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Electrical properties and AC degradation characteristics of low voltage ZnO varistors doped with Nd_2O_3

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Abstract

The electrical properties and degradation characteristics of low voltage ZnO varistors were investigated as a function of Nd_2O_3 content. The varistor ceramics with 0.03 mol% Nd_2O_3 sintered at 1250 °C were far more densified than those with 0.06, 0.09 and 0.12 mol% Nd_2O_3. The addition of Nd_2O_3 to the low voltage ZnO varistors greatly improved the current–voltage characteristics; the nonlinear coefficient of varistors increase from 12.2 to 34.6 with increasing Nd_2O_3 content. The samples with 0.03 mol% Nd_2O_3 showed excellent stability due to high density and relatively good *V–I* characteristics, with the nonlinear coefficient of 22.5 and the leakage current of 9.6 μA. Their variation rate of varistor voltage and nonlinear coefficient and leakage current were −4.7%, −5.4%, 18.3%, respectively, under AC degradation stress (1.0 $V_{1\ mA}$/125 °C/24 h).
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Keywords: Varistors; Degradation; Nd_2O_3; Electrical characteristics; Stability

1. Introduction

ZnO varistors with high nonlinearity in their current–voltage characteristics are extensively used as protecting devices against transient voltage in electronic and industrial equipment and as surge arrestors. The most important property of a varistor is its nonlinear current–voltage characteristic, which can be expressed by the equation $I = KV^{\alpha}$, where α is the nonlinear coefficient, which characterizes the nonlinear properties of varistors, the higher the value of α, the better the clamp. Moreover, ZnO varistors possess excellent surge withstanding capabilities [1–3].

The ZnO varistors are suited for high-voltage applications. However, an increasing number of low voltage varistors is being used for surge protection in integrated circuits and automobiles. Since the breakdown voltage (varistor voltage) is proportional to the number of ZnO grains in series between the electrodes, low voltage varistors can be obtained by either decreasing the thickness of the specimen or increasing the size of ZnO grains. The thin ZnO varistors are difficult to prepare and apt to break. Note also that the energy absorption capability of thin ZnO varistors is very poor due to its small volume. On the other hand, low voltage ZnO varistors with grains of large size have been fabricated by using grain growth-enhancing additives. TiO_2 can greatly enhance the grain growth of ZnO, thus widely used in producing low voltage ZnO varistors, but the doping of TiO_2 have restricted nonlinear current-voltage characteristics, and the α value is very low. Consequently, its microstructure exhibits a nonuniform distribution of grain size, which causes an irregular current distribution and makes the varistor susceptible to hot spots [4,5].

More recently, the published literature reported that ZnO varistors added with rare-earth metal oxides, such as CeO_2 and Y_2O_3, exhibits high nonlinearity and stability [6,7]. In this paper, the effect of Nd_2O_3 content on electrical properties and AC degradation characteristics of low voltage ZnO varistor ceramics was investigated.

2. Experimental

2.1. Sample preparation

Reagent-grade raw materials were prepared for low voltage ZnO varistors, the base composition was: 95.95% ZnO + 0.75% Bi_2O_3 + 0.8% TiO_2 + 0.5% NiO + 1.0%

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Co_2O_3 + 0.5% $MnCO_3$ + 0.5% SnO_2 (all in mol%). The other samples were Nd_2O_3-doped low voltage varistors (the base composition plus 0%, 0.03%, 0.06%, 0.09%, 0.12% Nd_2O_3). The powder mixtures were wet ball-milled in a polyethylene bottle with ZrO_2 balls of 24 h in deionized water. After dried and granulated, the powder was pressed into discs of 10 mm in diameter and 1.2 mm in thickness at a pressure of 80 MPa. The discs were sintered at 1250 °C in air for 1 h, with heating and cooling rates of 300 °C/h. The size of the final samples was about 8 mm in diameter and 1.0 mm in thickness. For the studies of electrical properties, silver paste was applied to the faces of the discs (which were subsequently heated at 600 °C for 20 min) to provide electrodes, the size of electrodes was 5 mm in diameter.

