Electrical characteristics of SrCoO$_3$-added zinc oxide varistors

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The electrical characteristics and interfacial trap levels at grain boundaries of SrCoO$_3$ (SCO)–added ZnO varistors were investigated. A marked nonlinearity was observed in the $V$–$J$ characteristics. The resistance to electrical degradation correlated with the orientation of the (100) plane of ZnO grains: the resistance was large when the (100) plane was parallel to the electrode. Isothermal capacitance transient spectroscopy revealed two kinds of interfacial trap levels. The deeper level was observed only in samples with 2.5 mol% or more added SCO. Each trap level had a concentration that increased in proportion to the temperature. At room temperature, the concentrations of all trap levels in samples with 2.0 mol% or less SCO were much lower. As a result, no transient capacitance was observed under an applied bias voltage. This suggests that the main cause of the nonlinearity observed in the $V$–$J$ characteristics of samples with 2.0 mol% or less SCO was not the presence of interfacial trap levels, but rather the Co and/or ZnSrO$_2$ in the ZnO grains.

1. Introduction

Zinc Oxide (ZnO)-based varistors exhibit a marked nonlinearity in voltage-current density ($V$–$J$) characteristics, and are used as surge arresters in power delivery systems and as protection against external surges in electrical devices. The nonlinearity in the $V$–$J$ characteristics of ZnO varistors can be explained by a model involving the double Schottky barrier that forms at the boundaries between the ZnO grains. The degradation in electrical characteristics due to an applied electric stress is very small. In order to achieve nonlinearity and improve the resistance to electrical degradation, ZnO varistors are made of polycrystalline ZnO with many kinds of additives. The main additive used for some commercial ZnO varistors is bismuth oxide (Bi$_2$O$_3$). Antimony oxide (Sb$_2$O$_3$) is added to these Bi-based varistors to improve their current characteristics. However, the electrical characteristics of Bi-based varistors degrade markedly upon the application of an electric stress or electrostatic discharge (ESD). It is reported that the thermal characteristics of the additives correlate with ESD suppression; additives with melting points lower than that of ZnO (1800°C) such as Bi$_2$O$_3$ (820°C) and Sb$_2$O$_3$ (656°C) affect electrical characteristics. Therefore, there is a demand for varistors consisting of oxides with melting points higher than that of ZnO.

It has been reported that only SrCoO$_3$ (SCO)-added ZnO varistors show both marked nonlinear $V$–$J$ characteristics and reliable performance against ESD. It is believed that the nonlinearity in the $V$–$J$ characteristics stems from the potential barrier and trap levels (interface states and bulk traps) near the grain boundary. Generally, the capacitance of varistors is induced by interface charges and exhibits bias voltage dependence. However, the electrical behavior of SCO-added varistors is reported to be different from that of Bi-based varistors. It has also been reported that the capacitance of SCO-added varistors is almost independent of the applied bias voltage at room temperature. Thus, typical capacitance–voltage ($C$–$V$) characteristics could not be observed. It is speculated that the electrical barrier structure at the boundaries between ZnO grains differs from that in Bi-based varistors. Koga et al. proposed an n-p-n heterostructure model in order to explain the anomalous behavior of the capacitance. However, this model does not take account of the existence of trap levels. The capacitance of varistors originates from the capacitance of the insulating depletion layer along the grain boundary, and the depletion layer capacitance is affected by both the capture and emission of electrons at the trap levels. The depletion layer capacitance shows a time response corresponding to the bias voltage applied to the depletion layer. This time response can be determined through isothermal capacitance transient spectroscopy (ICTS). This paper investigated the basic electrical characteristics of SCO-added varistors, the relationship between electrical characteristics and crystal structure, and the effect of interfacial trap levels on electrical characteristics.

