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Microstructure and electrical properties of ZnO-Pr_6O_{11}-CoO-Cr_2O_3-Dy_2O_3-based varistor ceramics

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ZnO varistors are electronic ceramic devices made by sintering ZnO powder with small amounts of various metal oxides, containing necessarily Pr_6O_{11} or Bi_2O_3. They exhibit highly nonlinear voltage-current (V-I) characteristics expressed by $I = kV^{\alpha}$, where k is a constant and α is a nonlinear exponent, inherent parameter of varistors, and they possess excellent surge withstanding capabilities. Therefore, they have been extensively used to protect semiconductor devices, electronic circuits, and electric power systems from dangerous overvoltage [1, 2]. The majority of commercial ZnO varistors necessarily contain Bi_2O_3 as varistor-forming oxides (VFO) and they exhibit excellent varistor properties. However, they have a few shortcomings due to the high volatility and reactivity of Bi_2O_3 melted at about 825 °C during a sintering above 1000 °C [3]. The former changes varistor characteristics with the variation of inter-composition ratio of additives, the latter destroys the multi-layer structure of chip varistors, and it generates an insulating spinel phase deteriorating surge-absorption capabilities. Furthermore, they need many additives to obtain the high nonlinearity and stability.

In the past few years, ZnO varistor ceramics containing Pr_6O_{11} as VFO have been studied to overcome these problems [4–10]. In the former work, Nahm *et al*. reported that ZnO-Pr_6O_{11}-CoO-Cr_2O_3-M_2O_3 (M = Er, Y)-based varistor ceramics exhibit high nonlinear properties and stability [6–10]. Many researchers who are interested in varistors wish to fabricate ZnO varistors exhibiting both higher nonlinearity and higher stability. It is very important to scrutinize the role of individual additive to apply ZnO-Pr_6O_{11}-based varistors in various areas. The purpose of this work is to investigate the effect of Dy_2O_3 incorporation on microstructure and electrical properties of ZnO-Pr_6O_{11}-CoO-Cr_2O_3-Dy_2O_3 (in short ZPCCD)-based varistors.

Reagent-grade raw materials were prepared for ZnO varistors with composition $(98.0 - x)$ mol% ZnO + 0.5 mol% Pr_6O_{11} + 1.0 mol% CoO + 0.5 mol% Cr_2O_3 + x mol% Dy_2O_3 (x = 0.0–2.0). After milling, the mixture was calcined in air at 750 °C for 2 h. The calcined powders were pressed into discs of 10 mm in diameter and 1.8 mm in thickness at a pressure of 80 MPa. The discs were sintered at 1350 °C in air for 1 h. 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 *V-I* characteristics of the varistors were measured using a Keithley 237 unit. The varistor voltage ($V_{1\,mA}$) was measured at a current density of 1.0 mA/cm^2 and the leakage current (I_L) was measured at 0.80 $V_{1\,mA}$. In addition, the nonlinear exponent (α) was determined from $\alpha = (\log J_2 - \log J_1)/(\log E_2 - \log E_1)$, where J_1 = 1.0 mA/cm^2, J_2 = 10 mA/cm^2, and E_1 and E_2 are the electric fields corresponding to J_1 and J_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 $(1/C_b - 1/C_{bo})^2 = 2(\phi_b + V_{gb})/q\varepsilon N_d$ [11], where C_b is the capacitance per unit area of a grain boundary, C_{bo} is the value of C_b when $V_{gb} = 0$, V_{gb} is the applied voltage per grain boundary, q is the electronic charge, ε is the permittivity of ZnO ($\varepsilon = 8.5\varepsilon_o$). The density of interface states (N_t) at the grain boundary was determined by the equation $N_t = (2\varepsilon N_d \phi_b/q)^{1/2}$ [11] and the depletion layer width (t) of the either side at the grain boundaries was determined by the equation $N_d\, t = N_t$ [12].

The microstructure was examined by a scanning electron microscope (SEM, Hitachi S2400). The average grain size (d) was determined by the lineal intercept method [13]. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku *D*/max 2100, Japan) with Cu K_α radiation. The density (ρ) of ZPCCD-based ceramics was measured by the Archimedes method.

