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# Influence of Space Charge on the Dielectric Properties of ZnO:Mn Epitaxial Films

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To control the magnetic property via piezoelectricity, the effects of Mn doping to ZnO on the leakage current and dielectric characteristics were studied. ZnO films with small leakage current were obtained by optimizing deposition conditions and Mn doping. The I-V measurement with DC bias voltage revealed that ZnO: 4 at% Mn showed the smallest leakage current. In addition, 3 and 4 at% Mn doped ZnO thin films showed the smallest dielectric loss (tanδ) evaluated with an AC amplitude of 10 mV. Space charge effect was not recognized in the ZnO film with 4 at% Mn evaluated with an AC amplitude of 2 V. The electro-optic coefficient of the ZnO: 4 at% Mn, which originated in only dipolar polarizability, was 1.14 pm/V.
Key words: ZnO, deposition condition, Mn, space charge, electro-optic effect

## 1. INTRODUCTION

It would be beneficial if the magnetic moment of magnetic materials as used in data storage media and in spin-electronic devices etc. [1] was able to be controlled by an external electric field. However, the magnetic spin does not directly coupled with the electric field.

Magnetic properties can be added to ZnO, which has the largest piezoelectricity among semiconductors, by doping a magnetic ion. Therefore, it is expected that the magnetic property of ZnO-based magnetic semiconductor is controlled by an external electric field. However, ZnO thin films have a large number of native carriers, which causes the large leakage current and impedes the application of sufficient electric field to develop its piezoelectricity. In order to apply a large electric field, it is necessary to reduce the origins of native carriers such as oxygen vacancies and zinc interstitials. To reduce them, it is necessary to deposit the films under oxygen-rich conditions. At first, therefore, optimization of deposition conditions was carried out to decrease the leakage current. We also tried to dope Mn ion for that purpose [2]. If Mn ion was used, the magnetic property was simultaneously added to ZnO. However, space charge is generated in ZnO:Mn thin films. This paper also describes how the space charge effect changes by Mn doping to ZnO thin films.

## 2. EXPERIMENT

ZnO:Mn thin films were prepared by pulsed laser deposition (PLD) method. In PLD method, a plume is formed by ablating a raw ceramic target. The optical emissions from atomic oxygen radicals (O*) and atomic zinc radicals (Zn*) in the plume were evaluated with a spectrometer (PMA-11, HAMAMATU). The optimum conditions for decreasing the oxygen defects were determined by the ratio of emission intensity, I(O*) and I(Zn*). Targets were prepared using ZnO (5N) and $Mn_3O_4$ (3N) powders. The mixed powder was milled, pressed with the weight of 1 ton at room temperature, and sintered at 1000 °C for 10 hours in air.

(0001) sapphire substrate was annealed at 1000°C in air for 10 hours to obtain a clear step and terrace structured surface. 200 nm-thick (111) Pt was deposited by rf sputtering as a bottom electrode. Subsequently, 1 μm-thick ZnO thin films with an Mn concentration below 5 at% were deposited on epitaxial Pt/(0001) sapphire at 600°C. Finally, 200 nm-thick Au top electrode was deposited.

The current-voltage (I-V) properties were measured using a picoampere with a voltage source (HP4140B). The dielectric properties were measured by an LCR meter (HP4284A).

To estimate the piezoelectricity of the ZnO:Mn, the electro-optic property was evaluated by measuring birefringence shift induced by the electric field [3], [4].

