Influence of Dysprosia Addition on Microstructure and Electrical Properties of Praseodymia-based Zinc Oxide Varistors

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The microstructure and electrical properties of varistor ceramics, which are composed of Zn-Pr-Co-Cr-Dy-oxide system, were investigated at various dysprosia (Dy_2O_3) addition contents. The Dy_2O_3 microstructurally played the role of inhibition for the densification and grain growth. As the Dy_2O_3 content increased, the density decreased in the range of 5.51-4.90 g/cm^3, reaching maximum at 0.5 mol% and the average ZnO grain size decreased in the range of 17.7-6.0 μm. The incorporation of Dy_2O_3 significantly improved the nonlinear properties of varistors, above 30 in nonlinear exponent, compared with that without Dy_2O_3. The varistors with the best performance of nonlinear properties was obtained Dy_2O_3 content of 1.0 mol%, 49 in nonlinear exponent and 0.5 μA in leakage current.

Keywords : Microstructure, Electrical properties, Varistors, Pr_6O_{11}, Dy_2O_3

1. INTRODUCTION

ZnO varistors are passive semiconductor-ceramic devices made by sintering ZnO powder with small amounts of various minor metal oxides. They exhibit highly nonlinear voltage-current (*V-I*) characteristics: resistance of a varistor decreases abruptly at increasing voltage, and at a certain point, they behave as a short circuit. They possess excellent surge-energy-absorption capabilities. As a result, they have been extensively used to protect various semiconductor devices, electronic equipments, and electric power systems from dangerous abnormal high voltage[1,2]. The nonlinear properties of ZnO varistors are attributed to a double Schottky barrier (DSB) formed at active grain boundaries containing many trap states.

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 flaws due to the high volatility and reactivity of Bi_2O_3 during liquid sintering[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 recent, to overcome these problems, ZnO varistor ceramics containing praseodymia (Pr_6O_{11}) as VFO are actively being studied[4-13]. Nahm et al. reported that the addition of rare-earth oxides, R_2O_3 (R = Nd, Er, Dy) to Zn-Pr-Co oxide-based varistors improves the non-linearity and electrical stability[6-8]. However, the varistors having a high stability exceeded never 40 in the nonlinear exponent and the varistors having a high nonlinearity exhibited very poor stability against DC stress. Meanwhile, the varistors added by Cr_2O_3 to Zn-Pr-Co-R (R = Er, Y) oxide system exhibited excellent nonlinear exponent, and the stability is greatly improved [9-13]. Furthermore, it is necessary to study electrical properties in the varistors composed of 5-components with dysprosia (Dy_2O_3).

The purpose of this work is to investigate the effect of incorporation of Dy_2O_3 on microstructure and electrical properties of Zn-Pr-Co-Cr oxide-based varistors.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Reagent-grade raw materials were prepared for ZnO varistors with composition (96.0-x) mol% ZnO, 0.5

mol% Pr_6O_{11}, 3.0 mol% CoO, 0.5 mol% Cr_2O_3, x mol% Dy_2O_3 (x = 0.0-2.0). Raw materials were mixed by ball milling with zirconia balls and acetone in a polypropylene bottle for 24 h. The mixture was dried at 120 °C for 12 h and calcined in air at 750 °C for 2 h. The calcined mixture was pulverized using an agate mortar/pestle and after 2 wt% polyvinyl alcohol (PVA) binder addition, granulated by sieving 200-mesh screen to produce starting powder. The powder was uniaxially pressed into discs of 10 mm in diameter and 2 mm in thickness at a pressure of 800 kg/cm². The discs were covered with raw powder in alumina crucible, sintered at 1350 °C for 1 h. The heating rate and cooling rate were 4 °C/min. The sintered samples were lapped and polished to 1.0 mm thickness. 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 samples and ohmic contact of electrodes was formed by heating at 600 °C for 10 min. The electrodes were 5 mm in diameter.

2.2 Microstructure examination

The either surface of samples was lapped and ground with SiC paper and polished with 0.3 μm-Al_2O_3 powder to a mirror-like surface. The polished samples were thermally etched at 1100 °C for 30 min. The surface microstructure was examined by a scanning electron microscope (SEM, Hitachi S2400, Japan). The average grain size (d) was determined by the lineal intercept method, given by $d = 1.56L/MN$, where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines[14]. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2100, Japan) with CuK_α radiation. The density (ρ) of ceramics was measured by the Archimedes method.

