

Dielectric relaxation of shallow donor in polycrystalline Mn-doped ZnO

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The dielectric properties of Mn-doped ZnO ceramics with electrically active grain boundaries at low temperatures of 10–70 K were investigated by admittance spectroscopy. It was observed that the dielectric relaxation of the main shallow donors, zinc interstitial, in these samples occurred in the temperature range of 20–50 K. Based on theoretical analysis, an expression for the admittance of an electrically active grain boundary at low temperatures was obtained. It was concluded that the relaxation of the shallow donors is Debye type with a thermally activated relaxation time and is related to the ionization process of these donors. The activation energy for the relaxation, i.e., the ionization energy of the shallow donors, was determined to be about 0.04 eV, the capture cross section of the shallow donors to be around 10^{-12} cm^2 , and the relaxation time at room temperature to be about 10^{-13} s . © 2003 American Institute of Physics. [DOI: 10.1063/1.1557781]

I. INTRODUCTION

Electrically active grain boundaries in polycrystalline semiconductors have been extensively studied experimentally and theoretically,^{1–6} since many technical applications are related to these electrically active grain boundaries, for example, ZnO varistors,^{1–3} polycrystalline silicon devices,^{4,5} and BaTiO₃ positive temperature coefficient resistors.⁶ Usually, a double Schottky barrier exists at an electrically active grain boundary. The information on the interface states and on the donor and acceptor states in the depletion regions, such as their energy levels and caption cross sections, can be determined from the admittance spectroscopy measurements of the grain boundaries.^{1,4,5}

Excellent theoretical models for the admittance of an electrically active grain boundary have been given by Pike,⁴ Werner,⁵ and Blatter and Greuter.¹ However, both Pike and Werner considered only the contributions of the interface states and of the completely ionized shallow bulk defects to the admittance of the grain boundary, neglecting the influence of the deep bulk traps. Therefore, only the information on the interface states can be obtained from their analyses. Blatter and Greuter further investigated the effect of the deep bulk traps on the static and dynamic properties of carrier transport through a grain boundary and obtained relevant information on these traps. All of these analyses are based on the assumption that the shallow defects are completely ionized in the bulk and their response times are therefore too short to observe the relaxation behavior of the shallow defects in the admittance spectra. Hence, the information on the

shallow defects can not be obtained from these analyses. The assumption is true when the temperature is relatively high to make the shallow defects completely ionized, which was the case in those works. However, when the temperature is low enough so that the shallow defects can only be partly ionized in the bulk, the relaxation of the shallow defects will make a significant contribution to the admittance of the grain boundary. This is the case analyzed in the present work.

It is well known that Mn doping in ZnO varistors can significantly improve the nonlinearity of current–voltage characteristic.^{2,7–9} However, the microscopic mechanism of this improvement effect is still unclear and very few investigations on the varistor behavior in Mn-doped ZnO binary ceramics are reported.^{10–13} In a recent work,^{14,15} we studied the current–voltage behavior of polycrystalline ZnO with Mn as the only additive and found that samples slowly cooled from the sintering temperature (1200 °C) show nonlinear current–voltage behavior (i.e., electrically active grain boundaries exist in these samples), whereas samples quenched from the sintering temperature show ohmic behavior. Defect equilibrium analysis^{14–16} suggested that the electrical activity of the grain boundaries in the slowly cooled samples, which resulted in the varistor behavior, is due to the oxidation of the doubly ionized zinc interstitials at the grain boundaries by ambient oxygen during slow cooling, and the presence of Mn induces this process.

In the present work, the dielectric behavior of Mn-doped ZnO samples with electrically active grain boundaries was investigated in the low temperature range from 10 to 70 K by admittance spectroscopy. A dielectric relaxation of the shallow donors in these samples was observed in the temperature range from around 20 to 50 K. Based on theoretical analysis, an expression for the admittance of an electrically active

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grain boundary at low temperatures was obtained, which provides reasonable interpretation to the experimental results.

II. EXPERIMENTAL PROCEDURE

Reagent grade ZnO powders (Aldrich, Milwaukee, WI) with 99.9% purity and mean particle size of $0.23\text{ }\mu\text{m}$ was used to make the ceramic samples. To dope with Mn, alcohol solutions of hydrated manganese nitrate, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, were prepared and mixed with ZnO powder in a planetary milling for 4 h. The amount of manganese ranged from 0.1 to 0.6 mol %. The slurry was dried at 80°C , and the obtained powder was calcined at 450°C for 1 h. Disk-shaped specimens of 10 mm diameter and 1–2 mm height were obtained by uniaxial pressing at 100 MPa, followed by isostatic pressing at 200 MPa.