2.2. Methods characterization

Sintered density (ρ) was determined by Archimede method. The microstructure and grain size distributions were carried out using a scanning electron microscope (SEM). Average grain size (d) was measured by the linear intercept method on the micrographs. The polished samples were lightly etched with dilute solution of hydrochloric for microstructure investigations.

The current–voltage (V–I) characteristics of low voltage ZnO varistors were measured using CJ1001 meters, the varistor voltage $V_{1\ mA}$ was determined at current density of 1 mA/cm^2, the leakage current I_L was determined at 0.83 $V_{1\ mA}$. In addition, the nonlinear coefficient α was determined from $\alpha = (\log I_2 - \log I_1)/(\log V_2 - \log V_1)$, where I_1 = 0.1 mA/cm^2, I_2 = 1.0 mA/cm^2, and V_1 and V_2 are the electrical fields corresponding to I_1 and I_2, respectively [8,9].

The AC (50 Hz) degradation tests were carried out under continuous conditions, such as 1.0 $V_{1\ mA}$rms/125 °C/24 h. Simultaneously, the leakage current was monitored at interval of 1 min during stressing using CJ1001 meter. The degradation rate coefficient (K_T) was calculated from the expression $I_L = I_{L0} + K_T t^{1/2}$, where I_L is leakage current at stress time (t) and I_{L0} is I_L at $t = 0$. After the stress, the V–I characteristics were measured at room temperature.

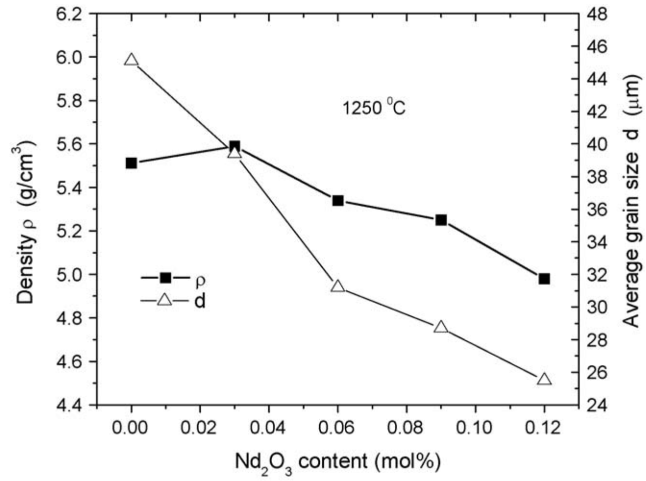

Fig. 1. The density (ρ) and average grain size (d) of low voltage ZnO varistors with Nd_2O_3 content.

The capacitance–voltage (C–V) characteristics of low voltage ZnO varistors were measured at 1 kHz with the variable applied bias in the pre-breakdown region of the V–I characteristics using a LRC meter.

3. Results and discussion

3.1. Density and microstructure

Fig. 1 shows the density (ρ) and average grain size (d) of varistor sintered at 1250 °C with various Nd_2O_3 content. The density of ceramics was gradually decreased from 5.60 to 4.79 g/cm^3, corresponding to the range of 98–85% of theoretical density (TD) of pure ZnO (TD = 5.61 g/cm^3 in ZnO). The ceramics with 0.03 mol% Nd_2O_3 sintered at 1250 °C exhibited the highest densification, reaching 98% of TD. The density greatly affects the resistance of degradation together with a leakage current. This will be discussed later in more