2.3 V-I characteristic measurement

The V-I characteristics of the varistors were measured using a high voltage source measure unit (Keithley 237). The varistor voltage ($V_{1\ mA}$) was measured at a current density of 1.0 mA/cm² 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/cm², $J_2 = 10$ mA/cm², and E_1 and E_2 are the electric fields corresponding to J_1 and J_2, respectively.

2.4 C-V characteristic measurement

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 $(1/C_b - 1/C_{bo})^2 = 2(\phi_b + V_{gb})/q\varepsilon N_d$[15], 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 (ε = $8.5\varepsilon_o$). The density of interface states (N_t) at the grain boundary was determined by the equation $N_t = (2\varepsilon N_d \phi_b/q)^{1/2}$[15] and the depletion layer width (t) of the either side at the grain boundaries was determined by the equation $N_d\ t = N_t$[16].

3. RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs of varistor ceramics with various Dy_2O_3 contents. The sintered ceramics seem

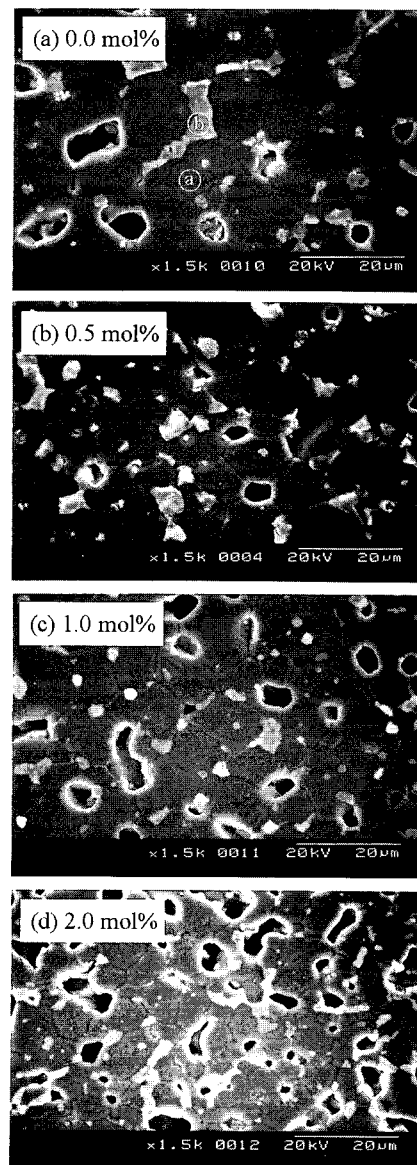Fig. 1. SEM micrographs of ZPCCD-based varistors with Dy_2O_3 contents; ⓐ ZnO grain and ⓑ intergranular layer.

to be less densified as the pore is increased with increasing Dy_2O_3 content. The sintered density was decreased in the range of 5.49-4.64 g/cm^3 corresponding to 95-80 % of theoretical density (TD = 5.78 g/cm^3 in ZnO). The average grain size was markedly decreased from 18.2 to 4.6 μm with increasing Dy_2O_3 content. It is supposed that this is attributed to the secondary phases generated by segregating at grain boundaries and nodal points with increasing Dy_2O_3 content. It is confirmed from XRD shown in Fig. 2 that secondary phases are the mixture of Pr- and Dy-rich phases. All varistor ceramics was consisted of only two phases, i.e. ZnO grain and intergranular layer comprising of Pr oxide and Dy_2O_3 regardless of Dy_2O_3 content. As a result, the incorporation of Dy_2O_3 deteriorates the densification and inhibits ZnO grain growth. The detailed microstructural parameters are summarized in Table 1.

