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Influence of cobalt oxide addition on electrical properties of ZnO-Pr_6O_{11}-based varistor ceramics

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ZnO varistors are smart ceramic semiconductor components made by ZnO sintered together with minor additives. They exhibit highly nonlinear voltage-current (V–I) characteristics expressed by $I = kV^{\alpha}$, where k is a constant and α is nonlinear exponent as an index or figure of merit indicating the effectiveness of a varistor. Furthermore, they possess excellent high energy-handling capabilities. As a result, they have been widely used to protect various semiconductor devices, electronic circuits, and electric power systems from dangerous abnormal transient voltage [1, 2]. ZnO varistors are greatly divided into Bi_2O_3- and Pr_6O_{11}-based with varistor-forming oxide (VFO). Most commercial ZnO varistors containing Bi_2O_3 exhibit excellent varistor properties, but they have a few flaws due to Bi_2O_3 having high volatility and reactivity [3]. And they need many additives to obtain the high performance. To overcome these problems, Pr_6O_{11}-based ZnO varistors are being studied [4–10]. In Pr_6O_{11}-based ZnO varistors, the most important two additives are Pr_6O_{11}, which in substance gives rise to nonlinear properties, and CoO, which improves them. However, the nonlinear properties in these varistors can be never improved by incorporating of any additives without CoO. Therefore, the CoO is indispensable additives in ZnO varistors. In Bi_2O_3-based ZnO varistors, CoO or Co_3O_4 content is limited to 0.5 mol% in general. No study of the influences of CoO additionon electrical properties in Pr_6O_{11}-based ZnO varistors has been reported. The goal of this paper is to investigate the influence of CoO addition on electrical properties of ZnO-Pr_6O_{11}-based ceramics.

Reagent-grade raw materials were prepared for ZnO varistors with composition expression, such as $(98.5 - x)$ mol% ZnO, 0.5 mol% Pr_6O_{11}, x mol% CoO (x = 0.5, 1.0, 2.0, 3.0, 5.0), 0.5 mol% Cr_2O_3, 0.5 mol% Dy_2O_3. The mixture was calcined in air at 750°C for 2 hr. The calcined powders were pressed into discs 10 mm in diameter and 2 mm in thickness at a pressure of 80 MPa. The discs were sintered at 1350 °C in air for 1 hr. The size of the final samples was about 8 mm in diameter and 1.0 mm in thickness. Silver paste was coated on both faces of the samples and ohmic contacts were formed by heating at 600 °C for 10 min. The size of electrodes was 5 mm in diameter.

The surface microstructure was examined by scanning electron microscopy (SEM, Model S2400, Hitachi, Japan). The average grain size (d) of varistor ceramics was determined by the lineal intercept method [11]. The density (ρ) of varistor ceramics was measured by the Archimedes method.

The V–I characteristics of the varistors were measured using a Keithley 237 unit. The varistor voltage (V_{1mA}) was measured at a current density of 1.0 mA/cm^2 and the leakage current (I_L) was measured at 0.80 V_{1mA}. In addition, the nonlinear exponent (α) was determined from $\alpha = 1/(\log E_2 - \log E_1)$, where E_1 and E_2 are the electric fields corresponding to 1.0 mA/cm^2 and 10 mA/cm^2, respectively.

The capacitance-voltage (C–V) characteristics of varistors were measured at 1 kHz using a RLC meter (QuadTech 7600) and an electrometer (Keithley 617). The donor concentration (N_d) and the barrier height (ϕ_b) were determined by the equation $(1/C_{gb} - 1/C_{b0})^2 = 2(\phi_b + V_{gb})/q\varepsilon N_d$ [12], where C_{gb} is the capacitance per unit area of a grain boundary, C_{b0} is the value of C_{gb} when $V_{gb} = 0$, V_{gb} is the applied voltage per grain boundary, q is the electronic charge, and ε is the permittivity of ZnO ($\varepsilon = 8.5\ \varepsilon_0$). The density of interface states (N_t) at the grain boundary was determined by the equation $N_t = (2\varepsilon N_d \phi_b/q)^{1/2}$ [12] and the depletion layer width (t) of the either side at the grain boundaries was determined by the equation $N_d\ t = N_t$ [13].

Fig. 1 shows the SEM micrographs of varistor ceramics sintered with various CoO contents. It is well known that the microstructure of Pr_6O_{11}-based ZnO varistor ceramics is consisted of only two phases [8]: ZnO grain (bulk phase, black) and intergranular layer (second phase, whitish) comprising of Pr- and Dy_2O_3-rich phase located at the boundaries. As the CoO contents increased, the sintered density was increased from 5.25 to 5.55 g/cm^3 corresponding 91 to 96% of theoretical density of pure ZnO (5.78 g/cm^3) up to 2.0 mol%, whereas the additions further did not affect density, saturating 5.55 g/cm^3. Therefore, the ceramics was more densified with increasing CoO contents. The average grain size increases from 9.9 to 27.2 μm with increasing CoO content. As a result, it can be seen that the CoO promotes grain growth. The grain size directly affects varistor voltage in voltage-current characteristics. The detailed V–I microstructural parameters are summarized in Table I.

