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Impedance and admittance spectroscopy of Mn_3O_4-doped ZnO incorporated with Sb_2O_3 and Bi_2O_3

Y.W. Hong, J.H. Kim*

Department of Inorganic Materials Engineering, Kyungpook National University, 1370 Sankyuk-Dong, Buk-Gu, Daegu 702-701, South Korea

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Abstract

ZnO–Bi_2O_3–Sb_2O_3 (Sb/Bi = 0.5) varistors were prepared with and without 1/3 mol% Mn_3O_4 along the conventional ceramic processing route. The bulk electron traps of ZnO were examined by admittance spectroscopy, and the respective electrical components such as resistance and capacitance of the specimens were determined by impedance–modulus spectroscopy. The bulk trap level of 0.25–0.32 eV in the depletion layer has been confirmed in all the specimens fired up to 1300 °C; those fired at 1300 °C, showed an additional trap level of 0.14 eV. It seems that the former represents $V_O^{\bullet}$ and the latter represents $Zn_i^{\bullet\bullet}$. In Mn-doped specimens, the bulk trap level of 0.33 eV and two interface states of 0.40 and 0.75–0.87 eV were confirmed by impedance–modulus spectroscopy. Among these, the interface trap level of 0.40 eV is thought to stem from the heterojunction of ZnO-intergranular phase modified by Mn.

Keywords: C. Impedance; E. Varistors; Admittance; Manganese oxide

1. Introduction

ZnO based varistors have been widely used for voltage stabilization or transient surge suppression in electronic circuits and electric power systems [1–3]. Excellent nonohmic properties in the current–voltage response of ZnO varistors are attributed to grain boundary phenomena in relation to the phase formation in sintering and dopant-induced point defects [2,5]. It is thought that the determination of both the deep bulk trap levels and the interfacial state levels formed by adsorbed oxygen and transition ion dopants is the key to the clarification of the conduction mechanism as well as the characteristics improvement of ZnO varistors [2,3]. Impedance spectroscopy is a powerful technique for the characterization of grain boundaries in ceramic materials. In addition, the use of combined impedance and modulus spectroscopic plots is known particularly useful for separating components with similar resistances but different capacitances or vice versa, i.e., similar capacitances with dissimilar resistances [4,6].

The present study aims at the examination of the effect of Mn_3O_4 doping on the bulk and grain boundary characteristics of ZnO–Bi_2O_3–Sb_2O_3 (Sb/Bi = 0.5) system using an impedance and admittance spectroscopy.

2. Experimental procedure

Reagent grade ZnO, Bi_2O_3, Sb_2O_3, and Mn_3O_4 powders were used as starting materials. ZnO–Bi_2O_3–Sb_2O_3 (97:2:1 in mol%) systems with and without 1/3 mol% Mn_3O_4 (named ZBSM and ZBS, respectively) were prepared by ball milling in a polyethylene jar with zirconia balls of 5 mm diameter as milling media in ethanol. The slurry was dried into a cake and was sieved through a 100 mesh screen to produce granules without binder. Granules were uniaxially pressed into pellets under 20 MPa and then CIPed at 98 MPa. The pellets were placed in an alumina crucible and sintered between 1000 and 1400 °C for 1 h in air at heating and cooling rates of 5 °C/min. Sintered pellets were trimmed into disks of 1.0 mm thickness and 8.0 mm diameter, and silvered on both sides for the electrical measurements. Commercial Ag-paste was used in the electroding, in which the disks were heat-treated at 600 °C for 10 min in air.

* Corresponding author. Tel.: +82-53-950-5637; fax: +82-53-950-5645.
E-mail address: jihkim@knu.ac.kr (J.H. Kim).

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The admittance spectroscopy measurements for identifying bulk trap levels were carried out using an impedance/gain phase analyzer (HP 4194A) at frequencies ranging from 10 to 82 kHz with five sampling points. In the examination of temperature response, the specimens were placed in a sample holder inside a furnace, and admittance was measured between 100 and 350 K at a cooling rate of 1.0 °C/min with a computer-aided data acquisition system.

The impedance spectroscopy measurements were conducted using an impedance/gain phase analyzer over a frequency range varying from 100 Hz to 15 MHz. The effect of temperature on the ac characteristics were examined between 280 and 580 K at 20 K increments with a computer-aided data acquisition system. Throughout the measurement, the specimens in the furnace were allowed to equilibrate at each temperature for 20 min.