Figure 3 shows the electric field-current density (E-J) characteristics of varistors with various Dy_2O_3 contents. 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. This clearly shows that the incorporation of Dy_2O_3 greatly improved the nonlinear properties of varistors. The varistor voltage ($V_{1\ mA}$) was greatly increased in the range of 70-405 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, whereas the varistors without Dy_2O_3 was only 1.2 V/gb. Therefore, it is assumed that the varistors without Dy_2O_3 has poor grain boundaries. these grain boundaries cause very low nonlinear properties. The detailed V-I characteristic parameters are summarized in Table 1.
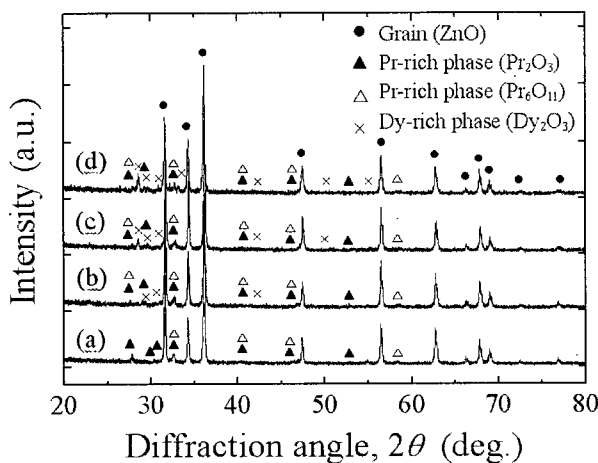
The α value in varistors without Dy_2O_3 was only 7, whereas the α value of the varistors with Dy_2O_3 was abruptly increased above 30. Then, the α value varied from maximum (49) in 1.0 mol% Dy_2O_3 to minimum (37) in 2.0 mol% Dy_2O_3. The I_L value in varistors without Dy_2O_3 was 74.3 μA, whereas the I_L value of the varistors with Dy_2O_3 very abruptly decreased in the range of 0.5-4.8 μA. The minimum value of I_L was obtained from 1.0 mol% Dy_2O_3, exhibiting 0.5 μA. It can be seen that the variation of I_L shows the inverse relationship to the variation of α. This is because the high α value leads to low leakage current due to relatively high tunneling current and the low α value leads to high leakage current due to relatively high thermionic emission current. As a result, the incorporation of Dy_2O_3 was confirmed to significantly improve the nonlinear properties. The detailed V-I characteristic parameters are summarized in Table 1.

Figure 4 shows the C-V characteristics of varistors with various Dy_2O_3 contents. The capacitance decreases due to the increase of depletion layer width at active grain boundaries with increasing DC bias. The modified C-V equation was used to calculate characteristic parameters, such as the donor concentration and barrier height. 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 are summarized in Table 2.

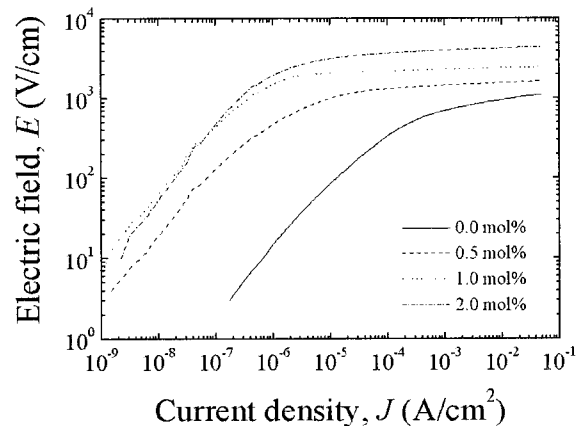Fig. 3. The E-J characteristics of ZPCCD-based varistors with Dy_2O_3 contents.

Fig. 2. XRD patterns of ZPCCD-based varistors with Dy_2O_3 contents; (a) 0.0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol%.

Table 1. Microstrucrural and V-I characteristic parameters of ZPCCD-based varistors with Dy_2O_3 contents.

Dy_2O_3 content (mol%)	ρ (g/cm^3)	d (μm)	$V_{1\ mA}$ (V/mm)	V_{gb} (V/gb)	α	I_L (μA)
0.0	5.39	17.7	69.9	1.2	7.4	74.3
0.5	5.51	16.8	143.4	2.4	30.7	4.8
1.0	5.40	10.6	234.0	2.5	49.4	0.5
2.0	4.90	6.0	405.3	2.4	36.8	2.1

