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Dependence of residual voltage ratio behavior of SnO_2-based varistors on Nb_2O_5 addition

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SnO_2-based varistor samples doped with Co_2O_3, Nb_2O_5 and Cr_2O_3 were prepared by ball-mixed oxide method. The microstructure, nonlinear *I-V* characteristic and surge current performances of these samples were investigated. This paper mainly focused on the dependence of the residual voltage ratio behavior of SnO_2-based varistors on Nb_2O_5 addition, different factors influencing the residual voltage ratio in different concentration of Nb_2O_5 were analyzed. The Nb_2O_5 addition influences its residual voltage ratio by changing the grain size, forming defects (especially the free electrons) and cumulative effect. The measured results indicated that the optimally obtained sample with 0.07mol% Nb_2O_5 possesses the lowest residual voltage ratio of 1.86, the corresponding nonlinear coefficient and the threshold electric field are 42.6 and 364.6 V/mm, respectively.

SnO_2-based varistor, Nb_2O_5, residual voltage ratio

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1 Introduction

With the unique nonlinear characteristics and high energy handling capabilities, varistors are widely used in electric and electronic systems to suppress the transient overvoltage and absorb surge energy to protect various devices and circuits. Presently, ZnO-based varistor is the prime choice due to its favorable non-ohmic behavior and high energy handling capability. However, as the large doping, ZnO-based varistors contain multiphase which also deteriorate their temperature stability and aging reaction [1–4].

Presently, new varistor materials still have been being explored. In 1995 [5], Pianaro firstly found that SnO_2 ceramics with small amount of doped additives had high density and nonlinear properties. Since then, much attention has been paid to this new material system. In most literatures on SnO_2-based varistors, the nonlinear coefficient α is in the range from 8 to 50 [6–10]. Bueno et al. reported that the nonlinear coefficient α of the varistors composed of 98.95 mol% SnO_2+1.0 mol% Co_2O_3+0.035 mol% Nb_2O_5+0.25 mol% Cr_2O_3+0.25 mol% La_2O_3 reached 142 [11]. Same to ZnO, SnO_2 is a kind of n-type semiconductor with rutile structure. But different from the multi-phase structure of the ZnO-based varistors, the SnO_2-based varistors have simple microstructures. The single-phase structure of this material gives rise to a high stability. Bueno et al. reported that the thermal conductivity of the SnO_2-based varistor system was two times higher than that of the ZnO-based varistor [12]. It is inferred that, when surge energy was injected into the tested specimens, higher thermal conductivity could improve the temperature uniformity of the ceramic materials and reduce the probability of the thermal-mechanical failure [13], this will also improve their impulse energy absorption capability. In addition, several advantages have been reported for the SnO_2-based varistors over the ZnO-based

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varistors [14], such as lower additive contents, higher threshold electric field, higher refractivity and better mechanical properties.

However, it is of great challenge for the SnO_2-based varistors to be utilized in lightning protection systems, concerning with their relatively high residual voltage ratio. Residual voltage ratio is a crucial parameter for a surge protective device that can intuitively reflect varistor overvoltage limiting ability and the nonlinear properties at high current region. It is defined as: $K_R=V_R/V_N$, i.e., under 8/20 μs wave, the ratio between the residual voltage under the impulse current of *m*-kA (normally, *m* is 5 for 110-kV sure arrester and 10 for 500-kV one) and the voltage under the current DC of 1 mA. Normally the value is smaller than 3 and lower residual voltage ratio will lead to better overvoltage suppressing performance. For this reason, it is expected that a good varistor device should have lower residual voltage ratio. Generally, the residual voltage ratio of commercial ZnO-based varistors is about 1.7, while the value of most SnO_2-based varistors is more than 2 [13]. If the residual voltage ratio can be lowered further by composition optimizing or new manufacture process, the withstanding capability of the SnO_2-based varistors to surge current will increase correspondingly.

Despite of its nonlinear coefficient and threshold electric field properties equivalent to the ZnO-based varistors, there is no report in literature with respect to the residual voltage ratio of the SnO_2-based varistors. Therefore, we drive a study of residual voltage ratio in the SnO_2-based varistors using 8/20 μs pulse current generator. In this paper we worked on the dependence of the residual voltage ratio behavior of the SnO_2-based varistors on Nb_2O_5 addition, the mechanism, and the method reducing the residual voltage ratio ensuring the nonlinear electric properties of the varistors. The Nb_2O_5 addition influences its residual voltage ratio by changing the grain size, forming defects (especially the free electrons) and cumulative effect. In this paper, we report for the first time the observation of excellent lower residual voltage ratio properties for the SnO_2-based varistors.