3. Results and discussion

The zero bias admittance (G) of ZBS and ZBSM system as a function of temperature at various frequencies is shown in Fig. 1. Single peak in G–T curve appeared in both systems sintered at 1200 °C. In 1300 °C sintered ones, on the contrary, two peaks were seen in each curve between 100 and 350 K. The peak temperature, T_{p}, seemed to increase with the increase of the angular frequency (ω). According to Greuter and Blatter [3], the bulk trap states introduce screening charge into double Schottky barrier and result in a dispersion and singular broadness in G. The characteristic relaxation time, τ_n, for a bulk trap is given by [3]

$$\tau_n = \frac{e}{2A^{*}T^{2}g\sigma_n}\exp\left(\frac{E_{\mathrm{bt}}}{kT}\right) \tag{1}$$

where e is the electron charge, A^{*} the effective Richardson's constant ($\sim$30 A/(cm^2 K^2) for ZnO), T the temperature, g (=1/2) the inverse of the degeneracy of the trap state, σ_n the capture cross section, E_{bt} the deep bulk trap below the conduction band edge, and k is the Boltzmann constant.

The bulk trap resonance occurs when $\omega\tau_n = 1$, that is, at a local maximum of G at each ω and related T_{p}. The bulk trap levels of Eq. (1) can be obtained from the slope of the Arrhenius plot of $\ln(\omega/T_{\mathrm{p}}^2)$ versus $1/T$ as the activation energies. Fig. 2 shows $\ln(\omega/T_{\mathrm{p}}^2)$ versus $1/T$ plots of ZBS and ZBSM redrawn from Fig. 1. The calculated values of E_{bt} and σ_n for each specimen determined from $\ln(\omega/T_{\mathrm{p}}^2)$ versus $1/T$ plots are listed in Table 1.