Samples were heated to 1200°C at constant heating rate of $5^\circ\text{C}/\text{min}$. After 2 h sintered at 1200°C , the samples were cooled to 600°C at a rate of $1^\circ\text{C}/\text{min}$ and then furnace cooled to room temperature.

Sintered samples were examined by x-ray diffraction, scanning electron microscopy (SEM), with energy dispersive x-ray spectroscopy (EDS), and transmission electron microscopy (TEM) with electron diffraction and EDS analyses. No second phase was observed in each sample even at high magnification (up to $10^6\times$) field-emission SEM and TEM images. All the samples show uniform equiaxed grains and no abnormal grain growth. The average grain sizes of the samples are between 5 and 10 μm , and their sintered relative densities range between 95% and 97%. Trace element analysis by inductively coupled plasma emission spectroscopy in the sintered samples indicates that the concentration of each background impurity of Bi, Ba, Sr, Ca, Pb, Co, Sb, Cu, Al, and Na, is very low ($<16\text{ ppm}$) and much lower than the Mn doping level.

Sintered samples were polished with 1200-grit SiC on both sides, ultrasonically cleaned, and then vacuum deposited with gold electrodes or covered with In–Ga electrodes. Using a computer aided system, the low temperature admittance spectra (from 10 to 300 K) of the samples were measured in a cryogenic system (Model HC-2, APD Cryogenics Inc., USA) by an impedance gain-phase analyzer (Model 1260, Solartron Instruments, England) in the frequency range from 1 Hz to 1 MHz. Temperature control and measurements were performed with a calibrated silicon diode and a microprocessor cryogenic temperature controller (Model 9650, Scientific Instruments, USA).

III. RESULTS AND DISCUSSION

A. Basic experimental phenomena

Figure 1 shows the temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the complex-permittivity at several frequencies for the sample of ZnO doped with 0.3 mol % Mn. The following features can be observed: ϵ' at 10 K is very low, which at 1 MHz is close to the dielectric constant of ZnO crystal (~ 10). With increasing temperature, ϵ' increases slowly up to around 25 K, then rises sharply to a much higher value, and thereafter again increases slowly. Corresponding to the jump of ϵ' , ϵ'' shows a peak in the

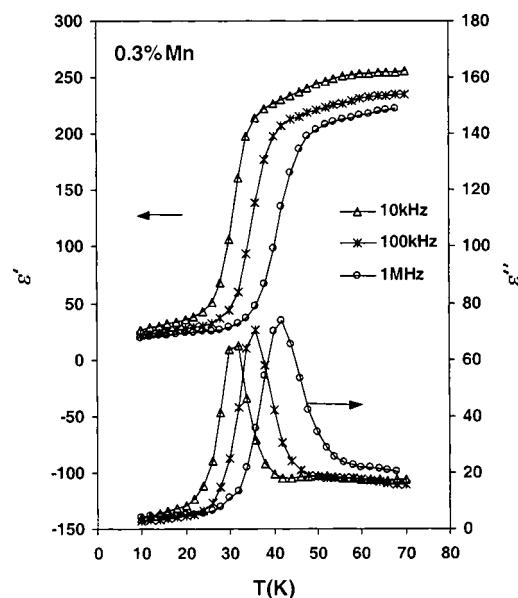


FIG. 1. Temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity at several frequencies for the sample of ZnO doped with 0.3 mol % Mn.

same temperature range. With the increase of frequency, both the jump of ϵ' and the peak of ϵ'' shift to higher temperatures. These features indicate that a dielectric relaxation occurred in these samples. However, a loss peak in the temperature spectrum does not prove that the relaxation response of the material is a Debye-like relaxation, only a frequency sweep can prove this point conclusively.¹⁷

The frequency dependence of the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity at several temperatures for the sample of ZnO doped with 0.3 mol % Mn, is presented in Fig. 2. At 10 K, both ϵ' and ϵ'' change slightly with frequency; while at a temperature within the