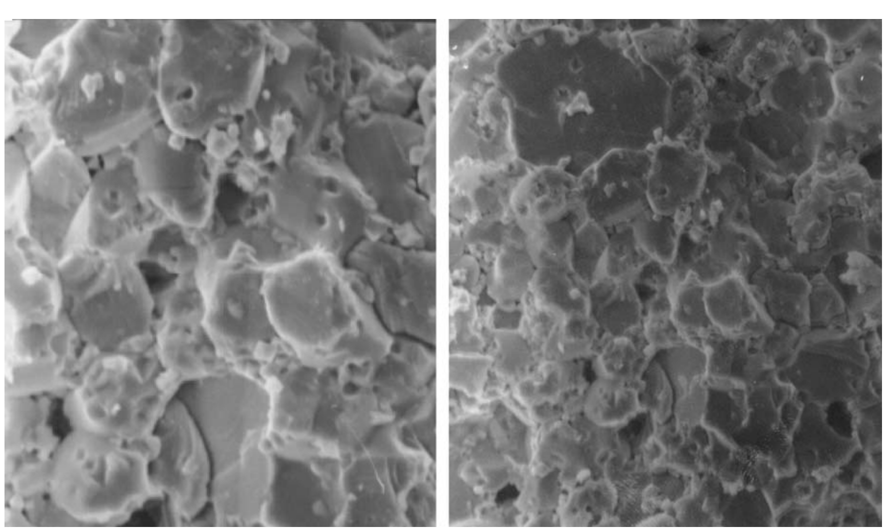

Fig. 2. SEM micrographs of varistor ceramics with various Nd_2O_3 content. (a) 0.06 mol% and (b) 0.12 mol%.

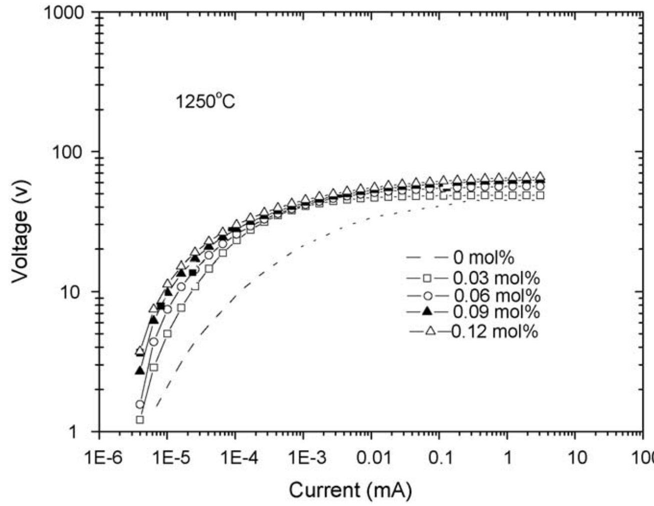

Fig. 3. The *V–I* characteristics of low voltage ZnO varistors with Nd_2O_3 content.

detail. Fig. 2 shows the SEM micrographs. It was observed that microstructure of the ceramics is very simple, composed of only two phases, namely ZnO grain and intergranular layer as secondary phases.

The average grain size was found to decrease in the range of about 39–25 μm at 1250 °C with increasing Nd_2O_3 content. It is believed that the decrease of the average grain size with Nd_2O_3 content is attributed to segregation of Nd_2O_3, which nearly insoluble in ZnO grains, to grain boundaries. This was nearly equal to that of ceramics doped with other rare-earth metal oxides [10].

3.2. Current–voltage (V–I) characteristics

The electrical properties of low voltage ZnO varistors were characterized by their current–voltage (*V–I*) characteristics. Fig. 3 shows the *V–I* characteristics of the samples sintered at 1250 °C with various Nd_2O_3 content. All the low voltage ZnO varistors are likely to exhibit good electric characteristics seemingly. It can be seen that the breakdown region of *V–I* curves with Nd_2O_3 is much flatter than that without Nd_2O_3. The variation of *V–I* characteristic parameters, including the varistor voltage ($V_{1\ mA}$), nonlinear coefficient (α), and leakage current (I_L) are shown in Fig. 4. The $V_{1\ mA}$ increased in the range of 32.8–64.5 V/mm with increasing Nd_2O_3 content. As the $V_{1\ mA}$ is directly related to the number of grain boundaries across a series between the electrodes, the increase of $V_{1\ mA}$ is attributed to the decrease of average grain size only. As the same meaning, a higher sintering temperature resulted in the decrease of $V_{1\ mA}$, due to the increase of average grain size. The V_{gb}, average breakdown voltage per grain boundaries, is defined as follows: $V_{gb} = (d/D)V_{1\ mA}$, where d is the average grain size and D is the thickness of sample. The V_{gb} was in the range of 2.0–2.5 V/gb for sintering temperature of 1250 °C with Nd_2O_3 content. This agrees to generally well-known 2–3 V/gb regardless of sintering processes and varistor compositions [11].