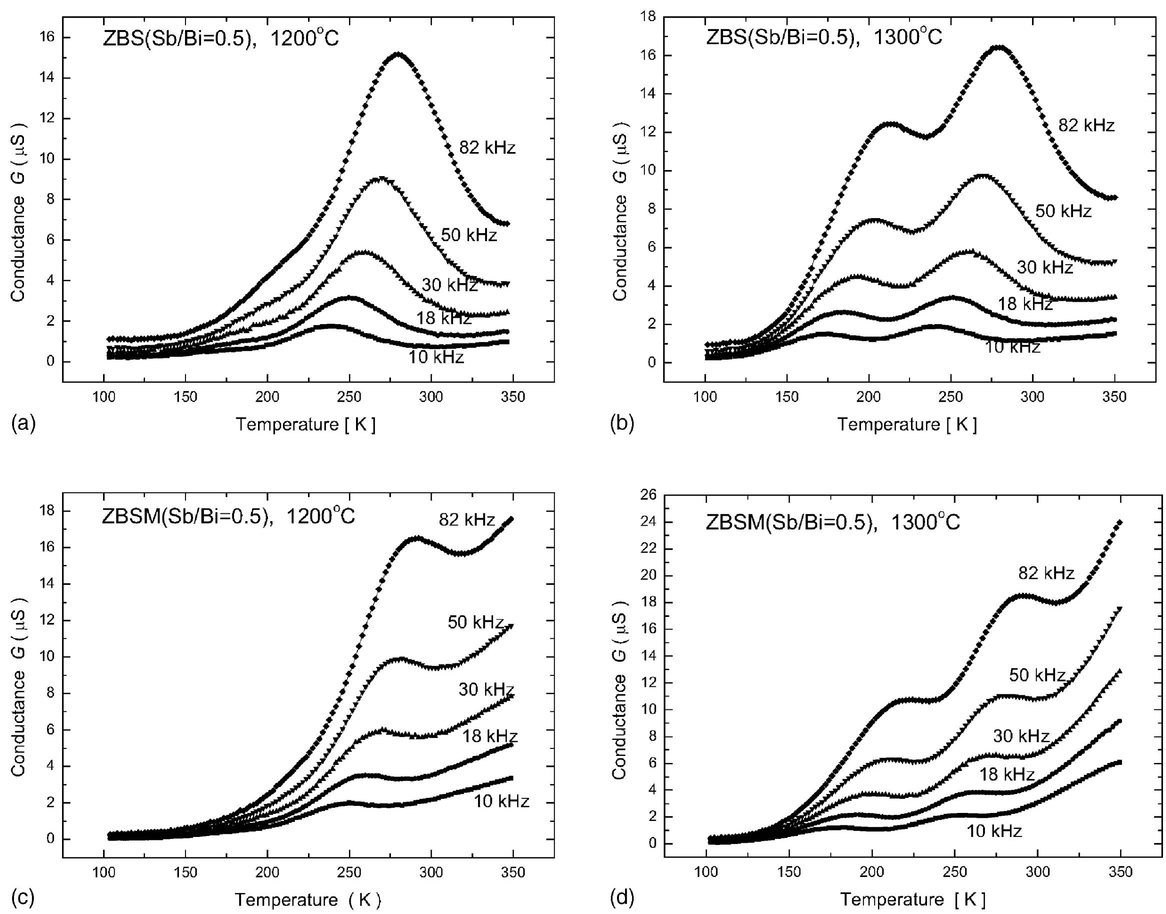

Fig. 1. Admittance spectra as a function of temperature for (a) and (b) ZBS (Sb/Bi = 0.5), and (c) and (d) ZBSM (Sb/Bi = 0.5) sintered at 1200 and 1300 °C for 1 h in air.

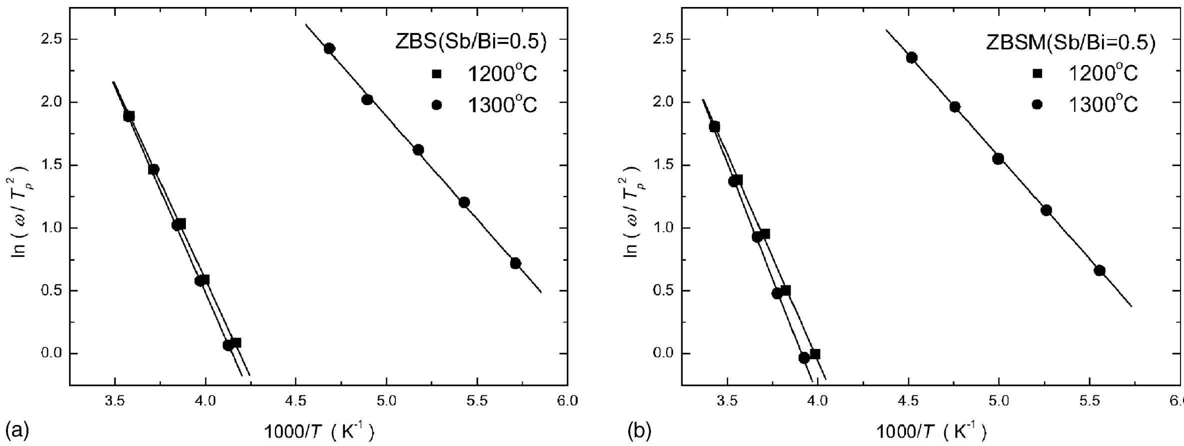

Fig. 2. Arrhenius plots of $\ln(\omega/T_p^2)$ vs. $1000/T$ (a) for ZBS (Sb/Bi = 0.5) and (b) ZBSM (Sb/Bi = 0.5) system sintered at 1200 and 1300 °C for 1 h in air.

The bulk trap levels obtained in ZBS and ZBSM can be classified into two categories: the deeper one between 0.25 and 0.32 eV is ascribed to $V_O^{\bullet}$ trap; the shallow one of 0.14 eV is ascribed to $Zn_i^{\bullet\bullet}$ trap. Although the above values are some what smaller than those of commercial ZnO varistors, the orders of σ_n ($\sim 10^{-15}$ cm^2 in $V_O^{\bullet}$ and $\sim 10^{-16}$ cm^2 in $Zn_i^{\bullet\bullet}$) support this assumption [2,3]. The presumed $V_O^{\bullet}$ trap existed in both systems irrespective of sintering temperature. The trap level, however, become deeper with Mn doping and/or high temperature sintering. The presumed $Zn_i^{\bullet\bullet}$ trap, on the contrary, protruded in 1300 °C sintered specimens. This result implies the close relation between $Zn_i^{\bullet\bullet}$ trap and the formation of Bi-rich intergranular phase [5].