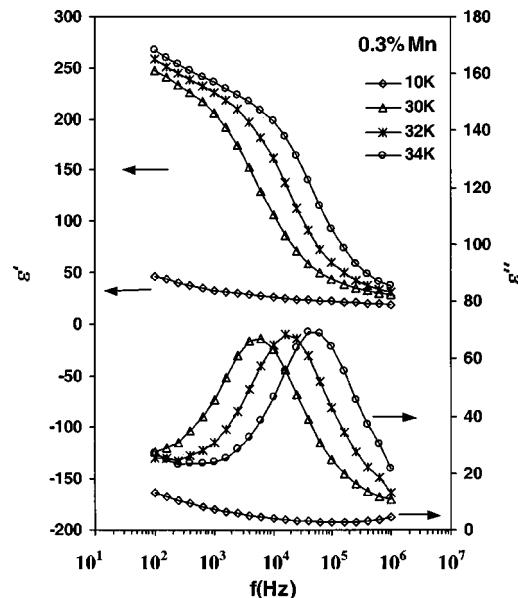


FIG. 2. Frequency dependence of the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity at several temperatures for the sample of ZnO doped with 0.3 mol % Mn.

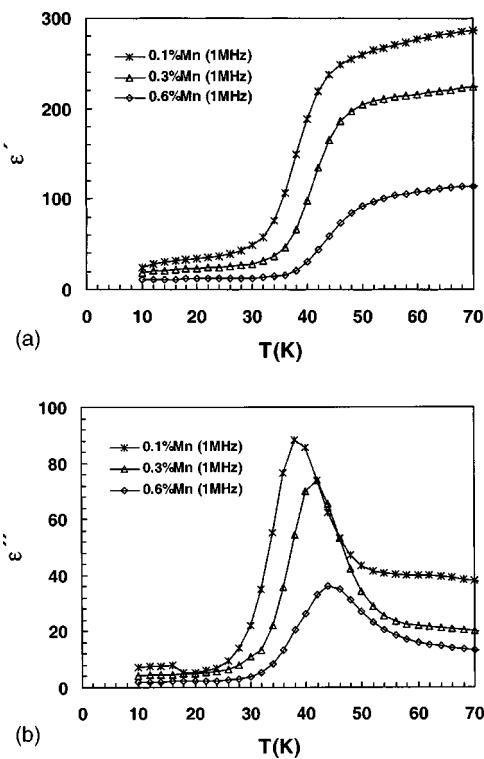


FIG. 3. Effects of the Mn concentration on the (a) real (ϵ') and (b) imaginary (ϵ'') parts of the complex permittivity.

range of 20–50 K, ϵ' shows a sharp decrease with frequency. Corresponding to the sharp decrease of ϵ' , there exists a significant peak of ϵ'' . Also, both the sharp decrease of ϵ' and the peak of ϵ'' shift to higher frequency with the increase in the temperature. Therefore, the dielectric relaxation in the sample seems to be a Debye-like relaxation. Our theoretical analysis has confirmed this point, as described in the following section.

The temperature and frequency dependences of the complex permittivity for the samples of ZnO doped with 0.1 and 0.6 mol % Mn, respectively, are similar as those of the 0.3 mol % Mn doped one, i.e., all of them exhibit the same features described above. The difference between them, i.e., the effect of the Mn concentration on the dielectric properties of the samples, is shown in Fig. 3. With increasing the Mn concentration, the value of ϵ' and the height of the ϵ'' peak decrease, and the ϵ'' peak position shifts slightly to higher temperatures.

B. Origin of the observed dielectric relaxation

As mentioned in Sec. I, Greuter and Blatter¹ have presented a detailed theoretical analysis and experimental observation of the dielectric behavior of ZnO varistors. Their analysis and observation were limited to temperatures greater than 80 K, where the shallow donors in ZnO varistors have already been ionized. Therefore, only the relaxation of the deep bulk traps and of the interface states can be observed in the admittance spectra of ZnO varistors. For example, several ϵ'' peaks, arising from the relaxation of several deep bulk traps, were observed in the temperature range from around 80 to 400 K.¹ The Mn-doped ZnO samples slowly

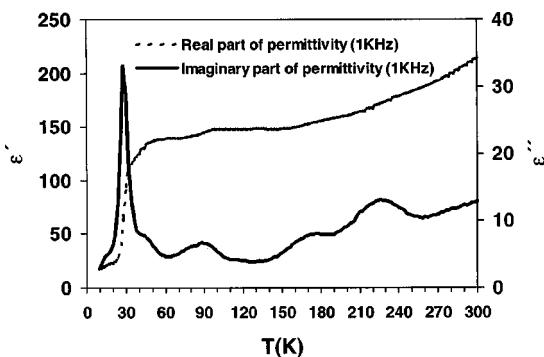


FIG. 4. Temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity from 10 to 300 K at 1 kHz for the sample of ZnO doped with 0.6 mol % Mn.

