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Influence of CoO on stability of nonlinear electrical properties and dielectric characteristics in Pr_6O_{11}-based ZnO varistor ceramics

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Abstract

The nonlinear electrical properties, dielectric characteristics, and stability of the varistor ceramics of Zn–Pr–Co–Cr–Dy oxide system were investigated at various CoO contents. The sintered density of varistor ceramics increased from 5.25 to 5.55 g cm^{-3} with increasing CoO contents. The varistor voltage decreased from 235.3 to 86.0 V mm^{-1} with increasing CoO contents. As the CoO content increased, the nonlinear exponent increased up to 1.0 mol.% CoO, whereas further incorporation decreased the nonlinear exponent. Varistor ceramics containing 1.0 mol.% CoO exhibited the highest nonlinearity, in which the nonlinear exponent was 66.6 and the leakage current was 1.2 μA. Furthermore, varistor ceramics containing 1.0 mol.% CoO exhibited the highest stability, where the variation rate of varistor voltage, nonlinear exponent, and leakage current were −1.9%, −10.9%, and +275%, respectively, under DC accelerated aging stress of $0.95V_{1\,\text{mA}}/150\,^{\circ}\text{C}/24\,\text{h}$.

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1. Introduction

Many electronic devices and electric power systems can be subjected to voltage transients (called surges) induced by lightning, switching, and electrostatic discharge (ESD). They are vulnerable to damage by surges in excess of their voltage ratings because of the weakness of insulating strength. This is severe problem in the light of electronic components with high quality, in particular. One way to overcoming this is to use the varistors. ZnO varistors are ceramic semiconductor components made by ZnO powder containing minor additives. This is one of well-known MOVs (metal-oxide-varistors). ZnO varistors exhibit highly nonlinear voltage–current (*V*–*I*) characteristics expressed by $I = kV^{\alpha}$, where k is a constant and α is the nonlinear exponent as an index or figure of merit indicating the varistor effectiveness. Furthermore, they possess excellent high energy-handling capabilities. As a result, they have been widely applied 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 drawbacks associated with the Bi_2O_3 with high volatility and reactivity [3]. And they need many additives to obtain the high performance. To overcome these problems, Pr_6O_{11}-based ZnO varistor ceramics have been studied [4–12]. In Pr_6O_{11}-based ZnO varistor ceramics, the most important additives are Pr_6O_{11}, which essentially gives rise to nonlinear electrical properties. But, the nonlinear electrical 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 influence of CoO on electrical properties and stability in Pr_6O_{11}-based ZnO varistor ceramics has been reported. The purpose of this paper reports is to investigate the influence of CoO on nonlinear electrical properties, dielectric characteristics, and stability against DC accelerated aging stress in the varistor ceramics of Zn–Pr–Co–Cr–Dy oxide system.

2. Experimental procedure

2.1. Sample preparation

Reagent-grade raw materials were used in proportions of $(98.5 - x)$ mol.% ZnO, 0.5 mol.% Pr_6O_{11}, x mol.% CoO ($x = 0.5$,

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1.0, 2.0, 3.0, 5.0), 0.5 mol.% Cr_2O_3, 0.5 mol.% Dy_2O_3. The chemicals were weighed and ball-milled with ZrO_2 balls and acetone in a polypropylene bottle for 24 h. The mixture was dried at 120 °C for 12 h and calcined 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 powders were uniaxially 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 electrodes were 5 mm in diameter.

2.2. *Microstructure measurement*

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 [13], given by $d = 1.56L/MN$, where L is the random line length on the micrograph, M the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines. The compositional analysis of the selected areas was determined by an attached energy dispersion X-ray analysis (EDX) system. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2100, Japan) with Cu Kα radiation. The density (ρ) of varistor ceramics was measured by the Archimedes method.