Fig. 1 shows SEM micrographs of ZPCCD-based ceramics with Dy_2O_3 content. SEM micrographs clearly show the influence of Dy_2O_3 incorporation on the density and grain size. The sintered microstructure was less densified due to increasing porosity as Dy_2O_3 content increases. The density of ceramics was decreased gradually from 5.53 to 4.43 g/cm^3 corresponding to 95.7–76.6% of theoretical density (TD = 5.78 g/cm^3 in ZnO). The average ZnO grain size was saliently decreased in the range of 18.6–4.7 μm with increasing Dy_2O_3 content. The decrease of grain size is attributed to the precipitation of secondary phase in the grain boundaries and nodal points.

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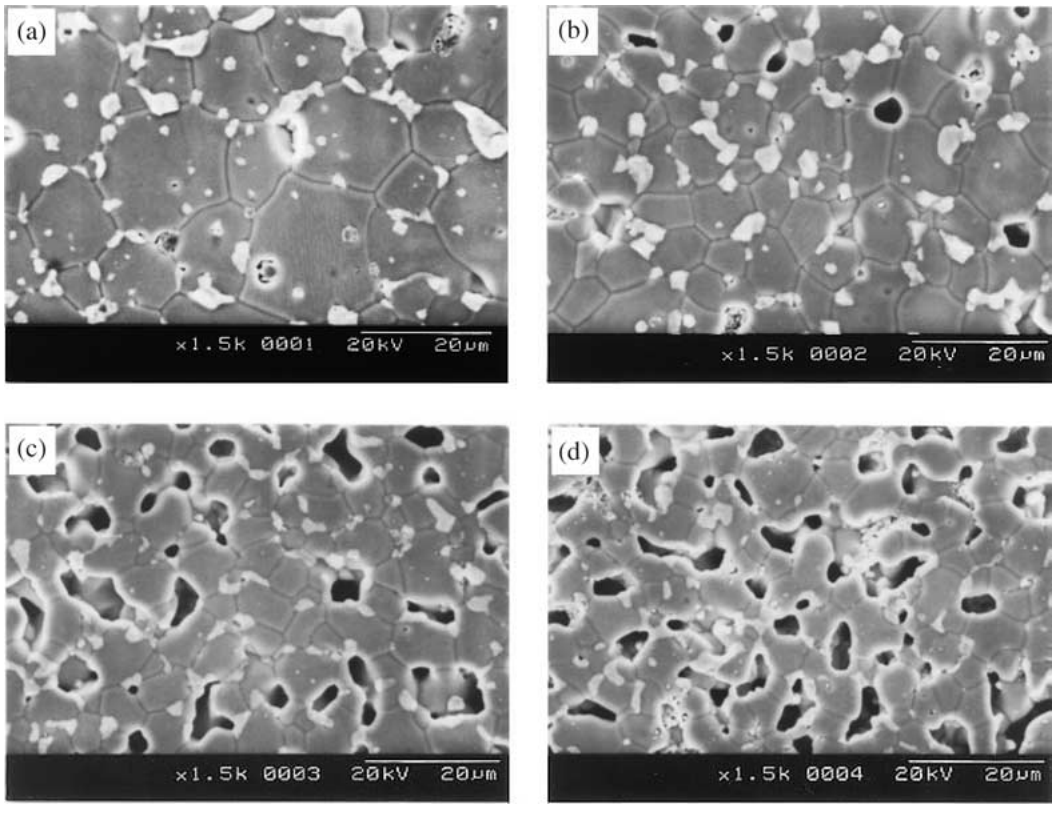

Figure 1 SEM micrographs of ZPCCD-based ceramics with Dy_2O_3 content: (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%.

