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Mn Doping Effects on Dielectric Properties of ZnO Epitaxial Films

T. Oshio, A. Ashida, T. Yoshimura and N. Fujimura

Graduate School of Engineering, Osaka Prefecture University

1-1, Gakuen-cho, Sakai, Osaka 599-8531, Japan

fujim@pe.osakafu-u.ac.jp

To control magnetic properties by means of piezoelectricity, the effects of Mn doping to ZnO on the dielectric and the electro-optic (E-O) properties were studied. Leakage current and dielectric loss (tanδ) of ZnO films are decreased by Mn doping up to 4%. However, these are increased by doping more than 4%. The temperature dependence of the conductivities revealed that origin of the leakage current and dielectric dispersion is the charge related to anti-site Zn (Zn_O). However, the large frequency dispersion in the birefringence shift (Δn) in the ZnO: 4% Mn thin film was observed, though the tanδ does not disperse. The dispersion originates in the space charge generated from the defect with low activation energy (Ea) of 8 meV. ZnO: 3 and 4% Mn with low AC conductivity (σ_{AC}) caused by Zn_O, showing a large E-O coefficient (1.14-1.18 pm/V) at the applied AC electric field of 20 kHz.

Key words: ZnO, space charge, electro-optic effect

Introduction

ZnO has the largest piezoelectric constant of 6.3 pC/N among semiconductors. Therefore, it is expected that the change of bond-angle caused by piezoelectric strain affects the spin-orbital interaction in ZnO doped with magnetic ions. In addition, Dietl predicted that p-type ZnO:Mn shows room-temperature ferromagnetic properties [1]. It would be possible to realize novel spintronics devices if the magnetic moment was controllable by an external electric field. In this study, we aimed to achieve a novel spin-control method by means of piezoelectric strain or change of charge distribution.

However, ZnO thin films have native carriers, which increase leakage current and prevent from applying electric field large enough to express the E-O phenomenon. Therefore, it is necessary to reduce the origin of native carriers, such as oxygen vacancies, to apply large electric field. We have previously reported that ZnO thin films with low leakage current and low tanδ were obtained by doping Mn [2], [3]. In this paper, we investigated the influence of space charge on dielectric and E-O properties, and succeeded in separating the piezoelectricity originating in dipolar polarization from the others caused by the space charges. In addition, we evaluated the E-O coefficient without the contribution of space charges.

Experimental

ZnO:Mn thin films were prepared by pulsed laser deposition method. The substrate temperature and O_2 gas pressure during depositions were 600°C and 1 mTorr, respectively. Targets were prepared using ZnO (5N) and Mn_3O_4 (3N) powders. The mixed powder was milled, pressed with 17 MPa 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 as a bottom electrode was epitaxially grown by rf sputtering. Subsequently, 1 μm-thick ZnO thin films with a Mn concentration from 0 to 10% were deposited at 600°C. Finally, 200 nm-thick Au top electrode was deposited.

I-V properties of the samples were measured using a picoampere meter with a voltage source (HP4140B). The dielectric properties were measured by an inductance-conductance-resistance meter (HP4284A). To evaluate the discharge properties following an applied electric field, a 300 pF capacitor was connected serially to the samples, and time dependence of the voltage was measured by a digital oscilloscope (HP54603B). To characterize the piezoelectricity, the E-O property was evaluated by measuring the birefringence shift caused by the electric field [4], [5] with a reflection configuration [2].

Results and Discussion

In order to decrease the leakage current, Mn was doped to the ZnO thin films. Figure 1 shows I-V properties of ZnO thin films with several concentrations of Mn. Leakage currents decreased with an increase of Mn concentration up to 4%. In this study, high resistivity ZnO thin films were obtained by doping 3-5% Mn.