2 Experimental procedure

All the oxides used were analytical grade: SnO_2 (99.5%), Co_2O_3 (99.0%), Nb_2O_5 (99.99%), Cr_2O_3 (99.5%). The studied systems correspond to the SnO_2-based system varistors of composition (99.46-*x*) mol% SnO_2+0.50 mol% Co_2O_3+ 0.04 mol% Cr_2O_3+*x* mol% Nb_2O_5 (*x*=0.05, 0.06, 0.07, 0.08). Samples were prepared by conventional ceramic fabricating processes. SnO_2 powder was blended with additives and ball milled with ethanol. The resulting mixture was cold pressed into round compacts under a pressure of 160 MPa and subsequently sintered at 1300°C for 1 h in air. Ceramic discs with a diameter of about 10 mm and a thickness of about 1.0 mm were obtained. Uniform coating of silver paint was pasted on both sides of the discs as electrodes and was cured at 500°C.

The current-voltage measurements were carried out using HVB4000 (Concept 80 Broadband Dielectric Spectrometer, Novocontrol Technologies GmbH & Co. KG., Germany). The nonlinear coefficient α was obtained by the equation $\alpha=\log(I_2/I_1)/\log(V_2/V_1)$ (I_1=0.1 mA, I_2=1 mA were used in this paper). The threshold electric field (E_b) was obtained at a current density of 1 mA/cm^2. The crystalline phase and microstructural graphs were measured by X-ray (D/max-2500) diffraction pattern and scanning electron microscope (JSM-6460LV), respectively. The Nyquist diagram was obtained by using HVB4000, too.

3 Results and discussion

Figure 1 shows the SEM micrographs of different SnO_2-based varistor samples studied here. It was confirmed that we obtained uniform and dense microstructures. Table 1 presents the nonlinear coefficient α, the threshold electric field E_b, the leakage current, the residual voltage ratio, the mean grain size, and the relative density. As can be seen, all the systems possess high densities (the relative densities are all above 97%) and present excellent nonlinear *I-V* characteristics, while the residual voltage ratios are much different. The effects of Nb_2O_5 concentration on the residual voltage ratio of the SnO_2-based varistors can be clearly seen from Figure 2. The lowest residual voltage ratio of 1.86 can be obtained when the Nb_2O_5 concentration is 0.07mol%, which is comparable with that of the ZnO-based varistors. Figure 3 is the Nyquist diagram obtained at 300°C for samples from which the diameters of each semicircle can reflect the resistances of grain boundaries.

Table 1 Relative density, mean grain size and electrical performance of samples

Nb_2O_5 concentration (mol%)	Nonlinear coefficient	E_b (V/mm)	Leakage current (μA)	Residual voltage ratio	Mean grain size (μm)	Relative density (%)
0.05	29.4	415.4	17.6	2.29	3.04	97.5
0.06	29.5	491.2	8.5	2.71	3.11	98.6
0.07	42.6	364.6	1.85	1.86	3.00	98.2
0.08	40.0	198.1	0.19	2.22	2.90	97.0

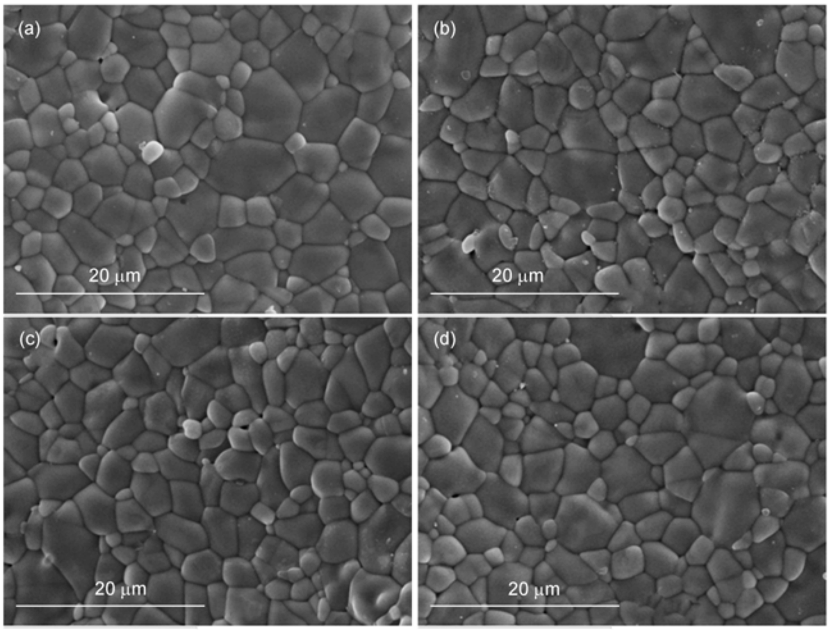

Figure 1 SEM fractographs of the sintered samples with different concentration (x mol%) of Nb_2O_5. (a) x=0.05; (b) x=0.06; (c) x=0.07; (d) x=0.08.