2. Experimental

2.1 Sample preparation

The starting material was a mixture of ZnO powder (99.9999% purity, MEIDENSHA) and the additive SrCoO$_3$ (SCO). First, SCO was synthesized by sintering a powder mixture of SrCO$_3$ and Co$_3$O$_4$ according to Refs. 3 and 4. The molar ratio of SrCo$_3$ to Co$_3$O$_4$ was 3:1. The powder mixture was pressed and calcined in air at 600°C for 5 h. The ground powder was pressed into tablets at 320 MPa and further sintered in air at 1150°C for 10 h. The ground SCO powder was added to the ZnO powder at amounts ranging from 0.25 to 3.0 mol%. The powder mixtures were wet-mixed for 24 h with ethanol. Pressed tablets of the mixture were calcined at 600°C for 5 h and ground in an agate mortar. The ground powder was pressed into 20-mm-diameter tablets at a pressure of 320 MPa. The tablets were sintered at 1150°C for 4 h in air and then allowed to cool to room temperature following the approach detailed in Refs. 3 and 4. Hereafter, each sample will be referred to by an abbreviated name...
corresponding to its composition. For example, the samples containing 1.0 mol % SCO and 1.0–2.5 mol % SCO will be referred to as SCO1.0 and SCO1.0–2.5, respectively.

2.2 Sample Characterization

After mirror polishing, 2.38-mm-diameter aluminum electrodes were fabricated on both pressed faces of each sample (3 × 3 mm) by vacuum evaporation in order to measure the V–J characteristics. The density of the sintered samples was measured by the Archimedes method. The relative density of all sintered samples, as calculated from the theoretical density of wurtzite-type ZnO (5.61 g/cm³), was approximately 92–95%. The V–J characteristics of the current density in the range of approximately 3 × 10⁻⁷ to 3 × 10⁻³ A/cm² were obtained by applying a constant direct current (dc) using source meters (2410 and 2657A, KEITHLEY). The nonlinearity index, α, of the V–J characteristics was estimated via $V = V_N (J/J_N)^{1/α}$, where $V$ and $V_N$ are the normalized voltages per mm of sample thickness, and $J$ and $J_N$ are the current densities. $V_N$ is the voltage at $J = J_N$. In this study, the $V_N$ at $J_N = 1 × 10^{-3}$ A/cm² is the varistor voltage. The V–J characteristics were nonlinear for $α ≠ 1$. The uniformity of the current flow inside each sample was estimated from the V–J characteristics. Electrical degradation was induced by applying a constant dc current of 100 mA to the sample holder.

2.3 ICTs

The transient capacitance $C(t)$ vs. time $t$ characteristics was measured under zero bias between 10⁻⁴ and 10⁴ s after applying a voltage pulse of 30–39 V for 20 ms. It is confirmed that the trap levels in a ZnO grain do not contribute to the transient capacitance above room temperature. The measurements were conducted using a capacitance meter (MI-401, MEASURE JIG; test frequency: 2 MHz) and a digital voltmeter (34410 and 34411, KEYSITE TECH.). $V_{R}$ and $V_{T}$ were used to estimate the capacitance above room temperature. The measurements were performed over the temperature range from 27 to 240°C, and the temperature was controlled to within 0.1°C.

3. Results and discussion

Figure 1 shows the typical V–J characteristics at room temperature before and after electrical degradation for SCO1.0. A marked nonlinearity was observed in the V–J characteristics of all samples. Figure 2 plots the relationship between averaged varistor voltage and inverse of grain size for samples with varying amounts of SCO addition. Though the varistor voltage changed abruptly at SCO contents between 1.5 and 1.75 mol %, overall, it was proportional to the inverse of the ZnO grain size. A maximum varistor voltage of approximately 300 V was obtained for SCO0.5. Thus, the varistor voltage was determined mainly by the number of grain boundaries between the electrodes. This suggests that the abrupt change in varistor voltage is due to the change in height of the symmetrical double Schottky barrier. The varistor voltage decreased with increasing amount of SCO. Figure 3 shows the nonlinearity index before and after electrical degradation, $α_{NS}$ and $α_{NS-d}$, respectively, for samples with varying amounts of SCO. The SCO content dependences of $α_{NS}$ and $α_{NS-d}$ were similar. Their maxima (~57 and ~14, respectively) occurred at an SCO content of 1.5 mol %. Both indices also showed an abrupt change at an SCO content between 1.5 and 1.75 mol %, similarly to the varistor voltage.