## 3. RESULTS AND DISCUSSION

To optimize the deposition conditions, optical emission spectra in the plume were evaluated. The emissions at 777 and 335 nm, which originated from the formation of O* and Zn*, respectively, were used. It is expected that the native carriers can be reduced with increasing the ratio of the emission intensities $I(O^*_{777})/I(Zn^*_{335})$. Dependence of the ratio on $O_2$ pressure ($P_{O2}$) and distance from the target (T-S) is shown in Fig. 1. The ratio becomes larger with increasing $P_{O2}$ and T-S. The effect of

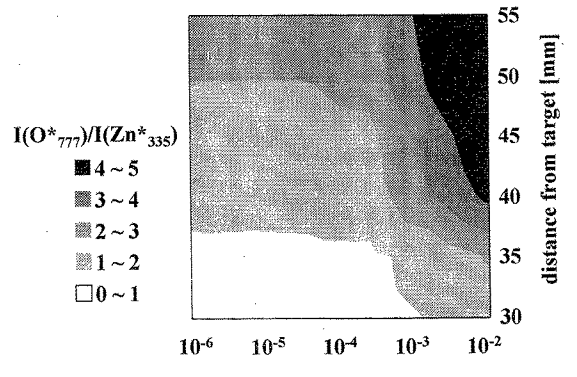


Fig. 1. Dependence of $I(O^*_{777})/I(Zn^*_{335})$ on $O_2$ pressure and distance from target.

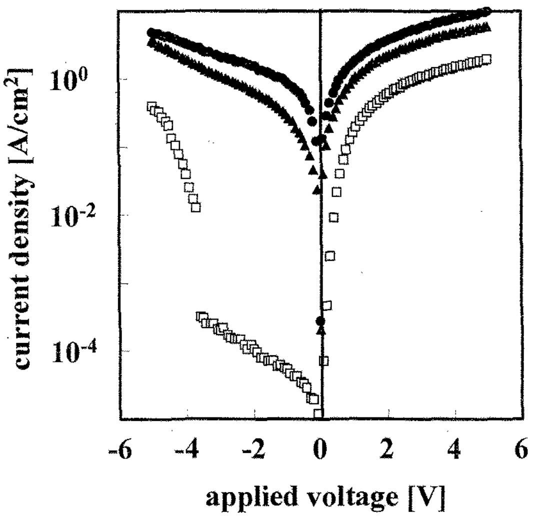


Fig. 2. I-V properties of ZnO films deposited at $1.0\times10^{-6}$ (•), $1.0\times10^{-4}$ (▲), and $5.0\times10^{-3}$ (□) Torr.

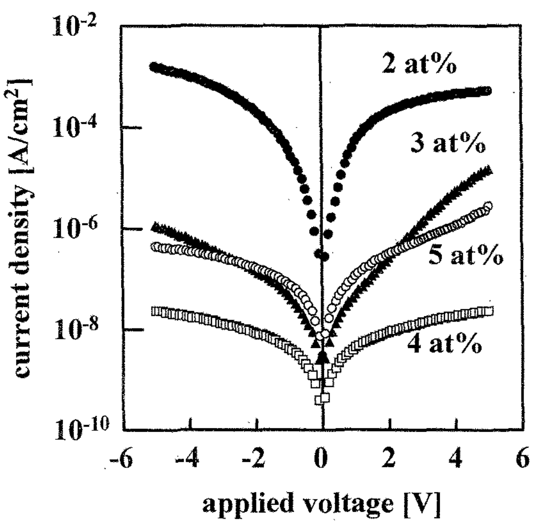


Fig. 3. I-V properties of 2(●), 3(▲), 4(□), and 5(○) at% Mn doped ZnO thin films.

$P_{O2}$ on the I-V properties of non-doped ZnO thin films is shown in Fig. 2. Leakage current decreases with an increase of $I(O^*_{777})/I(Zn^*_{335})$. The carrier concentration was decreased from $1.45\times10^{18}$ to $8.15\times10^{15}$ $cm^{-3}$ with increasing $P_{O2}$ from $1.0\times10^{-6}$ to $5.0\times10^{-3}$ Torr. Based on these results, $P_{O2}$ and T-S distance were determined as $5.0\times10^{-3}$ Torr and 50 mm, respectively. However, the leakage current of ZnO thin film deposited under this condition was $10^{-1}$ $A/cm^2$ at 2 V, which is not enough to apply a large electric field.