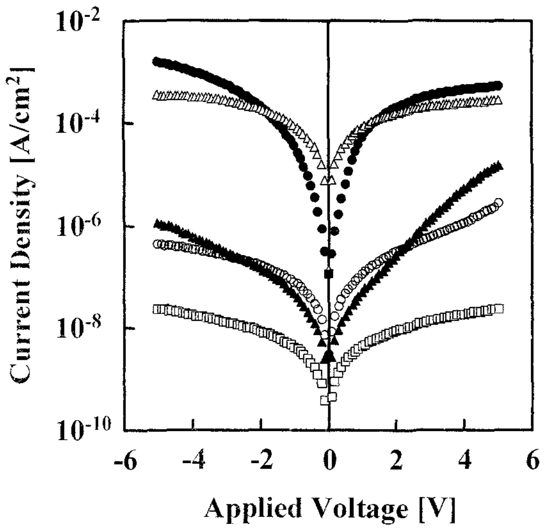

Fig. 1. I-V properties of 2(●), 3(▲), 4(□) 5(○) and 10(Δ) at% Mn doped ZnO thin films.

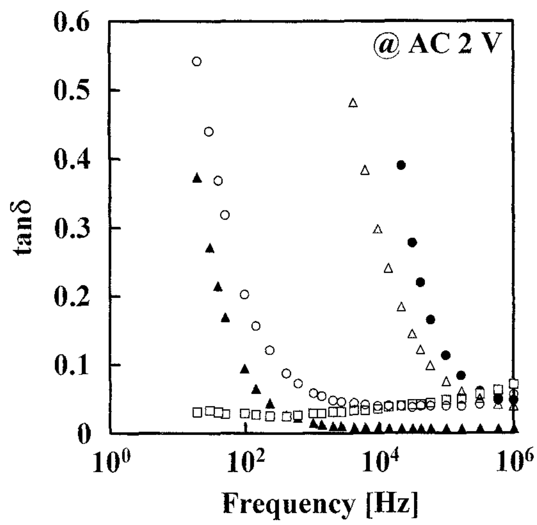

Fig. 2. Frequency dependence of tanδ of 2(●), 3(▲), 4(□), 5(○) and 10(Δ) at% Mn doped ZnO thin films evaluated with AC 2 V.

However, in order to investigate the E-O phenomenon, an evaluation of dielectric properties in the AC electric field is required. Frequency dependence of tanδ measured with AC 2 V, at which the piezoelectric effect is expected to appear, is shown in Figure 2. The dielectric dispersion expected to originate in the space charge decreases with an increase of Mn concentration as same as the leakage current. However, the dispersion increased with an increase of Mn concentration over 4%. It is therefore necessary to investigate the correlation between Mn and space charge.

To reveal the origins of the space charges in ZnO:Mn films, the σ_{AC} was measured. The frequency of the applied AC bias was set at 100 Hz, because the tanδ of the ZnO: 3 - 5% Mn films disperses around this frequency. Figure 3 shows temperature dependence of the σ_{AC}. In the undoped ZnO, a defect level with activation energy (Ea) of 52 meV was observed. It is close to an Ea of oxygen vacancy (V_O) [6]. However, the Ea is not observed in ZnO doped with Mn of 2% or more. A possible cause of this is that Mn acts as an oxidizing agent. With an increase in Mn concentration, the conductivity of ZnO decreases and defects with Ea of 370 meV and 8 meV appear. The defect with Ea of 370 meV is related to Zn atom at the oxygen site, Zn_O [7]. In this study, low AC conductivity ZnO thin films were obtained by doping 3-5% Mn. Carrier originating from Zn_O dominates the conduction of the ZnO: 3 and 5% Mn at room temperature. Therefore, the origin of the leakage current and dielectric dispersion in the two samples is expected to be Zn_O. On the other hand, a carrier with Ea of 8 meV dominates the conduction of the ZnO: 4% Mn. It is expected that the carrier of 8 meV is caused by a defect generated by Mn doping because of its absence in undoped ZnO.