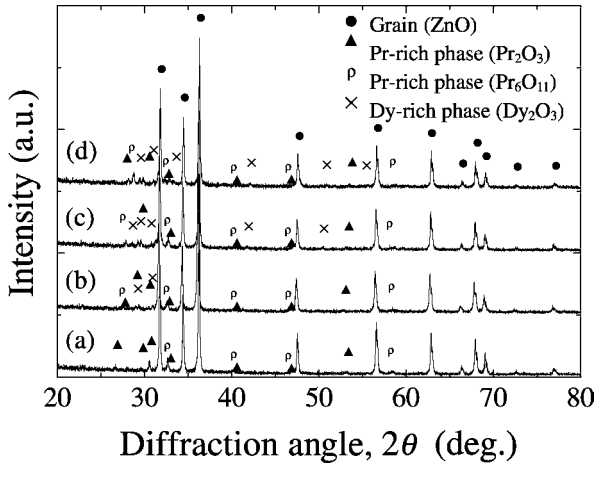

Figure 2 XRD patterns of ZPCCD-based ceramics with Dy_2O_3 content: (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%.

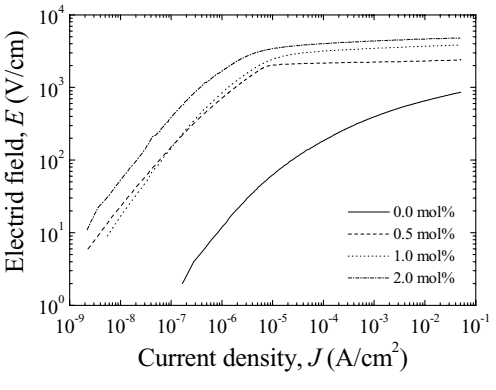

Figure 3 E-J characteristics of ZPCCD-based varistors with Dy_2O_3 content.

Fig. 2 shows the XRD patterns of ZPCCD-based ceramics with Dy_2O_3 content. All varistor ceramics have only two phases, i.e., ZnO grain and intergranular layer, as revealed in the former work [7, 10]. Intergranular layer was composed of Pr_6O_{11} (or Pr_2O_3) and Dy_2O_3 and identified by EDS analysis to coexist in the grain boundaries and the nodal points. These phases could be indicated to SEM micrographs. The detailed microstructural parameters are summarized in Table I.

Fig. 3 shows the *E-J* characteristics of ZPCCD-based varistors with Dy_2O_3 content. It can be seen that the knee region of *E-J* curves with Dy_2O_3 is much keener than that without Dy_2O_3 and especially, for the varistors with 0.5 mol% Dy_2O_3. Clearly, the incorporation of Dy_2O_3 greatly improved the nonlinear properties of varistors. The detailed *V-I* characteristic parameters were summarized in Table I. The varistor voltage ($V_{1\,mA}$) was greatly increased in the range of 39.4–436.6 V/mm. This is attributed to the increase of the number of grain boundaries due to the decrease of ZnO grain size with increasing Dy_2O_3 content. The breakdown voltage per grain boundaries (V_{gb}) was in the range of 2–3 V/gb in the varistors with Dy_2O_3, but the V_{gb} of varistor without Dy_2O_3 was only 0.7 V/gb.

TABLE I Microstructural and *V-I* characteristic parameters of ZPCCD-based varistors

Dy_2O_3 content (mol%)	d (μm)	ρ (g/cm^3)	$V_{1\,mA}$ (V/mm)	V_{gb} (V/gb)	α	I_L (μA)
0.0	18.6	5.53	39.4	0.7	4.5	87.9
0.5	11.5	5.43	223.8	2.6	66.6	1.2
1.0	6.8	4.64	345.4	2.3	34.2	3.7
2.0	4.7	4.43	436.6	2.1	37.0	2.4

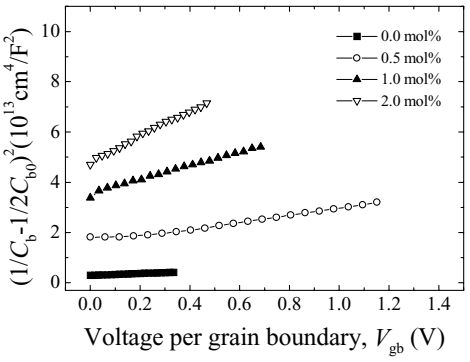

Figure 4 *C-V* characteristics of ZPCCD-based varistors with Dy_2O_3 content.