Fig. 2 shows the E–J characteristics of varistors with various CoO contents. The shape of curves is somewhat complex without having any remarkable tendency in the light of CoO content only. The characteristic curves of varistors are greatly divided into two regions,

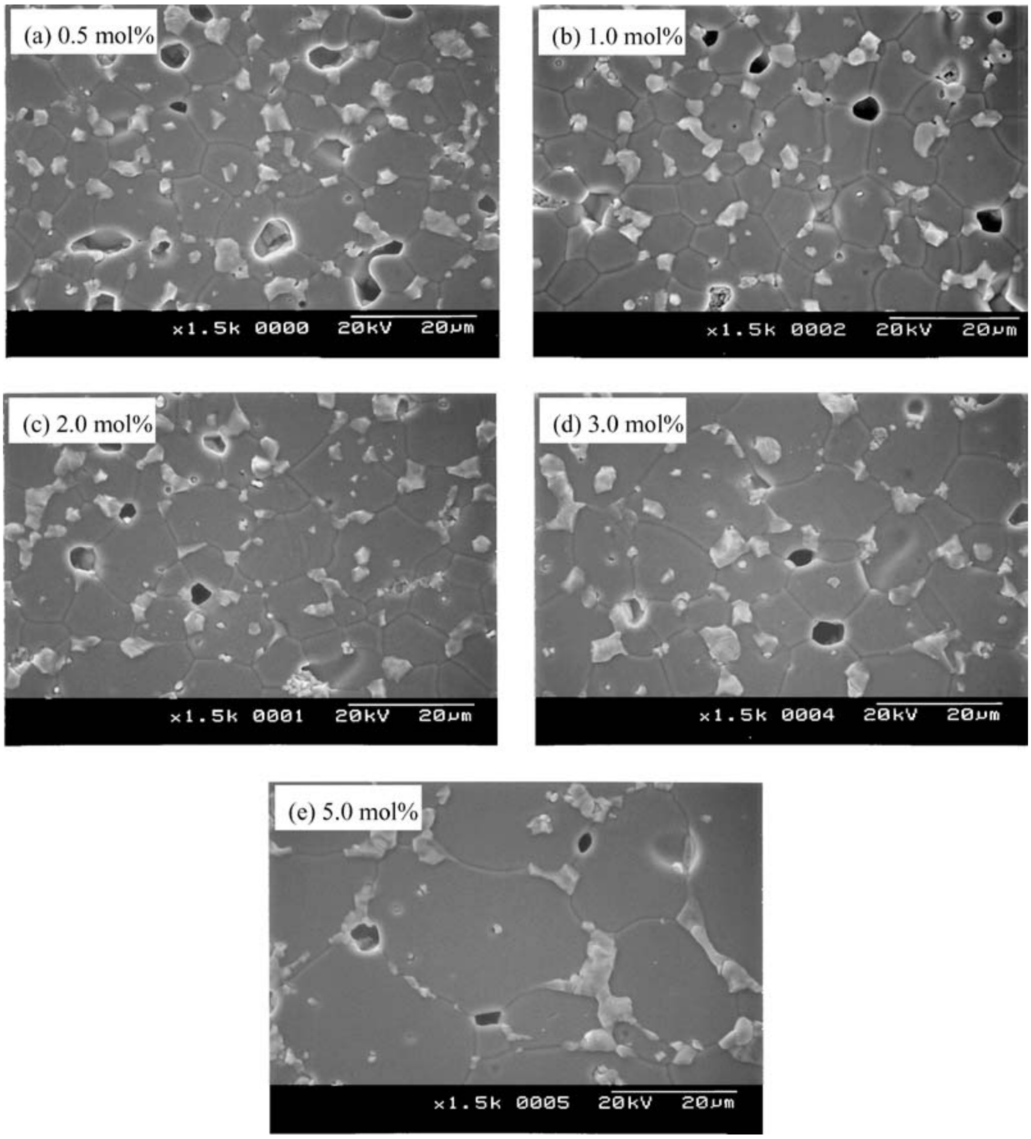

Figure 1 SEM micrographs of varistor ceramics with various CoO contents.

that is, prebreakdown at low voltage region and nonlinear properties at high voltage region. The detailed V–I characteristic parameters are summarized in Table I. The $V_{1\mathrm{mA}}$ monotonously abruptly decreased from 235.3 to 86.0 V/mm as the CoO contents increase. This is attributed to the decrease of the number of grain boundaries due to the increase of grain size. In general, the smaller the grain size, the higher the varistor voltage.