The ac response of ZnO varistor can be expressed in any of the following four basic formalisms [4]

$$\text{Admittance}: A^* = Z^{*-1} = j\omega C_0 \varepsilon^* = G + j\omega C = A' + jA'' \quad (2)$$

$$\text{Impedance}: Z^* = A^{*-1} = [j\omega C_0 \varepsilon^*]^{-1} = Z' - jZ'' \quad (3)$$

$$\text{Electric modulus}: M^* = \varepsilon^{*-1} = j\omega C_0 Z^* = M' + jM'' \quad (4)$$

$$\text{Relative permittivity}: \varepsilon^* = M^{*-1} = [j\omega C_0 Z^*]^{-1} = \varepsilon' - \varepsilon'' \quad (5)$$

where C_0 is the vacuum capacitance of the cell.

For ZBSM sintered at 1300 °C, the Z'' and M'' versus $\log f$ plots were shown in Fig. 3. The Z'' spectrum shows one peak but the M'' spectrum shows two peaks. It is clearly shown that the Z'' spectrum of single peak is converted to a double-peak M'' spectrum which enables further analysis on the defect structure of ZnO varistor.

To extract resistance and capacitance values, it is necessary to have an equivalent circuit to model the electrical response of spectrum. ZnO varistors consist of bulk and grain boundary regions, and the equivalent circuit used for data analysis consists of two parallel resistor–capacitor (RC) elements in series connection [6]. Each parallel RC element results in a semicircle in the impedance (Z^*) and the electric modulus (M^*) complex plane plots, and in a Debye peak in spectroscopic plots of imaginary components, Z'' and M'' versus $\log f$. The Debye peak in the Z'' and M'' spectra is described by

$$Z'' = R\left(\frac{\omega RC}{1+(\omega RC)^2}\right), \quad M'' = \frac{C_0}{C}\left(\frac{\omega RC}{1+(\omega RC)^2}\right) \quad (6)$$

The frequency at the semicircle maxima, ω_{max}, for each RC element is given by

$$\omega_{max} = 2\pi f_{max} = (RC)^{-1} = \tau^{-1} \quad (7)$$

where $\tau = RC$ is the time constant of the RC element. The peak heights of Z'' and M'' are proportional to R and C^{-1}, respectively. Consequently, Z'' spectra are dominated by the largest R values, whereas, M'' spectra are dominated by the smallest C values. Therefore, the magnitudes of Z''_{max} and

Table 1
Calculated parameters from the Arrhenius plots shown in Fig. 2

Sintering temperature (°C)	ZBS (Sb/Bi = 0.5)		ZBSM (Sb/Bi = 0.5)	
	E_t (eV)	σ_n (cm^2)	E_t (eV)	σ_n (cm^2)
1200	0.25	1.30×10^{-15}	0.27	1.71×10^{-15}
1300	0.27	3.19×10^{-15}	0.32	1.13×10^{-14}
	0.14	1.31×10^{-16}	0.14	0.89×10^{-16}

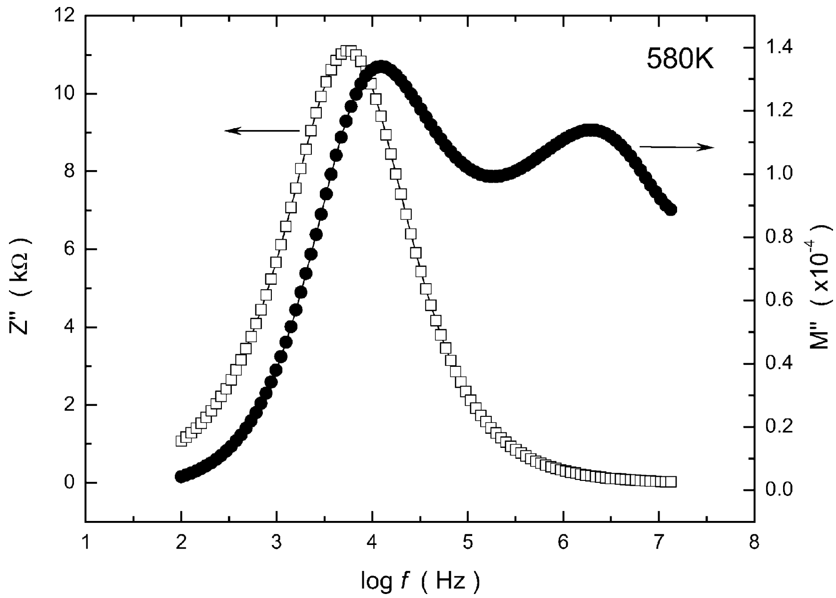

Fig. 3. Z'' and M'' vs. log f plots for ZBSM system at 580 K.