cooled from the sintering temperatures in the present work also exhibit varistor behavior.¹⁵ As expected, when we extended the admittance spectrum measurements up to 300 K, the temperature spectra similar to those in Greuter and Blatter's work have been observed in these samples, as shown in Fig. 4. The temperature spectra exhibit a series of ϵ'' peaks arising from several deep bulk traps, and most of the energy levels of these deep traps are the same as those obtained by Greuter and Blatter (the detailed analysis on these deep traps was presented elsewhere).¹⁸ It can be observed in Fig. 4 that the ϵ'' peak in Fig. 1 is the lowest temperature one and has the highest amplitude in the temperature range up to 300 K. Since the lower ϵ'' peak temperature corresponds to the lower ionization energy of the trap, and the height of the ϵ'' peak represents the trap concentration, the ϵ'' peak in Fig. 1 can be assigned to the shallowest donor with the highest concentration, i.e., to the main shallow donor. This point is further confirmed by the following experimental results.

The temperature dependence of the dc electrical conductivity was measured for samples with the same compositions but quenched rather than slowly cooled from the sintering temperature. Different from the case of the slowly cooled samples, there is no time enough to oxide the grain boundaries during quenching. As a result, electrical barriers were not formed at the grain boundaries and these quenched samples showed ohmic behavior at room temperature,¹⁴ with conductivities around 10^{-1} – $10^{-2} \Omega^{-1} \text{cm}^{-1}$, i.e., a typical semiconductor property. Therefore, the measured conductivity should reflect the property of the bulk. Figure 5 shows the

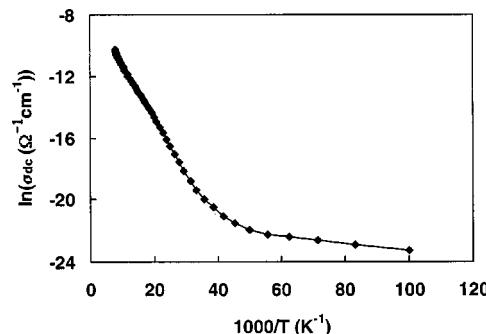


FIG. 5. Arrhenius plot of the dc conductivity of the sample of ZnO doped with 0.6 mol % Mn, quenched from 1200 °C.

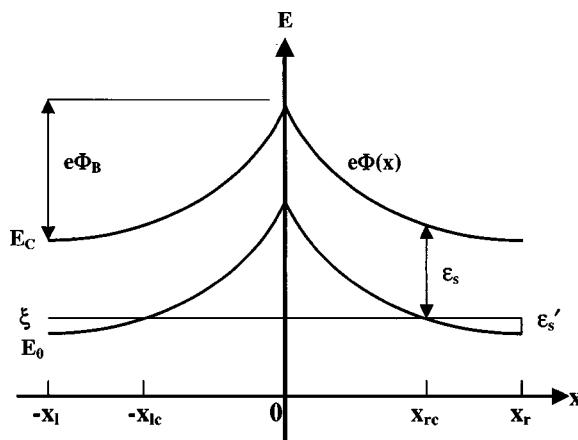


FIG. 6. Schematic energy band diagram of an electrically active grain boundary at low temperatures (only the upper part of the diagram is represented).

Arrhenius plot of the dc electrical conductivity of the sample doped with 0.6 mol % Mn. An activation energy of 0.03–0.04 eV was found at temperatures above 30 K. Similar temperature dependence of the dc electrical conductivity was also observed in undoped ZnO samples with room temperature conductivities of $\sim 10^{-1} \Omega^{-1} \text{cm}^{-1}$ and an activation energy of 0.03–0.04 eV at temperatures above 30 K.¹⁴ It is well known that the main intrinsic shallow donor in pure ZnO has an ionization energy of about 0.05 eV.^{19,20} Further analysis will show that the activation energy of the relaxation process in the admittance measurements is also about 0.04 eV. The defect chemistry calculation in a previous work¹⁶ showed that the main shallow donor in undoped and Mn-doped ZnO samples is the zinc interstitial. Therefore, based on the above ac and dc experimental results, it becomes clear that the main shallow donor, i.e., zinc interstitial, begins to significantly ionize in the temperature range from 20 to 50 K. This phenomenon gives a relaxation response of the material showing in the admittance spectroscopy measurements on samples with electrically active grain boundaries, and it is also responsible for the activation energy of 0.03–0.04 eV obtained by dc electrical conductivity measurements on samples with ohmic behavior.