Figure 4 shows the XRD patterns for synthesized SCO. The diffraction peaks were in agreement with those for Sr₁₋ₓCoO₃, Sr₁₋ₓCoO₃, Sr₁₋ₓCoO₃, and Sr₁₋ₓCoO₃, but were not in agreement with those for Sr₁₋ₓCoO₃. Figure 5 and 6 show the XRD patterns for SCO0.25–3.0 and the same patterns extended along the vertical axis. ZnO has a wurtzite-type crystal structure. It has been reported that there is a correlation between the orientation of ZnO particles, the nonlinearity index, and the resistance to electrical degradation. Changes in the orientation of the (100), (002), and (101) planes of a ZnO particle will manifest themselves as differences in the intensities of the diffraction peaks, as shown in Fig. 5. A marked
change in orientation was observed upon the addition of SCO. Figure 7 shows a detailed view of the relative intensity \( RII \) of diffraction peaks from the (100), (002), and (101) planes of a ZnO particle for SCO0.25–3.0. The \( RII \) for a given compound is defined as the ratio of the sum of the integrated intensities of all the diffraction peaks of the compound to those of ZnO. Both \( \alpha_{as} \) and \( \alpha_{deg} \) correlated strongly with the \( RII \) of the diffraction peaks from (100), as seen in Fig. 8. This indicates that large \( \alpha_{as} \) and \( \alpha_{deg} \) values will be obtained when the (100) plane is parallel to the electrode. The electrical degradation factor that has been reported to date has been due to oxide ions (\( O^{2-} \)) or \( Zn^{2+} \) ions around grain boundaries moving across the boundaries by drift motion under the influence of an applied voltage, because the electric field strength at grain boundaries is much larger than that within ZnO grains. The shape and height of the potential barriers, which affect the nonlinearity indices of the \( J-V \) characteristics, \( \alpha_{as} \) and \( \alpha_{deg} \), and the diffusion of \( O^{2-} \) and \( Zn^{2+} \) ions through the grain boundary is affected by the crystal orientations of the two ZnO grains forming the grain boundary. Therefore, the resistance to electrical degradation might be due to the suppression of \( O^{2-} \) or \( Zn^{2+} \) diffusion through the (100) planes of ZnO grains facing the grain boundaries relative to the diffusion through other planes under an applied voltage.

Diffraction peaks of ZnSrO2 were observed for all samples, as shown in Fig. 6.10) The SCO content dependence of \( RII \) for ZnSrO2 might be caused by the change in the orientation of ZnO grains, as shown in Figs. 6 and 7. SCO peaks were observed in the case of SCO2.5 and SCO3.0. This shows that excess SCO segregated in samples with 2.5 mol% or more SCO. Unidentified diffraction peaks were observed in only SCO1.75, whose \( RII \) of the (002) plane was much higher than those for other samples. The above results suggest that for SCO0.25–2.0, with the exception of SCO1.75, Co occurs in metallic form in the ZnO grains, i.e., without forming a compound with Sr or Zn.