In order to decrease the longitudinal leakage current, Mn was doped to the ZnO thin films. Fig. 3 shows I-V properties of ZnO thin films with a Mn concentration of 2(●), 3(▲), 4(□), and 5(○) at%. Leakage current at 2 V was decreased from $10^{-1}$ to $10^{-8}$ $A/cm^2$. The value of leakage current seems to be sufficient to apply the large bias. For device application, however, the evaluation of dielectric properties under the AC amplitude is required.

The dielectric properties with AC amplitude were measured. Frequency dependence of tanδ measured with AC amplitude of 10 mV is shown in Fig. 4. ZnO with 2 and 5 at% Mn indicated dielectric dispersion at less than 10 kHz, which is caused by space charge. On the other hand, tanδ of 3 and 4 at% Mn-doped ZnO were less than 0.1 in the frequency range from 20 Hz to 1 MHz.

For obtaining sufficient pizoelectricity, large amplitude voltage should be applied to the sample. Therefore, dielectric properties with AC amplitude of 2 V were measured. As shown in Fig. 5, distinct dielectric dispersion at frequency below 200 Hz is observed in the ZnO thin film with 3 at% Mn. Meanwhile, the dispersion is not recognized in ZnO: 4 at% Mn at the frequency range from 20 Hz to 1 MHz.

To estimate the piezoelectricity of the ZnO: 4 at% Mn, measurement of the electro-optic property was performed. The measurement was carried out in a reflection configuration, because the optical axis coincided with the

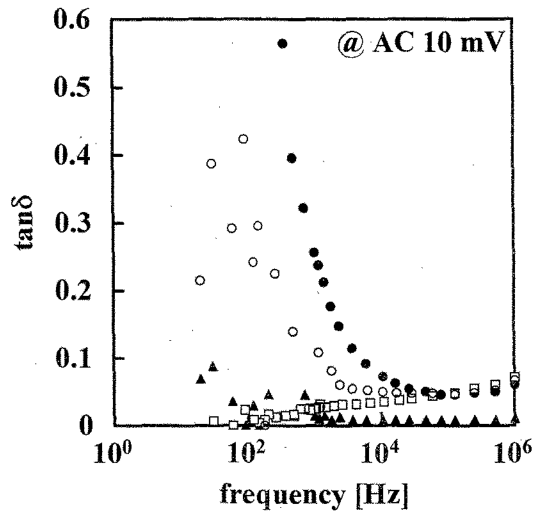


Fig. 4. Frequency dependence of dielectric loss (tanδ) of 2(•), 3(▲), 4(□), and 5(○) at% Mn-doped ZnO thin films evaluated with AC 10 mV.

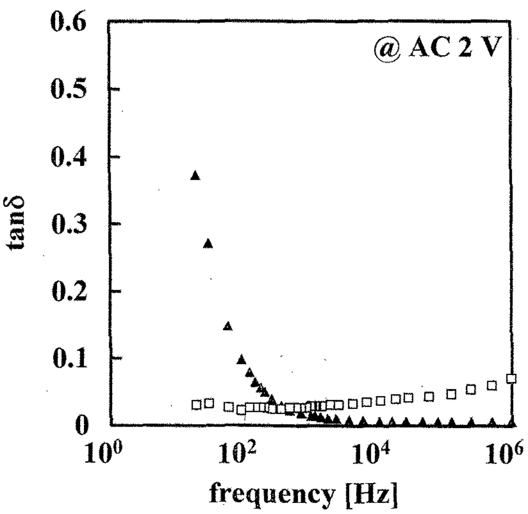


Fig. 5. Frequency dependence of dielectric loss of 3(▲) and 4(□) at% Mn doped ZnO thin films evaluated with AC 2 V.