C. Expression for the admittance of an electrically active grain boundary at low temperatures

In the following, a theoretical analysis of the admittance of an electrically active grain boundary is presented for the low temperature range where the main shallow donor is only partly ionized in the bulk, i.e., the shallow donor level energy E_0 is very close to the Fermi level ξ in the bulk. In other words, the absolute value of ε_s' , defined by $|\varepsilon_s'| = |\xi - E_0|$ in the bulk, is very small. Note that the shallow donor level can be below or above the Fermi level in the bulk, i.e., ε_s' can be positive or negative. The energy-band diagram of this kind of grain boundary is schematically shown in Fig. 6 (the zero energy is assumed to be at the top of the valence band). In this figure, E_C is the energy level of the conduction band edge, $\varepsilon_s = E_C - E_0$, Φ_B is the potential barrier, the interface is at $x = 0$, and the band bending, $\Phi(x)$, ends at $x = -x_l$ and

$x = x_r$ on the left and right side, respectively. Note also that the ε_s' is shown as being positive in the diagram and its value is exaggerated to better show its presence.

In the temperature range under consideration, if ε_s' is positive, it must be small enough to have the shallow donors significantly ionized in the bulk. Otherwise, the grains become insulating and the space charge regions will extend into the bulk so that the influence of the grain boundaries is better viewed as a large perturbation on the bulk Fermi level rather than a double Schottky barrier,²¹ while in the case of $\varepsilon_s' \leq 0$, the absolute value of ε_s' must also be small enough to have some shallow donors not ionized in the bulk, otherwise, its dielectric relaxation cannot be observed.^{1,4,5}

Assuming that N_0 is the total concentration and f_0 the electron-occupation probability of the shallow donors, in the bulk the concentrations of the unionized and ionized shallow donors should be $f_0 N_0$ and $(1 - f_0)N_0$, respectively. In this case $f_0 = 1/(1 + g \exp(-\varepsilon_s'/kT))$, where g is the degeneracy factor of the shallow donors ($g = 0.5$ for a simple defect donor). In the depletion region, when $\varepsilon_s' > 0$, the Fermi level crosses the shallow donor level at two points, x_{lc} and x_{rc} in Fig. 6, and these points are close to the edges (points x_l and x_r) of the depletion region due to the very small value of ε_s' . Therefore, it is reasonable to assume that in the part of the depletion region where the donor level is above the Fermi level, i.e., for $-x_{lc} < x < x_{rc}$, the donors are completely ionized, while in the other parts, the concentration of the unionized donors is $f_0 N_0$. On the other hand, when $\varepsilon_s' \leq 0$, the shallow donors are completely ionized in the whole depletion region.

When a small ac signal, $\delta V = \delta V_m \exp(i\omega t)$, is applied to the grain boundary, the response of the shallow donors must be analyzed for the two above cases, $\varepsilon_s' > 0$ and $\varepsilon_s' \leq 0$, separately. For each case, due to the symmetry of the double Schottky barrier without a dc bias applied at the grain boundary, the response of both sides of the grain boundary should be equal, and therefore, one can first consider the response of one of the sides, say the right side.

In the case of $\varepsilon_s' > 0$, when the applied voltage is changed from 0 to δV the crossing point moves from x_{rc} to $x_{rc} + \delta x_{rc}$, and the edge of the depletion region moves from x_r to $x_r + \delta x_r$. As a result, electrons are emitted from the shallow donors to the conduction band when the moving direction of x_{rc} is to the right, while when the moving direction is opposite, electrons are recaptured from the conduction band to the shallow donors. The charge emitted or recaptured δQ is

$$\delta Q = e f_0 N_0 A_{gb} \delta x_{rc}, \quad (1)$$

where e is the electron charge, and A_{gb} the grain-boundary area. Due to the fact that x_{rc} is very close to x_r , it can be assumed that δx_{rc} is equal to δx_r . Therefore,

$$\delta Q = e f_0 N_0 A_{gb} \delta x_r. \quad (2)$$

In the case of $\varepsilon_s' \leq 0$, when the applied voltage is changed from 0 to δV the edge of the depletion region moves from x_r to $x_r + \delta x_r$, which results in the electron emission and recapture between the shallow donors and the conduction band. The charge emitted or recaptured, δQ , is

equal to $e f_0 N_0 A_{\text{gb}} \delta x_r$. In other words, for both cases, the charge emitted or recaptured has approximately the same value.