$M''_{\max}$ at the peak maxima are given by

$$Z''_{\max} = \frac{R}{2}, \quad M''_{\max} = \frac{C_0}{2C} \tag{8}$$

The magnitudes of R and C can be estimated from either $Z''_{\max}$ or $M''_{\max}$, using Eqs. (7) and (8). For detailed explanation about data analysis for ZnO varistor see the reference [6].

Resistivity values, ρ, referred to the grain boundary components are plotted against reciprocal temperature in Arrhenius format to estimate the activation energy (E_a), as described by

$$\ln \rho = \ln \rho_0 + \left(\frac{E_a}{k}\right)\frac{1}{T} \tag{9}$$

From the $M''_{\max}$ peak data, we can also calculate the activation energies for the bulk traps and the interface states about capacitance components as following:

$$\ln \tau = \ln \tau_0 + \left(\frac{E_a}{k}\right)\frac{1}{T} \tag{10}$$

In Fig. 4(a), M''–log f plots of ZBSM are shown. Three kinds of $M''_{\max}$ peaks (P_{M1}, P_{M2}, P_{M3}) appeared in the temperature range of 280–580 K. The Z'' peak (P_{Z3}) was shown as a function of temperature in Fig. 4(b). Using Eqs. (7) and (8), the resistance and the capacitance extracted from each peak of M''–log f and Z''–log f spectra were shown in Fig. 5(a). The resistances of P_{Z1} and P_{Z2} hidden in P_{Z3} of Fig. 4(b) have been obtained from P_{M1} and P_{M2} of Fig. 4(a). The capacitance values of P_{M1}, P_{M2}, and P_{M3} ($C1$, 1.6 nF; $C2$, 1.2 nF; and $C3$, 1.0 nF, respectively, as shown in Fig. 5(a)) were very close to one another. With increasing temperature slightly, a decrease ($C2$ and $C3$) or an increase ($C1$) was seen. In contrast to the capacitance, the resistances

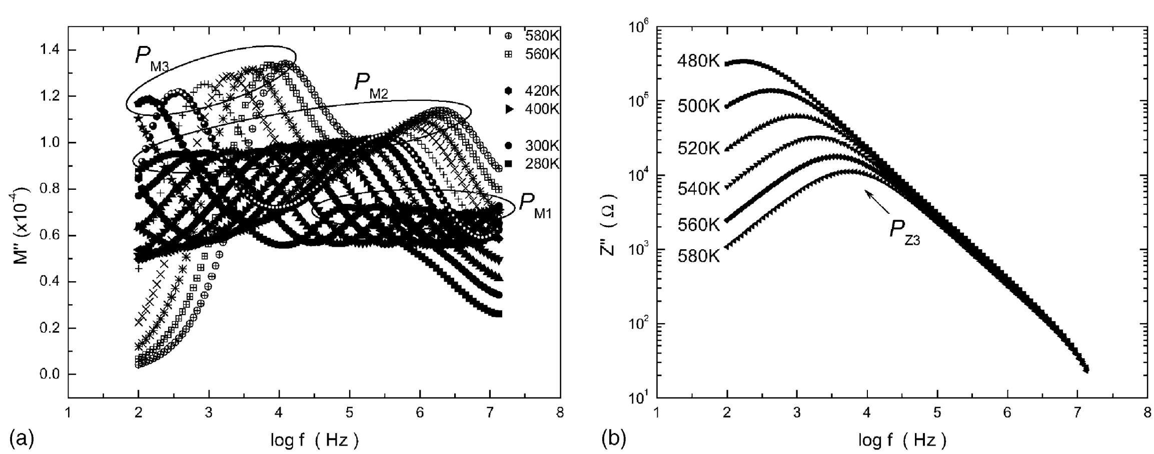

Fig. 4. (a) M''–log f and (b) Z''–log f plots redrawn from the M^* and Z^* data of ZBSM sintered at 1300 °C for 1 h in air, measured between 280 and 580 K at 20 K increments.