Fig. 3 shows the variation of nonlinear exponent (α) and leakage current (I_L) of varistors with various CoO contents. The α value was abruptly increased with increasing CoO contents up to 1.0 mol%, reaching a maximum value (66.6), whereas the additions further caused the decrease of α value. Therefore, it can be seen that the incorporation of moderate CoO contents significantly increases the α value. This is different from what optimum CoO addition in Bi_2O_3-based ZnO varistors is 0.5 mol%. Meanwhile, the I_L value was decreased

TABLE I Microstructural and V–I characteristic parameters of varistors with various CoO contents

CoO contents (mol%)	ρ (g/cm^3)	d (μm)	$V_{1\mathrm{mA}}$ (V/mm)	α	I_L (μA)
0.5	5.25	9.9	235.3	35.5	4.9
1.0	5.43	11.5	223.8	66.6	1.2
2.0	5.49	14.5	181.9	55.3	0.1
3.0	5.51	16.8	143.4	30.7	4.8
5.0	5.55	27.2	86.0	14.4	45.0

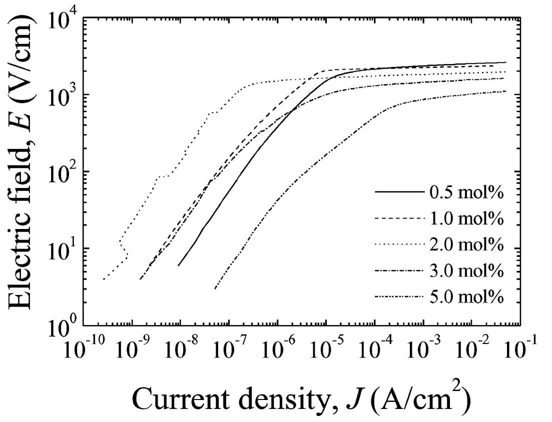

Figure 2 E–J characteristics of varistors with various CoO contents.

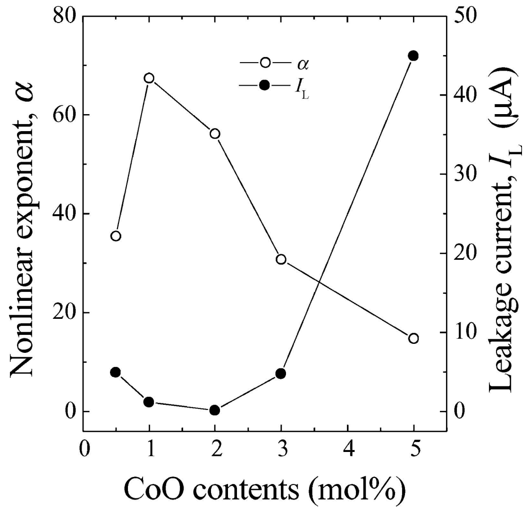

Figure 3 Variation of nonlinear exponent and leakage current of varistor with various CoO contents.

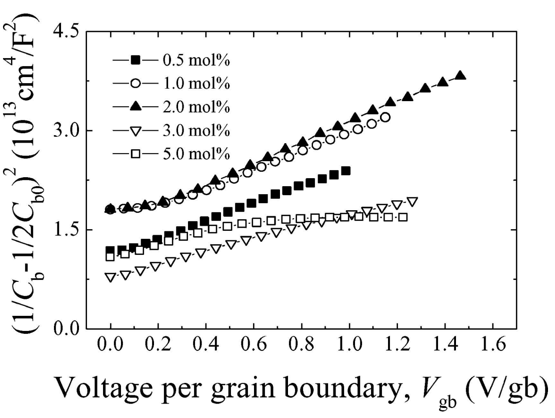

Figure 4 *C–V* characteristics of varistors with various CoO contents.

with increasing CoO contents up to 2.0 mol%, reaching a minimum value (0.1 μA), whereas the additions further caused abrupt increase of I_L value.

Fig. 4 shows the *C–V* characteristics of varistors with various CoO contents. It can be forecasted that the CoO affects *C–V* characteristics from the line slope and distributions. The detailed *C–V* characteristic parameters are summarized in Table II. The N_d was in the range of $1.06 \times 10^{18} - 1.69 \times 10^{18}$/cm^3 and the density of interface states (N_t) was in the range of $3.11 \times 10^{12} - 3.56 \times 10^{12}$ cm^2, reaching a maximum at 3.0 mol% CoO with increasing CoO contents. The depletion layer width (t) was opposite to the variation tendency of donor concentration. Really, the t is wider at side of lower doping region. With increasing CoO contents, the barrier height (ϕ_b)was increased up to 1.0 mol%, reaching a maximum (1.07 eV) and thereafter decreased. Related to the potential barriers at grain boundary, the variation of ϕ_b properly agreed to the variation of α in $V–I$ characteristics.

TABLE II *C–V* characteristic parameters of varistors with various CoO contents

CoO contents (mol%)	N_d (10^{18}/cm^3)	N_t (10^{12}/cm^2)	Φ_b (eV)	t (nm)
0.5	1.25	3.11	0.83	24.9
1.0	1.15	3.40	1.07	29.6
2.0	1.06	3.15	0.99	29.7
3.0	1.69	3.56	0.80	21.1
5.0	1.45	3.54	0.92	24.4

In summary, the varistor with CoO of 1.0 mol% exhibited the best nonlinear properties, with 66.6 in the nonlinear exponent and 1.2 μA in the leakage current. The additions further deteriorated the nonlinear properties. It was found that the nonlinear properties of varistors could be improved by incorporating CoO of moderate contents, approximately 1.0 mol%.

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