2.3. *Electrical measurement*

The voltage–current (V–I) characteristics of the varistor ceramics were measured using a high voltage source-measure unit (Keithley 237). The varistor voltage ($V_{1\,\mathrm{mA}}$) was measured at a current density of 1.0 mA cm^{-2} and the leakage current (I_L) was measured at $0.80V_{1\,\mathrm{mA}}$. In addition, the nonlinear exponent (α) was determined from $\alpha = (\log J_2 - \log J_1)/(\log E_2 - \log E_1)$, where $J_1 = 1.0\,\mathrm{mA\,cm^{-2}}$, $J_2 = 10\,\mathrm{mA\,cm^{-2}}$, and E_1 and E_2 are the electric fields corresponding to J_1 and J_2, respectively. The dielectric characteristics, such as the apparent dielectric constant ($\varepsilon'_{\mathrm{APP}}$) and dissipation factor ($\tan\delta$) were measured in the range of 100 Hz–2 MHz using a RLC meter (QuadTech 7600).

The DC accelerated aging stress test was performed under four continuous states: (i) $0.85V_{1\,\mathrm{mA}}$/115 °C/24 h (first stress), (ii) $0.90V_{1\,\mathrm{mA}}$/120 °C/24 h (second stress), (iii) $0.95V_{1\,\mathrm{mA}}$/125 °C/24 h (third stress), and (iv) $0.95V_{1\,\mathrm{mA}}$/150 °C/24 h (fourth stress). Simultaneously, the leakage current was monitored at intervals of 1 min during stressing using a high voltage source-measure unit (Keithley 237). After the respective stresses, the V–I and dielectric characteristics were measured at room temperature.

3. Results and discussion

Fig. 1 shows the SEM micrographs of varistor ceramics sintered for 1 h at 1350 °C 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 [4]: ZnO grain (bulk phase) and intergranular layer (secondary phase). The intergranular layers were Pr- and Dy-rich phases as determined by XRD analysis, as shown in Fig. 2. As can be seen in the figure, three diffraction peaks were revealed in the ceramics, namely, ZnO grains, Pr oxides, and Dy oxide. It was found from EDX in Fig. 3 that these coexist at the grain boundaries and the nodal points as if they were a single phase. It is believed that this is attributed to the ionic radius difference for Zn. Because the Co^{2+} ionic radius is the same as that of Zn^{2+}, completely substitution in the ZnO garin is possible. Therefore the CoO content does not affect microstructure phases.

As the CoO content increased, the sintered density increased from 5.25 to 5.55 g cm^{-3} up to 2.0 mol.%, whereas the further addition did not affect density, reaching 5.55 g cm^{-3}. The average grain size increased from 9.9 to 27.2 μm with increasing CoO content, as shown in Fig. 2. It can be seen that the CoO promotes grain growth. The grain size directly affects varistor voltage in voltage–current characteristics. The detailed microstructure parameters are summarized in Table 1.

Fig. 4 shows the E–J characteristics of varistor ceramics with various CoO contents. The conduction characteristics are greatly divided into the pre-breakdown region under knee part and the breakdown region above knee part. This curve is similar to that of zener diode. The shape of curves is somewhat complex without exhibiting any remarkable tendency in the light of CoO content only. The characteristic curves of varistors are greatly divided into the two regions, that is, prebreakdown at low voltage region as off-state and nonlinear electrical properties at high voltage region as on-state. The characteristic parameters, such as varistor voltage ($V_{1\,\mathrm{mA}}$), nonlinear exponent (α), and leakage current (I_L) obtained from Fig. 2 are summarized in Table 1. The $V_{1\,\mathrm{mA}}$ value monotonously greatly decreased from 235.3 to 86.0 V mm^{-1} as the CoO content increased. This is attributed to the decrease of the number of grain boundaries due to the increase of the average grain size. In general, the smaller the grain size, the higher the varistor voltage.

The α value was abruptly increased with increasing CoO content up to 1.0 mol.%, reaching a maximum value 66.6, whereas the further addition caused the decrease of α value. Therefore, it can be seen that the incorporation of moderate CoO content significantly increased the α value. This is different from Bi_2O_3-based ZnO varistor which optimum CoO content is 0.5 mol.%. Meanwhile, the I_L value decreased with increasing CoO content up to 2.0 mol.%, reaching a minimum value 0.1 μA, whereas the further addition caused abrupt increase of I_L value.

Fig. 5 shows the frequency dependence of dielectric parameters of varistor ceramics with various CoO contents. The apparent dielectric constant ($\varepsilon'_{\mathrm{APP}}$) decreased gradually without a sharper dispersive drop evident up to 2.0 mol.% CoO as the frequency increased, which is associated with the polarization of dielectrics. The more the CoO content increases, the more

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