To investigate the influence of Zn_O and the defect with 8 meV on the piezoelectricity, the frequency dependence of E-O properties of the three samples was evaluated as shown in Figure 4. The dispersions appear around 1 kHz, which does not correspond to that in tanδ-f properties as shown in Figure 2. Furthermore, the peak order in Δn of the samples does not correspond to the order in tanδ-f. It is expected that the origins of the dispersion in Δn are different from that in tanδ. As shown in Figure 3, the dominant origin of the

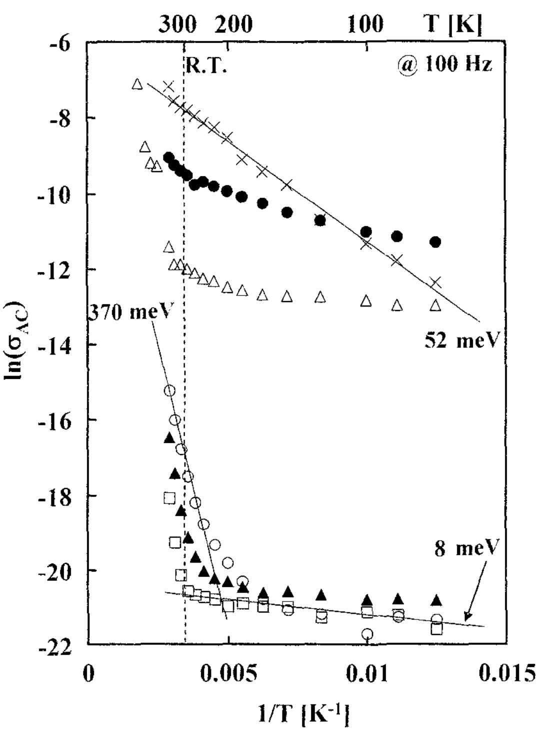

Fig. 3. Temperature dependence of σ_{ac} of ZnO: 0(x), 2(●), 3(▲), 4(□), 5(○) and 10(Δ) at% Mn thin films evaluated at 100 Hz.

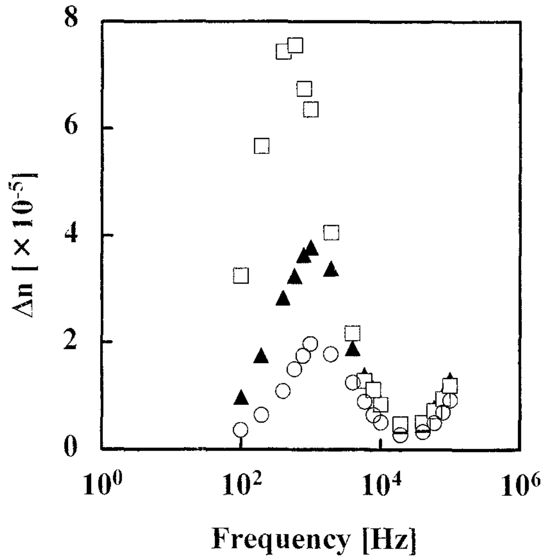

Fig. 4. Frequency dependence of Δn of ZnO: 3(▲), 4(□) and 5(○) at% Mn thin films evaluated with AC 2 V.

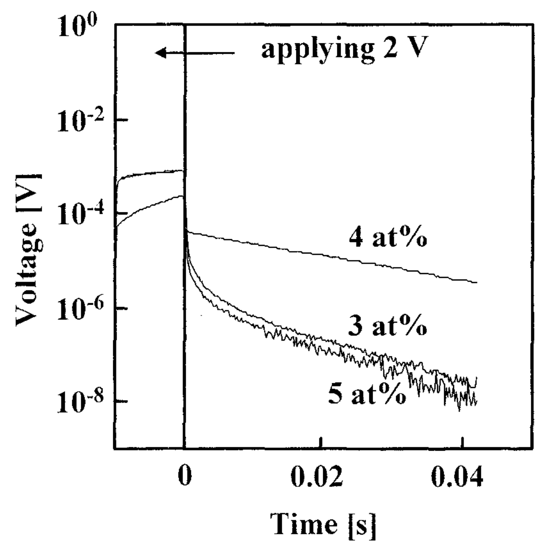

Fig. 5. Decay of discharge of ZnO: 3, 4 and 5 at% Mn thin films.

conduction of ZnO: 4% Mn at room temperature is different from that of 3 and 5% Mn doped samples. Therefore, it is expected that the space charge affecting on Δn is different from that on tanδ.