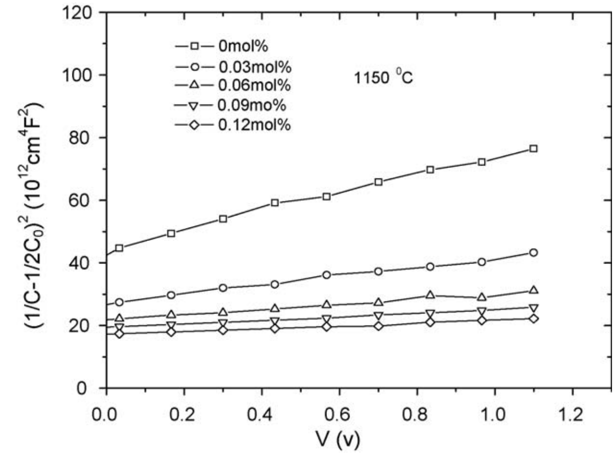

Fig. 5. The *C–V* characteristics of low voltage ZnO varistors with various Nd_2O_3 content.

One of the most important parameter in varistor is the nonlinear coefficient (α), which characterizes the native properties of varistor itself. Fig. 4 shows the nonlinear coefficient (α) and leakage current (I_L) as a function of Nd_2O_3 content. The value of α in the sample without Nd_2O_3 was low to be 12.2, whereas, in varistor with Nd_2O_3 was in the range of 22.5–34.6 with increasing Nd_2O_3 content, in particular, the low voltage varistor with 0.12 mol% Nd_2O_3 exhibited the best nonlinear characteristics, in which the value of α and I_L is 34.6 and 5.2 μA, respectively. It can be seen that the nonlinearity of

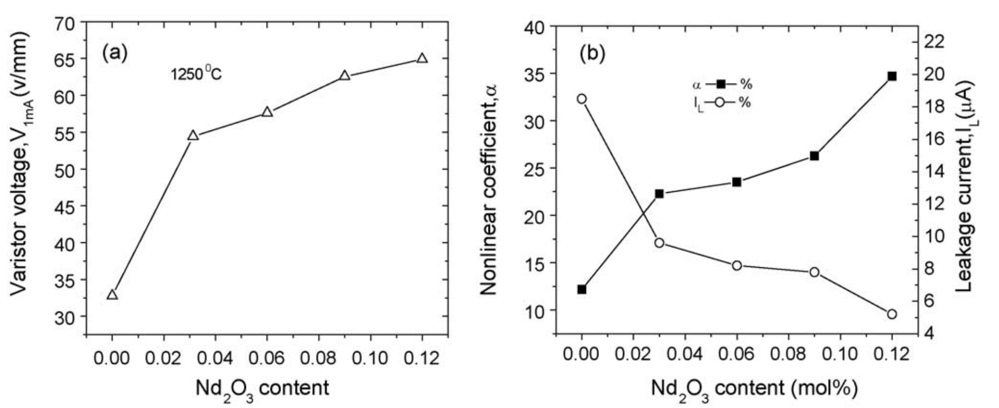

Fig. 4. Effect of Nd_2O_3 content on the electrical characteristics of low voltage ZnO varistors.

low voltage ZnO varistors are greatly improved when Nd_2O_3 is incorporated into the ZnO–Bi_2O_3–TiO_2 system.

3.3. Capacitance–voltage (C–V) analysis

On the basis of a symmetrical double Schottky barrier model for the grain boundary region, parameters such as the barrier height (φ_b), donor density (N_d), interface state density (N_t), and depletion layer width (t) can be determined from the capacitance–voltage relation [12]:

$$\left(\frac{1}{C}-\frac{1}{2C_0}\right)^2=\frac{2(\varphi_b+V)}{qN_d\varepsilon}$$

where

$$\frac{1}{2C_0}=\left(\frac{2\varphi_b}{qN_d\varepsilon}\right)^{1/2}$$

q is the electronic charge, ε is permittivity of ZnO ($\varepsilon = 8.5\varepsilon_0$), C is the capacitance of per grain boundary, C_0 is the value of C when $V = 0$, V is the applied voltage per grain boundary. Fig. 5 shows the C–V characteristics of low voltage ZnO varistors with various Nd_2O_3 content. From the slope as well as the intercept of the C–V straight line of the graph $(1/C - 1/2C_0)^2$ versus V, N_d and φ_b can be evaluated.