The emission and recapture of electrons between the shallow donors and the conduction band leads to an additional current in the external circuit of the grain boundary. The expression for this current can be found with the expression of the charge emitted or recaptured δQ [Eq. (2)]. Considering the similar case in Ref. 22 which calculated the current associated with traps in GaP Schottky barriers, we use the calculation method described in Ref. 22 to calculate the current in the present samples. The obtained current has two components, one in phase and the other in quadrature with δV

$$I_{\text{phase}} = \frac{e_n \omega^2}{e_n^2 + \omega^2} \frac{f_0 N_0}{n} A \left(\frac{e \varepsilon \varepsilon_0 N_+}{2 \Phi_B} \right)^{1/2} \cdot \delta V_m \exp(i \omega t) \quad (3)$$

$$I_{\text{quad}} = \frac{e_n^2 \omega}{e_n^2 + \omega^2} \frac{f_0 N_0}{n} A \left(\frac{e \varepsilon \varepsilon_0 N_+}{2 \Phi_B} \right)^{1/2} \delta V_m \exp \left[i \left(\omega t + \frac{\pi}{2} \right) \right], \quad (4)$$

where e_n is the emission rate of electrons in the shallow donors, ω the angular frequency of the applied voltage, n the free-electron concentration in the bulk, N_+ is the positive-charge concentration in the depletion region, ε is the dielectric constant of ZnO, and ε_0 is the vacuum dielectric permittivity. Therefore, this current introduces a conductance G_s and a capacitance C_s given by

$$G_s = \frac{I_{\text{phase}}}{\delta V} = C_{\text{HF}} \frac{f_0 N_0}{n} \omega^2 \frac{\tau_0}{1 + \omega^2 \tau_0^2}, \quad (5)$$

$$C_s = \frac{1}{\omega} \frac{I_{\text{quad}}}{\delta V} = C_{\text{HF}} \frac{f_0 N_0}{n} \frac{1}{1 + \omega^2 \tau_0^2}, \quad (6)$$

where C_{HF} is the high-frequency capacitance of the barrier

$$C_{\text{HF}} = A_{\text{gb}} \left(\frac{e \varepsilon \varepsilon_0 N_+}{2 \Phi_B} \right)^{1/2} \quad (7)$$

and the characteristic relaxation time τ_0 of the shallow donors is given by

$$\tau_0 = \frac{1}{e_n} = \frac{e}{2 g A^* T^2 c_0} \exp(\varepsilon_s/kT). \quad (8)$$

A^* is the effective Richardson constant ($\sim 30 \text{ A cm}^{-2} \text{ K}^{-2}$ for ZnO, considering the electron effective mass, $m_e^* = 0.28 m_0$, where m_0 is the free electron mass),¹ and c_0 and ε_s are the capture cross section and the ionization energy of the shallow donors, respectively.

Up to now only one side of the double Schottky barrier was considered. For two sides of the double Schottky barrier, the conductance G_s , the capacitance C_s , and the high-frequency capacitance C_{HF} , should become half of the above values due to the serial connection of two symmetric sides in the circuit. Thus, the expression for C_{HF} should be changed to

$$C_{\text{HF}} = \frac{1}{2} A_{\text{gb}} \left(\frac{e \varepsilon \varepsilon_0 N_+}{2 \Phi_B} \right)^{1/2} \quad (9)$$

and then the expressions for G_s and C_s can keep their forms of Eqs. (5) and (6), respectively. The expressions for C_{HF} , G_s , and C_s should be the same for the two cases of $\varepsilon'_s > 0$ and $\varepsilon'_s \leq 0$, due to the fact that they arise from the same emitted or recaptured charge δQ . Hence, in the following discussion, the two cases are no longer distinguished.