The donor concentration was decreased in the range of 3.93×10^{18} to 0.53×10^{18} /cm^3 with increasing Dy$_2$O$_3$ content. This means Dy$_2$O$_3$ acts as an acceptor. The rare-earth oxides in Pr$_6$O$_{11}$-based varistors are found to act as an acceptor[7,8,12]. Although Dy^{3+} ions have much larger radius (0.091 nm) than Zn^{2+} ions (0.074 nm), a limited substitution within the ZnO grains is possible. Dy substitutes for Zn and creates lattice defect in ZnO grains. The chemical-defect reaction using Kroger-Vink notation can be written as $Dy_2O_3 \xrightarrow{\quad ZnO \quad} 2Dy^{\cdot}_{Zn} + V''_{Zn} + 2O^{\times}_O$ $+1/2O_2$, where $Dy^{\cdot}_{Zn}$ is a positively charged Dy ion substituted for Zn lattice site, V''_{Zn} is a negatively charged Zn vacancy, and $O^{\times}_O$ is a neutral oxygen of oxygen lattice site. The oxygen generated in reaction above affects the donor concentration. In other words, N_d is related to the partial pressure of oxygen (Po_2), namely, $N_d \propto Po_2{}^{-1/4}$ or $Po_2{}^{-1/6}$. It is, therefore, believed that the decrease of donor concentration with Dy$_2$O$_3$ content is attributed to the increase of partial pressure of oxygen. The increase of the depletion layer width (t) is attributed to the decrease of donor concentration. In general, the

depletion region extends farther into the side with a lighter doping. The increase of Dy$_2$O$_3$ content led to the decrease of the density of interface states (N_t) from 5.51×10^{12} to 1.71×10^{12} /cm^2. With increasing Dy$_2$O$_3$ content, the barrier height (ϕ_b) very gradually increased up to 1.0 mol% and thereafter decreased. The barrier height is directly associated with the donor concentration and density of interface states. In other words, the barrier height is estimated by the variation rate in the density of interface states and donor concentration. In general, the barrier height is increased with increasing density of interface states and decreasing donor concentration. If the variation rate of donor concentration is much larger than that of density of interface states with an additive content, the barrier height is much more strongly affected by the donor concentration than the density of interface states. According to this reason, it can be understood that the barrier height is increased or decreased with increasing Dy$_2$O$_3$ content.

4. CONCLUSION

The microstructure, voltage-current (V-I) characteristics, and capacitance-voltage (C-V) characteristics of Zn-Pr-Co-Cr-Dy oxide-based varistors were investigated with various Dy$_2$O$_3$ contents. The varistor ceramics revealed a simple microstructure composing of ZnO bulk grain and intergranular layer containing Pr- and Dy-rich phase. The density of ceramics was decreased with increasing Dy$_2$O$_3$ content. The nonlinear properties were greatly enhanced by incorporation of Dy$_2$O$_3$. The varistors with 1.0 mol% Dy$_2$O$_3$ exhibited the highest nonlinear exponent, with the nonlinear exponent of 49 and the leakage current of 0.5 μA.

Fig. 4. C-V characteristics of ZPCCD-based varistors with Dy$_2$O$_3$ contents.

Table 2. The C-V characteristic parameters of ZPCCD-based varistors with Dy$_2$O$_3$ contents.

Dy$_2$O$_3$ content (mol %)	N_d (10^{18}/cm^3)	N_t (10^{12}/cm^2)	Φ_b (eV)	t (nm)
0.0	3.93	5.51	0.82	14.0
0.5	1.69	3.56	0.80	21.1
1.0	1.40	3.30	0.83	23.5
2.0	0.53	1.71	0.59	32.3

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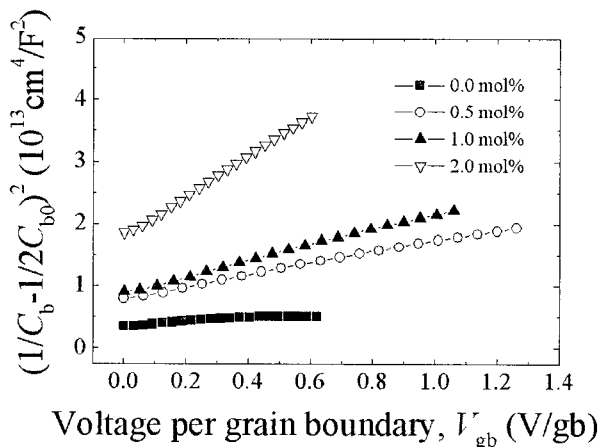
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