Using these values the depletion layer width (t) can be obtained from equation:

$$t=\left(\frac{2\varepsilon\varepsilon_0\varphi_b}{q^2N_d}\right)^{1/2}$$

The density of interface state (N_t) at the grain boundary was determined from:

$$N_t=\left(\frac{2N_d\varepsilon\varepsilon_0\varphi_b}{q^2}\right)^{1/2}$$

Once the donor concentration and barrier height are known, the depletion layer width (t) of the either side at the grain boundaries was determined by the equation:

$$N_d t = N_t$$

The grain boundary characteristics of the low voltage ZnO varistors doped with Nd_2O_3 were summarized in Table 1, the characteristic C–V parameters indicate that doping with Nd_2O_3 results in a increase in the barrier height (φ_b), donor density (N_d) and interface state density (N_t), the depletion layer width (t)

Table 1
Grain boundary characteristics of low voltage varistors with various Nd_2O_3 content.

Nd_2O_3 content (mol%)	N_d ($\times10^{18}$ cm^{-3})	φ_b (eV)	N_t ($\times10^{12}$ cm^{-2})	w (nm)
0	1.62	1.51	4.16	25.7
0.03	1.47	1.38	3.85	26.4
0.06	1.89	2.12	4.73	25.0
0.09	2.55	2.30	5.96	23.4
0.12	3.04	2.37	6.81	20.1

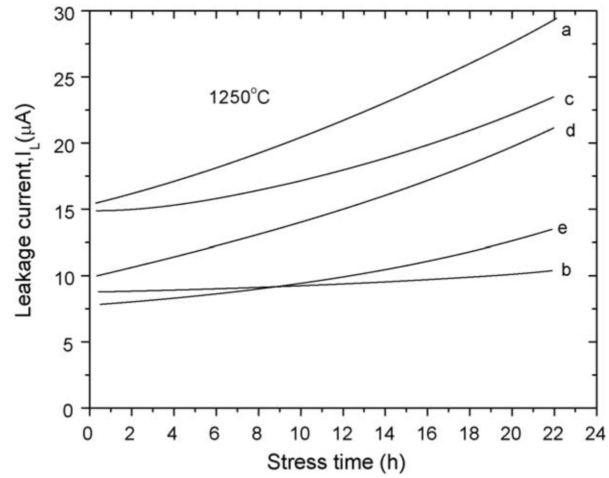

Fig. 6. The leakage current variation of low voltage ZnO varistors with Nd_2O_3 content during voltage stresses. (a) 0.0 mol%, (b) 0.03 mol%, (c) 0.06 mol%, (d) 0.09 mol%, (e) 0.12 mol%.

decrease from 25.7 to 20.1 nm with increasing amounts of Nd_2O_3. The measurement of the electrical properties of the varistors doped with Nd_2O_3 indicate that Nd_2O_3 has a strong donor effect which contributes to the increase of nonlinearity of low voltage ZnO varistors.

3.4. AC degradation characteristics

ZnO varistors are always subjected to a continuous electrical stress. If the stability against electrical stress is poor, the application of such varistors is extremely limited even if their nonlinearity is very superior. In practice, the ZnO varistors begin to degrade because of gradually increasing leakage current with stress time. Eventually, they cause thermal runaway and loss of varistor function. The stability of varistors is more important than any other properties. From this point of view, in addition to nonlinearity, the electrical stability is a technologically important characteristic of ZnO varistors. Fig. 6 shows the leakage current of low voltage ZnO varistors during AC degradation stresses. The varistors with 0.03 mol% Nd_2O_3 exhibited much higher stability, compared the varistors with 0.06, 0.09 and 0.12 mol% Nd_2O_3. It can be seen that their leakage current is nearly constant until the stress and shows weak positive creep during the stress. This result can be attributed to the much higher ceramic density. Therefore, the density of varistor ceramics affects the degradation characteristics more than the leakage current.