The discharging properties of ZnO: 3-5% Mn were evaluated by applying a pulse voltage equal to that in the measurement of Δn as shown in Fig. 5. The decay time constant (τ) of ZnO: 4% Mn was evaluated as about 30 msec. On the other hand, that of ZnO: 3 and 5% were evaluated as about 10 msec. It is expected that ZnO: 3 and 5% Mn have the same space charge differing from that in ZnO: 4 %. In Figure 3, the space charge with τ = 10 and 30 msec originate in the defect

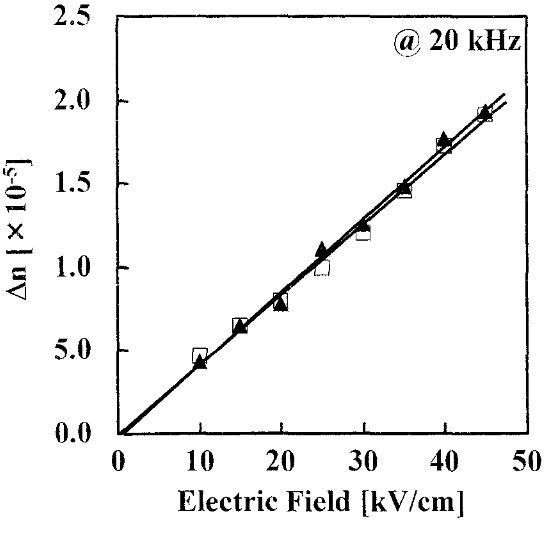

Fig. 6. Δn of ZnO: 3(▲), and 4(□) at% Mn thin films as a function of AC electric field at 20 kHz.

with Ea of 8 meV and Zn_O, respectively. It is considered that the space charge generated from the defect with Ea of 8 meV disperses Δn.

In Figure 4, the Δn minimum is around 20 kHz. It is expected that the E-O properties at this frequency are not greatly influenced by the space charges. Therefore, the E-O properties of the samples were evaluated at 20 kHz. The electric field dependence of Δn of ZnO: 3 and 4% Mn with very low σ_{AC} are shown in Figure 6. In both, Δn linearly increases with an increase in electric field, showing that the samples indicate the Pockels effect. We successfully separated the piezoelectricity witch originated in dipolar polarization from the others caused by space charges. The E-O coefficients of ZnO: 3 and 4% Mn thin films were calculated to be 1.18 and 1.14 pm/V, respectively.

Conclusions

The leakage current and tanδ of ZnO thin films are decreased by doping Mn up to 4%. The decrease is caused by the decrease of V_O and a defect with Ea of 8 meV. However, these are increased by doping more than 4% which is caused by increase of Zn_O. The Zn_O dominates the conduction of ZnO: 3 and 5% Mn at room temperature. However, that of ZnO: 4% Mn with the lowest leakage current and tanδ is dominated by the defect with Ea of 8 meV. ZnO: 4% Mn are found to have the lowest conduction caused by Zn_O. However, the ZnO: 4% Mn has the largest frequency dispersion caused by the space charge in Δn. In this sample, the carrier with a large time constant of 30 msec is expected to be caused by the defect with Ea of 8 meV. Therefore, it is considered that the space charge with Ea of 8 meV disperses the Δn. The dispersion has a minimum value around 20 kHz. Therefore, the E-O properties of ZnO: 3 and 4% Mn with very low σ_{AC} caused by Zn_O were evaluated at 20 kHz. As a result, E-O coefficients without the contribution of space charges were evaluated as 1.18 and 1.14 pm/V for ZnO: 3 and 4% Mn thin films.

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