Therefore, it is assumed that the ZPCC-based varistor without Dy_2O_3 has poor grain boundaries.

The α value in varistors without Dy_2O_3 was only 4.5, whereas the α value of the varistors with Dy_2O_3 was abruptly increased above 30. Then, the α value varied from maximum (66.6) in 0.5 mol% Dy_2O_3 to minimum (34.2) in 1.0 mol% Dy_2O_3. The maximum α value is much higher than that for incorporation of Er_2O_3 and Y_2O_3 reported previously in equivalent conditions [7, 10]. The I_L value in varistors without Dy_2O_3 was 87.9 μA, whereas the I_L value of the varistors with Dy_2O_3 was very abruptly decreased below 4 μA. The minimum value of I_L was obtained from 0.5 mol% Dy_2O_3, exhibiting 1.2 μA. The variation of I_L value revealed to be opposite to that of α value. As a result, the incorporation of Dy_2O_3 was confirmed to significantly improve the nonlinear properties.

The capacitance-voltage (*C-V*) characteristics of ZPCCD-based varistors with Dy_2O_3 content are shown in Fig. 4. It can be forecasted that Dy_2O_3 greatly affects *C-V* characteristics from the line slope and distribution. The detailed *C-V* characteristic parameters were summarized in Table II. It was found that the increase of Dy_2O_3 content leads to the decrease of the donor concentration (N_d) from 4.19×10^{18} to $0.33 \times 10^{18}/cm^3$ as well as the decrease of density of interface states (N_t) from 5.38×10^{12} to $1.74 \times 10^{12}/cm^2$. Therefore, Dy_2O_3 serves as an acceptor. The increase of the depletion layer width (t) is attributed to the decrease of donor concentration. Really, the t is wider at side of lower doping region. With increasing Dy_2O_3 content, the barrier height (ϕ_b) was increased up to 1.0 mol% and thereafter decreased. The ϕ_b is directly connected with the N_d and N_t. In other words, the ϕ_b is estimated by the variation rate in the N_t and N_d. In general, the ϕ_b increases with increasing N_t and decreasing N_d.

TABLE II *C-V* characteristic parameters of ZPCCD-based varistors

Dy_2O_3 content (mol%)	N_d ($10^{18}/cm^3$)	N_t ($10^{12}/cm^2$)	Φ_b (eV)	t (nm)
0.0	4.19	5.38	0.74	12.9
0.5	1.15	3.40	1.07	29.5
1.0	0.60	2.68	1.28	44.8
2.0	0.33	1.74	0.97	52.3

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References

1. L. M. LEVINSON and H. R. PILIPP, *Amer. Ceram. Soc. Bull.* **65** (1986) 639.
2. T. K. GUPTA, *J. Amer. Ceram. Soc.* **73** (1990) 1817.
3. Y. S. LEE and T. Y. TSENG, *ibid.* **75** (1992) 1636.
4. A. B. ALLES and V. L. BURDICK, *J. Appl. Phys.* **70** (1991) 6883.
5. Y.-S. LEE, K.-S. LIAO and T.-Y. TSENG, *J. Amer. Ceram. Soc.* **79** (1996) 2379.
6. C.-W. NAHM, H.-S. YOON and J.-S. RYU, *J. Mater. Sci. Lett.* **20** (2001) 393.
7. C.-W. NAHM, *Mater. Lett.* **47** (2001) 182.
8. *Idem.*, *J. Mater. Sci. Lett.* **21** (2002) 201.
9. C.-W. NAHM and B.-C. SHIN, *J. Mater. Sci: Mater. Electro.* **12** (2002) 111.
10. C.-W. NAHM, *Mater. Lett.* **57** (2003) 1317.
11. M. MUKAE, K. TSUDA and I. NAGASAWA, *J. Appl. Phys.* **50** (1979) 4475.
12. L. HOZER, "Semiconductor Ceramics: Grain Boundary Effects" (Ellis Horwood, 1994) p. 22.
13. J. C. WURST and J. A. NELSON, *J. Amer. Ceram. Soc.* **55** (1972) 109.

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