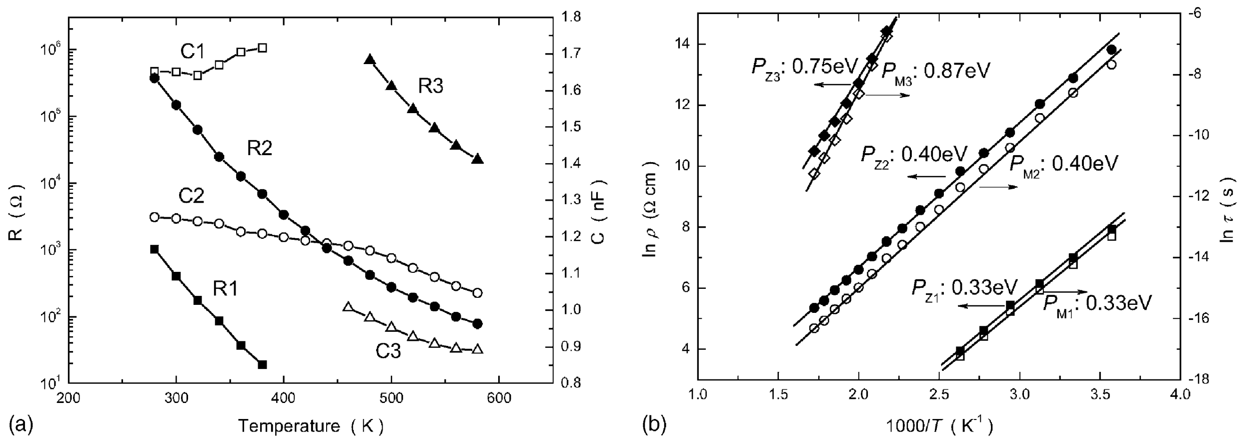

Fig. 5. (a) Changes in resistance (*R*1, *R*2, and *R*3) and capacitance (*C*1, *C*2, and *C*3) values extracted from impedance and modulus peaks with temperature. (b) Arrhenius plots of $\ln \rho$ and $\ln \tau$ vs. 1000/*T* for Z'' and M'' peaks, respectively.

of P_{Z1}, P_{Z2}, and P_{Z3} (*R*1, *R*2, and *R*3, respectively, as shown in Fig. 5(a)) drastically decreased with temperature.

Arrhenius plots of $\ln \rho$ and $\ln \tau$ versus 1000/*T* corresponding to *R* and *C* components, respectively, are shown in Fig. 5(b). The activation energies are 0.33 eV for the bulk trap, and 0.40 and 0.75–0.87 eV for the interface states. The interface state of 0.40 eV has been reported in Mn-doped ZnO varistors [7,8]. Yano et al. [7] suggested that 3d character of the doped transition-metals is one of the origins of interface states, as well as π character of the adsorbed excess oxygen. In relation to the nature of the interface states, two types of grain boundary junctions have been suggested: ZnO–ZnO homojunction (0.97 eV) and ZnO–Bi_2O_3–ZnO heterojunction (0.64 eV) defined by impedance spectroscopy [6]. It is quite possible that the compositions of the Bi-rich intergranular phases responsible for the interface states in ZnO varistors are varied with doping constituents and heat-treatment condition [2,5]. Moreover, the peak of modulus (P_{M2}) corresponding to 0.40 eV persisted up to 580 K along with the main grain boundary resistance peak (P_{M3}) corresponding to 0.75–0.87 eV. Consequently, it is reasonable to assign the energy level of 0.4 eV to the interface state of ZnO-intergranular phase heterojunction modified by Mn.

4. Conclusion

The bulk traps and the interface states of ZnO–Bi_2O_3–Sb_2O_3 (Sb/Bi = 0.5) varistors with and without 1/3 mol% Mn_3O_4 have been studied by admittance spectroscopy and impedance–modulus spectroscopy.

Using admittance spectroscopy, the bulk trap level of 0.25–0.32 eV in the depletion layer has been confirmed in both ZBS and ZBSM sintered at 1200 and 1300 °C; additional trap level of 0.14 eV appeared in 1300 °C sintered specimens. Both levels are the typical of intrinsic defect of ZnO: 0.25–0.32 eV for $V_O^{\bullet}$ and 0.14 eV for $Zn_i^{\bullet\bullet}$.

By impedance–modulus spectroscopy, the bulk trap level of 0.33 eV and two interface states of 0.40 and 0.75–0.87 eV were confirmed in ZBSM. Among these, the interface trap level of 0.40 eV is thought to stem from the heterojunction of ZnO-intergranular phase modified by Mn.

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