Considering both the dc conductance G_{dc} arising from the electron flow over the barrier, and the frequency-independent barrier capacitance C_{HF} , the full expression for the admittance of the grain boundary $Y_a(\omega, T)$, defined as $Y_a(\omega, T) = G_{\text{ac}}(\omega, T) + i \omega C(\omega, T)$, under zero bias is

$$G_{\text{ac}}(\omega, T) = G_{\text{dc}} + C_{\text{HF}} \frac{f_0 N_0}{n} \omega^2 \frac{\tau_0}{1 + \omega^2 \tau_0^2}, \quad (10)$$

$$C(\omega, T) = C_{\text{HF}} + C_{\text{HF}} \frac{f_0 N_0}{n} \frac{1}{1 + \omega^2 \tau_0^2}, \quad (11)$$

with C_{HF} and τ_0 in the forms of Eqs. (9) and (8), respectively. G_{dc} is usually very small in the low temperature range, and thus can be neglected in Eq. (10).

If the donor–acceptor compensation in the material is small enough to be negligible, n and N_+ are equal to $(1 - f_0)N_0$ and N_0 , respectively. From the defect equilibrium analysis,¹⁶ we know that the concentrations of the acceptors, the zinc vacancies, in the Mn-doped samples are less than 10% of the concentrations of the donors, thus the compensation is not important here. Therefore, Eqs. (9), (10), and (11) become

$$C_{\text{HF}} = \frac{1}{2} A_{\text{gb}} \left(\frac{e \varepsilon \varepsilon_0 N_0}{2 \Phi_B} \right)^{1/2}, \quad (12)$$

$$G_{\text{ac}}(\omega, T) = G_{\text{dc}} + G_{\text{HF}} \frac{f_0}{1 - f_0} \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2} \\ = G_{\text{dc}} + C_{\text{HF}} g^{-1} \exp \left(\frac{\varepsilon'_s}{kT} \right) \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2}, \quad (13)$$

$$C(\omega, T) = C_{\text{HF}} + C_{\text{HF}} \frac{f_0}{1 - f_0} \frac{1}{1 + \omega^2 \tau_0^2} \\ = C_{\text{HF}} + C_{\text{HF}} g^{-1} \exp \left(\frac{\varepsilon'_s}{kT} \right) \frac{1}{1 + \omega^2 \tau_0^2}. \quad (14)$$

In a similar way, the expression for the admittance under a dc bias can also be obtained, but it is omitted here since the present experiments are under the zero-bias condition.

D. Comparison of the experimental results with the theoretical analysis

Equations (13) and (14) indicate that the zero-bias admittance exhibits a Debye-like relaxation, which is in agreement with the experimental observations in the present samples (Note that $\varepsilon' = C/C_e$ and $\varepsilon'' = G_{\text{ac}}/(\omega C_e)$, with $C_e = \varepsilon_0 A/H$, where ε_0 is the vacuum permittivity, and H and A are the thickness and the electrode area of the sample, respectively). Therefore, as shown in Figs. 1 and 2, the relaxation peaks were observed in both temperature and frequency spectra, whenever the condition of $\omega \tau_0 \approx 1$ is satisfied, and the peaks shift to higher frequency with increasing

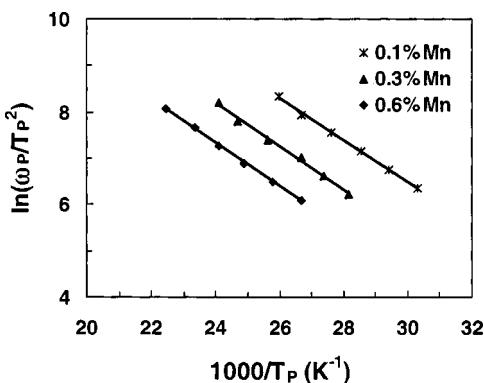


FIG. 7. Arrhenius plots of $\ln(\omega_p/T_p^2)$ vs $1000/T_p$, where ω_p and T_p are the relaxation-peak frequency and temperature, respectively.

temperature because of the thermal activation of the relaxation time τ_0 . Note that the term $g^{-1} \exp(\varepsilon_s'/kT)$ may also lead to a slight shift of the peaks, but its influence is negligible due to the very small value of ε_s' .