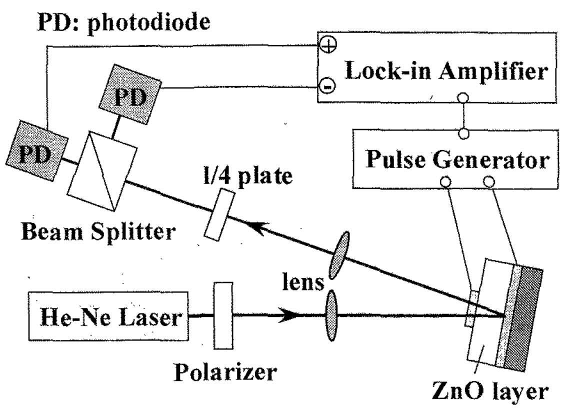


Fig. 6. A schema of the evaluation system for the electro-optic property.

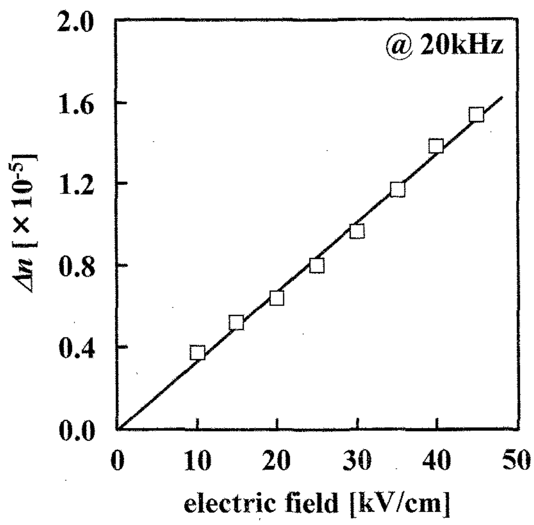


Fig. 7. Δn of ZnO: 4 at% Mn thin film as a function of electric field at 20 kHz.

polarization axis of ZnO thin films. The schematic view of the measurement system is shown in Fig. 6. The beam from the He-Ne laser ($\lambda$ = 632.8 nm) was linearly polarized and focused on the sample. AC square-wave bias voltage from 100 Hz to 100 kHz was applied to the sample by a pulse generator. The reflected beam was collimated and passed through a quarter-wave plate. A beam splitter was used to split the beam into two orthogonally polarized ones. A lock-in amplifier was used to amplify the differential signals. The small polarization shift, δ, of the reflected light was then determined by the difference between the signals. The birefringence shift, Δn , was obtained using the equation [3],

$$\Delta n = \frac{\lambda \delta}{2\pi n_0 d} \quad (1)$$

where $\lambda$ is the wavelength of the beam of the He-Ne laser, $\delta$ is the measured polarization shift, $n_0$ is the ordinary refractive index, and $d$ is the total optical path length. $n_0$ of the ZnO film was evaluated with a ellipsometer (Photal FTM-7700).

To evaluate the electro-optic response, which originated in only dipolar polarizability, Δn of ZnO with 4 at% Mn was evaluated at the frequency of 20 kHz. Change in Δn against the electric field is shown in Fig. 7. The applied electric field was changed from 10 to 45 kV/cm. Δn linearly increases with increasing the electric field. The electro-optic coefficient was calculated to be 1.14 pm/V.

4. CONCLUSIONS

To decrease the leakage current of ZnO thin films, $P_{O2}$ and T-S distances during depositions were determined by evaluating the optical emission spectra in the plume. Furthermore, Mn doping was carried out. As a result, the leakage current was decreased to $10^{-8}$ A/cm$^2$ at 2 V, at which piezoelectric effect appears. The tanδ of 3 and 4 at% Mn-doped ZnO evaluated with AC amplitude of 10 mV are less than 0.1. However, tanδ of ZnO: 3 at% Mn evaluated with an AC amplitude of 2 V shows dielectric dispersion at less than 200 Hz. On the other hand, tanδ of ZnO: 4 at% Mn is less than 0.1 with AC 2 V. The electro-optic coefficient of the ZnO: 4 at% Mn, which originated in only dipolar polarizability, was calculated to be 1.14 pm/V.

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