The elemental compositions and the distribution of each element on the fractured surface of samples were determined by EDS and BSE to analyze the XRD data in detail. It has been reported that ZnO fracture surfaces were formed by grain boundary and trans-crystalline fracture.11) Thus, the correlation between the resistance to electrical degradation and the distribution of impurities on the surface of the ZnO grain was investigated. Figure 9 shows a BSE image and elementary mappings obtained by EDS for SCO1.5–2.5. The gray-scale brightness in both BSE and EDS images increases as the amount or atomic weight of an element increases. Comparison of the BSE images with elementary mappings of Zn, Sr, Co [see Figs. 9(a)–9(c)] and the XRD results (Fig. 6) both suggest that the SCO in the SCO0.25–2.0 samples decomposed, that Co dissolved homogeneously in ZnO, and that Sr partly formed ZnSrO2 in ZnO grains. By contrast, excess SCO segregated to the grain boundaries in SCO2.5 and SCO3.0 as.
shown in Fig. 9(d), because both Sr and Co were identified at the ZnO grain boundaries, and XRD diffraction peaks of SCO were observed as shown in Fig. 6. Granular compounds having Sr as their main ingredient (hereafter, “Sr-compounds”) were observed for SCO0.5–2.0. The number of Sr-compounds increased with increasing SCO content. The morphology of SCO1.75 was particularly different from the others (see Fig. 10). Furthermore, narrow XRD diffraction peaks for unidentified compounds were observed in the case of SCO1.75 (see Fig. 6). Thus, the Sr-compounds were noncrystalline for all samples except SCO1.75, in which case the Sr-compound was crystalline. Clearly, the added SCO decomposed, Sr formed ZnSrO2 in the ZnO grains and Sr-compound, and Co dissolved homogeneously into ZnO in the case of SCO0.25–2.0. It has been reported that the barrier height $\varphi$ of the double Schottky barrier is changed by the addition of Co, which affects the donor density $N_D$ in ZnO grains, and the nonlinearity of the $V-J$ characteristics and the resistance to electrical degradation were affected by the Co concentration.6) Because $\varphi$ is proportional to $\sqrt{N_D}$, the nonlinearity of the $V-J$ characteristics was improved by the dissolution of Co atoms into ZnO grains at low SCO contents.

It has been reported that the depletion layer capacitance is not measured because the capacitance remains constant at zero upon the application of a bias voltage.3),4) Thus, the electrical characteristics of SCO-added varistors could not be determined by $C-V$ measurements at room temperature. The $C-V$ measurement method is effective in yielding the values of $\varphi$ and $N_D$; however, it becomes ineffective when the emission and/or capture of carriers by the trap levels at the grain boundaries and in ZnO grains do not occur. Thus, trap levels were analyzed by using ICTS.

Figure 11 shows the inverse of capacitance versus time $[1/C(t)-t]$ characteristics for SCO2.0 and SCO2.5. The capacitance of SCO0.25–2.0 showed a roughly constant value after a single pulse voltage was applied at room temperature [see Fig. 11(a)]. As a result, the change in the transient capacitance $\Delta C$ was approximately zero. However, $\Delta C$ increased with increasing temperature. This indicates that active trap levels are generated thermally. On the other hand, a significant $\Delta C$ was observed for SCO2.5 at room temperature and various other temperatures, as shown in Fig. 11(b). $\Delta C$ also increased with increasing temperature. The anomalous characteristics of an SCO-added varistor, in which no capacitance change is observed when a bias voltage is applied at room temperature, appear in samples with 2.0 mol %

![Graph](image-url)
or less SCO. Because the existence of at most two kinds of interfacial trap levels was suggested by Fig. 11(b), the transient capacitance \( C(t) \) was analyzed using Eq. (1):

\[
\frac{1}{C(t)} = \frac{1}{C_0} + A_1 \exp \left\{ -\left( \frac{t}{\tau_1} \right)^{\beta_1} \right\} + A_2 \exp \left\{ -\left( \frac{t}{\tau_2} \right)^{\beta_2} \right\},
\]

where

\[
\frac{1}{C_0} = \sum_{i=1}^{2} \frac{Q_{i0}(\infty)}{q\epsilon N_D}, \quad A_1 = \frac{N_{SI}}{\epsilon N_D}, \quad A_2 = \frac{N_{SC}}{\epsilon N_D},
\]

and \( Q_{i0}(\infty) \) \((i = 1, 2)\) is the number of electrons captured at the \( i \)-th interface trap level, \( q \) is the electric charge, \( N_D \) is the donor density, \( N_{SI} \) is the \( i \)-th active interface trap density, \( \epsilon \) is the dielectric constant of ZnO \((\epsilon = 8.5\epsilon_0, \epsilon_0 = 8.854 \times 10^{-12} \text{F/m})\), \( \tau_i \) is the time constant of the emission process from the \( i \)-th interface trap level, and \( \beta_i \) is the \( \tau_i \) distribution.\(^{35}\) \( A_i \) is proportional to the interfacial trap density \( N_{SI} \). The time constant \( \tau_i \) for electron emission can be expressed by\(^{35}\)