According to Eq. (8), the ionization energy, ε_s , and the capture cross section, c_0 , of the shallow donor can be determined from the slope and intercept of an Arrhenius plot of $\ln(\omega_p/T_p^2)$ versus $1/T_p$, where ω_p and T_p are the relaxation-peak angular frequency and temperature. The values of ω_p and T_p can be obtained from the frequency spectra in Fig. 2. These plots are shown in Fig. 7, and the determined ionization energies and capture cross sections are presented in Table I. With the values of ε_s and c_0 , the relaxation times, τ_0 , at room temperature (300 K) were calculated from Eq. (8) and were also presented in Table I. It can be seen that the ionization energies of the shallow donors are ~ 0.04 eV for all the samples, which are in good agreement with the values obtained from the temperature dependence of the dc conductivity in the quenched samples, and also close to the ionization energy of the intrinsic shallow donor in pure ZnO. The capture cross sections for all the samples are around 10^{-12} cm 2 , a reasonable value for a shallow donor in semiconductor materials.²³

Figure 3(a) shows that ε' at 1 MHz decreases with increasing Mn concentration. At relatively high temperatures, i.e., $T > 60$ K, $\varepsilon'(1\text{ MHz}) \approx C_{HF}/C_e$ due to the nearly complete ionization of the shallow donor, it is thus expected that C_{HF} decreases with the increase in Mn concentration. On the other hand, as shown in Fig. 3(b), the maximum value of the ε'' peak, denoted as ε''_p , at 1 MHz also decreases with increasing Mn concentration. Since

TABLE I. Determined ionization energies, ε_s , capture cross sections, c_0 , and relaxation times, τ_0 , at 300 K of the shallow donors in the slowly cooled samples.

Sample	ε_s (eV)	c_0 (cm 2)	τ_0 at 300 K (s)
0.1% Mn	0.039	2.64×10^{-12}	1.02×10^{-13}
0.3% Mn	0.040	1.43×10^{-12}	1.95×10^{-13}
0.6% Mn	0.041	0.72×10^{-12}	4.03×10^{-13}

$$\varepsilon''_p = \frac{1}{C_e} \left(\frac{G_{dc}}{\omega} + \frac{1}{2} C_{HF} g^{-1} \exp\left(\frac{\varepsilon_s'}{kT}\right) \right) \quad (\text{due to } \omega\tau_0 \approx 1) \quad (15)$$

and G_{dc}/ω is very small at 1 MHz, it is again expected that C_{HF} decreases with the increase in Mn concentration. From Eq. (12), it can be seen that the decrease of C_{HF} arises mainly from the decrease of N_0 and/or the increase of Φ_B . It means that when the Mn concentration is increased, the shallow-donor concentration, N_0 , decreases, and/or Φ_B increases. In a previous work,¹⁶ we showed that Mn depresses the concentration of the shallow donor in the Mn-doped ZnO samples at the sintering temperatures, which results in the decrease of the shallow-donor concentration at and below room temperature with increasing Mn concentration. This is consistent with the present result. It is also observed in Fig. 3(b) that the ε'' peak slightly shifts to higher temperature with the increase in Mn concentration, which indicates that the apparent ionization energy of the shallow donor slightly increases with increasing Mn concentration, in agreement with the results in Table I. This phenomenon further supports the conclusion that the concentration of the shallow donor decreases with increasing Mn concentration, due to the fact that the apparent ionization energy of the shallow donor should increase slightly with decreasing shallow-donor concentration in a semiconductor material.²⁴ Based on the above analysis, it is reasonable to believe that the phenomena in Fig. 3, i.e., the decrease of ε' and ε'' and the slight shift of ε'' peak with increasing Mn content, are due to the decrease of the shallow donor concentration.

One last point should be mentioned here. The above theoretical analysis is concerned with a single electrically active grain boundary. In fact, ceramic samples contain a large number of grain boundaries. The difference among these grain boundaries could result in a distribution of the relaxation time. Therefore, the curves in Fig. 2 show some strong distribution. The detailed discussion about this distribution is out of scope of the present article and will be addressed in a forthcoming article.

IV. CONCLUSIONS

From the experimental observation and theoretical analysis of the dielectric properties of the Mn-doped ZnO samples with electrically active grain boundaries, it is found that the main shallow donor, zinc interstitial, in ZnO exhibits a Debye-like dielectric relaxation behavior with a thermally activated relaxation time in the low temperature range from 20 to 50 K, which is related to the ionization process of this donor. With increasing Mn concentration, the relaxation peak in the temperature spectrum decreases and also slightly shifts to higher temperature, which probably arises from the decrease of the shallow-donor concentration.

Based on the theoretical analysis, an expression for the admittance of an electrically active grain boundary at low temperatures was obtained. Furthermore, the activation energy for the relaxation, i.e., the ionization energy of the shallow donors, was determined to be about 0.04 eV, the capture

cross section of the shallow donors to be around 10^{-12} cm^2 , and the relaxation time at room temperature to be about 10^{-13} s .

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