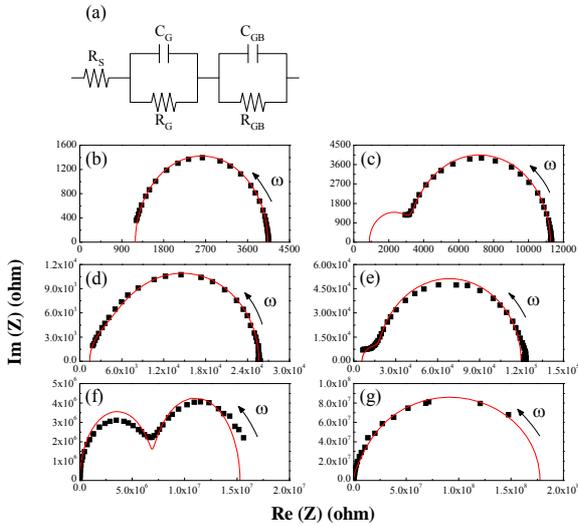


Fig. 3 (a) proposed  $C$ - $R$  equivalent circuit; (b-g) Impedance spectra of sample A to G at room temperature, respectively. The solid squares represent the experimental data whereas the solid lines are the best fitting results.

Table I Magnitudes of parameters extracted from fitting to IS experimental data.

Parameters	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
$R_G$ ( $\Omega$ )		2.3730E+03	3.1660E+03	1.2067E+04	6.9183E+06	7.2391E+06
$R_{GB}$ ( $\Omega$ )	2.8450E+03	7.9910E+03	2.1041E+04	1.0175E+05	8.3573E+06	1.7040E+08
$C_G$ (F)		2.9780E-10	1.5950E-10	4.2690E-11	2.2160E-12	2.7800E-11
$C_{GB}$ (F)	6.5700E-10	3.8730E-10	1.9810E-10	1.9280E-10	1.5790E-10	1.2860E-11
$\tau_G$ (s)		7.0668E-07	5.0498E-07	5.1514E-07	1.5331E-05	2.0125E-04
$\tau_{GB}$ (s)	1.8692E-06	3.0949E-06	4.1682E-06	1.9617E-05	1.3196E-03	2.1913E-03

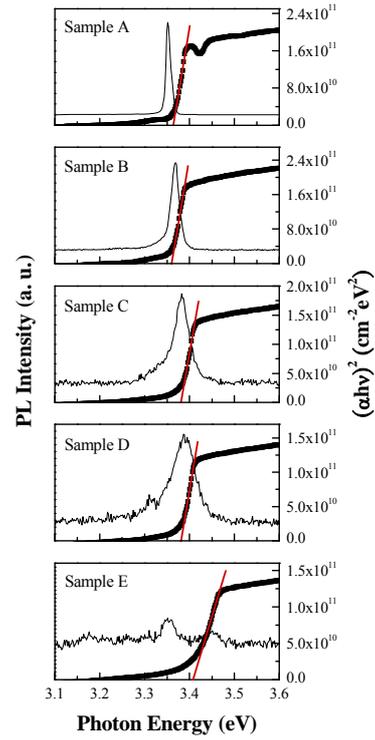


Fig. 4 Plot of  $(ahv)^2$  against  $hv$  of ZnMnO thin films at 10 K.

### 3. Conclusions

We have systematically performed the electrical and optical characterizations of ZnMnO thin films using XRD, Hall measurements, impedance spectroscopy, and optical absorption measurements. Films are single phase for manganese cell temperature less than 760 °C, and their crystal quality and grain size decrease with increasing Mn composition. The incorporation of Mn in Zn site accounted for the change of the optical band gap. If Mn atom acts as a deep donor in ZnO, it will depress the carrier concentration. We also find that the relaxation time of the grain and grain boundary increases with increasing the Mn composition.

### Acknowledgements

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