\[
\tau_i T^2 = B_i \exp \left( \frac{E_c - E_T}{kT} \right), \quad B_i = \frac{h^2 g_i}{4\pi^2 \hbar^2 k^2 m^* i \sigma_{si}},
\]

where \( E_c - E_T \) is the depth of the \( i \)-th interface trap level measured from the bottom of the conduction band, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( m^*_i \) is the effective mass of an electron in ZnO \((m^*_i = 0.27m_0; m_0: \text{rest mass of an electron})\), \( \sigma_{si} \) is the capture cross-section of the \( i \)-th interface trap level, \( \hbar \) is Planck’s constant, and \( g_i \) is the degeneracy of the \( i \)-th trap level \((g_i = 1)\). Figure 12 shows the measured and fitted \( 1/C(t)-t \) characteristics for SCO2.5 at 130°C as an example. The fitted characteristics, which were obtained by calculations using Eq. (2), were in good agreement with the measured characteristics. The deeper level is defined as level 1 and the shallower level as level 2. The fitting parameters were \( 1/C_0 = 1.465 \times 10^{-2} \pm 2 \times 10^{-6} \text{pF}, A_1 = 1.79 \times 10^{-3} \pm 2 \times 10^{-5} \text{pF}, \tau_1 = 5.1 \pm 0.1 \text{s}, \beta_1 = 0.493 \pm 0.007, A_2 = 1.04 \times 10^{-2} \pm 2 \times 10^{-5} \text{pF}, \tau_2 = 6.4 \times 10^{-3} \pm 2 \times 10^{-4} \text{s}, \) and \( \beta_2 = 0.47 \pm 0.01 \).

Level 1 was observed in all samples, while the shallower level, i.e., level 2, was observed only in samples with 2.5 mol% or more SCO. It is speculated on the basis of both the XRD and element mapping results that level 2 might be caused by the formation of SCO at the grain boundaries. Figure 13 shows the temperature dependence of \( A_1 \) and \( A_2 \) for SCO0.5–3.0.
samples with 2.0 mol % or less SCO. This shows that it is hard to observe a nonzero ΔC caused by level 1 at room temperature. However, a prominent nonlinearity was observed in the V–J characteristics of samples with 2.0 mol % or less SCO at room temperature (see Fig. 1). $A_1$ increased in proportion to temperature. These results suggest that trap level 1 becomes more active with increasing temperature. $A_2$ decreased with rising temperature and had a relatively large value compared to $A_1$. As a result, $\Delta C$ can be observed in samples having 2.5 mol % or more SCO. At room temperature, the concentration of each trap level was much smaller, as a result of which no transient capacitance was observed. Consequently, the capacitance was constant under an applied bias voltage. Thus, it appears that the main cause of the marked nonlinearity observed in the V–J characteristics of samples with 2.0 mol % or less SCO is not the presence of interfacial trap levels, but rather the Co and/or ZnSrO$_2$ in the ZnO grains.

4. Summary

A marked nonlinearity was observed in V–J characteristics. The resistance to electrical degradation correlated with the orientation of the (100) plane of ZnO grains: it was large when the (100) plane was parallel to the electrode. Two kinds of interfacial trap levels were observed. The deeper level was observed in all samples. The shallower level was observed only in samples with 2.5 mol % or more SCO. The concentrations of all active trap levels increased with increasing sample temperature. At room temperature, the concentration of each trap level was much smaller, as a result of which no transient capacitance was observed. Consequently, the capacitance was constant under an applied bias voltage. Thus, it appears that the main cause of the marked nonlinearity observed in the V–J characteristics of samples with 2.0 mol % or less SCO is not the presence of interfacial trap levels, but rather the Co and/or ZnSrO$_2$ in the ZnO grains.

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