On the other hand, the stability of varistors can be explained by degradation rate coefficient (K_T), indicated by the expression: $I_L = I_{L0} + K_T t^{1/2}$ [13]. The lower the K_T, the higher the stability. The AC degradation rate coefficient (K_T) are listed in Table 2. It is clear that the degradation rate coefficient (K_T) was influenced by the Nd_2O_3 content, the K_T value of varistors without Nd_2O_3 content was 2.64 μA h$^{-1/2}$ after the stress. However, that was the highest in the all samples, and greatly decreased with the Nd_2O_3 content, achieving a minimum for samples doped with 0.03 mol% Nd_2O_3. But the K_T increased with the Nd_2O_3 content increasing further, the low voltage ZnO

Table 2
The variation of *V–I* characteristics parameters of low voltage varistors after voltage stress with Nd_2O_3 content.

Nd_2O_3 content (mol%)	K_T (μA $h^{-1/2}$)	$V_{1\ mA}$ (V/mm)	$\%\Delta V_{1\ mA}$	α	$\%\Delta\alpha$	I_L (μA)	$\%\Delta I_L$
0.0	2.64	60.8	−16.4	12.2	−22.3	18.5	68.8
0.03	0.36	71.6	−4.7	22.5	−5.4	9.6	18.3
0.06	0.93	73.9	−6.7	23.1	−7.8	8.2	41.5
0.09	0.95	81.4	−7.4	27.4	−8.4	7.8	59.6
0.12	1.08	74.5	−8.8	34.6	−9.6	5.2	100.3

varistor with 0.03 mol% Nd_2O_3 are expected to show the best stability. From these results, it is concluded that Nd_2O_3-doping significantly improves the nonlinearity and the stability against AC degradation stress.

More detailed variation of *V–I* characteristic parameters after AC degradation stress is summarized in Table 2, such as variation rate of the varistor voltage ($\%\Delta V_{1\ mA}$), variation rate of the nonlinear coefficient ($\%\Delta\alpha$), and variation rate of the leakage current ($\%\Delta I_L$) after AC degradation stress, for the low voltage ZnO varistors sintered at 1250 °C, with no thermal runaway even under the stress. In an aspect of the stability of *V–I* characteristics, the $\%\Delta V_{1\ mA}$ should be lower than any other variation rate of parameters. In general, the allowed specifications of $\%\Delta V_{1\ mA}$ for the commercial varistors are less than 10% under 0.85 $V_{1\ mA}$/85 °C/1000 h. Even though the stressing time in this study is short, the stressing voltage and the ambient temperature are very severe. Therefore, it is believed that the AC degradation stress is very severe. On the whole, the varistor voltage exhibited comparatively much lower variation rate than that of other parameters with AC stress strength. The low voltage ZnO varistors with 0.03 mol% Nd_2O_3 sintered at 1250 °C exhibited a high stability by marking $\%\Delta V_{1\ mA} = -4.7\%$, $\%\Delta\alpha = -5.4\%$, and $\%\Delta I_L = 18.3\%$ after AC degradation stress (1.0 $V_{1\ mA}$/125 °C/24 h). It is forecasted that these varistors will be sufficiently applied to transient voltage absorber.

4. Conclusions

The microstructure, voltage–current (*V–I*) characteristics, capacitance–voltage (*C–V*) analysis and AC degradation characteristics of low voltage ZnO varistors were investigated with Nd_2O_3 content at sintering temperature of 1250 °C. The ceramics with 0.03 mol% Nd_2O_3 were far more densified, compared with the varistors with 0.06, 0.09 and 0.12 mol% Nd_2O_3. The addition of Nd_2O_3 to the low ZnO voltage varistors greatly enhance the nonlinearity of the varistor's behavior. The capacitance–voltage (*C–V*) measurement showed that in the samples with additions of Nd_2O_3 the donor density (N_d) at the grain boundaries increases from 1.62 to 3.04×10^{18} cm^{-3}, the barrier height (φ_b) increases from 1.51 to 2.37 eV, the depletion layer width (t) decreases from 25.7 to 20.1 nm. The varistors with 0.03 mol% Nd_2O_3 showed excellent stability due to high density and relatively good nonlinear *V–I* characteristics, in which $K_T = 0.36$ μA $h^{-1/2}$, $\%\Delta V_{1\ mA} = -4.7\%$, $\%\Delta\alpha = -5.4\%$ and $\%\Delta I_L = 18.3\%$ in AC degradation stress (1.0 $V_{1\ mA}$/125 °C/24 h).

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