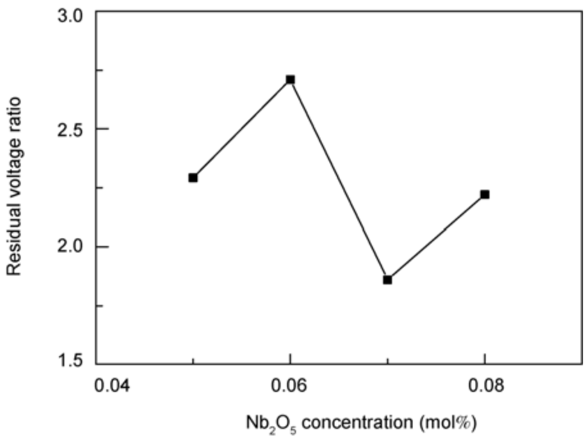

Figure 2 Relationship between the Nb_2O_5 concentration and the residual voltage ratio of samples.

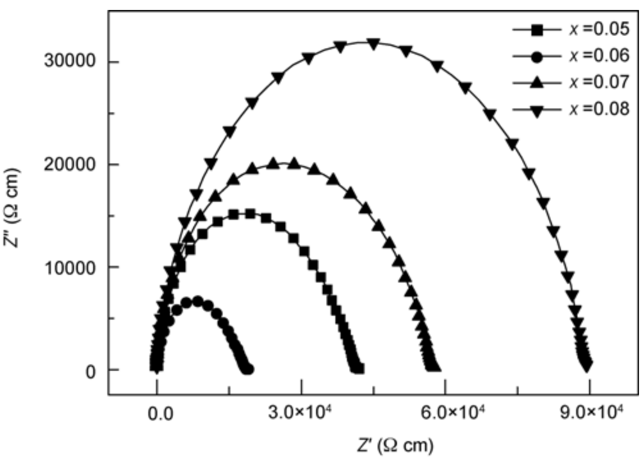

Figure 3 Nyquist diagram obtained at 300°C for samples with different Nb_2O_5 concentration x mol% (x=0.05, 0.06, 0.07, 0.08).

Ions are distributed in different locations for their difference of the ion radius. As Co^{2+} ions (0.074 nm) are larger than Sn^{4+} ions (0.071 nm), the substitution of Sn^{4+} ions by Co^{2+} ions will lead to significant lattice distortion. As a result, most of the Co^{2+} ions will stay in the grain boundary and only a spot of the Co^{2+} ions will leak into the shallow SnO_2 lattice, substitute Sn^{4+} ions around the grain boundary, and form depletion layer with donors.

$$CoO \rightarrow Co''_{Sn} + V_O^{\cdot\cdot} + O_O^{\times} \tag{1}$$

The production of oxygen vacancies would accelerate the diffusion, and thus promote grain growth.

Since the radius of Nb^{5+} ions (0.070 nm) is very close to that of Sn^{4+} ions (0.071 nm), Nb^{5+} ions will replace Sn^{4+} ions sites and enter the location of the inner grains easily.

$$Nb_2O_5 \rightarrow 2Nb^{\cdot}_{Sn} + 2e' + 4O_O^{\times} + 1/2O_2 \tag{2}$$

$$2Nb_2O_5 \rightarrow 4Nb^{\cdot}_{Sn} + V''''_{Sn} + 5O_2 \tag{3}$$

In order to reduce the residual voltage ratio, we could extend and flatter the nonlinear zone in the *I-V* curve. It means that more electron carriers are required to participate conducting. Doping Nb^{5+} produces a large number of free electrons that can greatly enhance the grain conductivity.

The residual voltage ratio is increased by adding Nb_2O_5 content in the first stage of the curve in Figure 2. This is because the residual voltage ratio is associated not only with the grain resistance, but also with the grain size. The residual voltage ratio is proportional to the grain size. When the Nb_2O_5 content is low, more Nb^{5+} enter the lattice to replace Sn^{4+} with increasing Nb_2O_5 content, damage the SnO_2 lattice and produce more defects. More defects improve the diffusion of ions, promote grain growth, and ulteriorly increase the residual voltage ratio. At the same time, grain growth and reduction of grain boundaries amounts make the grain boundary resistance lower, as shown in Figure 3.

In the second stage of the curve in Figure 2, the effect of grain growth is no longer important, while the production of large number of free electrons in the crystal reduces the grain resistivity and lowers the corresponding residual voltage obviously. Excess of free electrons will make the grain boundary depletion layer to be weakened or disappear, also reduce the grain boundary resistance as shown in Figure 3.

Nevertheless, when the substitution of Sn^{4+} by Nb^{5+} becomes saturated, the extra Nb^{5+} would not enter SnO_2 lattice any more but accumulate at the grain boundary. These Nb^{5+} ions in turn hinder the transport of electrons and other defect ions, which increase the residual voltage ratio and the grain boundary resistance.

Besides residual voltage ratio, other parameters of SnO_2 varistor's electrical properties, for instance, the nonlinear coefficient α, the threshold electric field E_b, and the leakage current, are also influenced by Nb_2O_5 content, as shown in Table 1. Nonlinear coefficient α heightens following the increase of Nb_2O_5 content. Figure 4 shows the effect of Nb_2O_5 content on the nonlinear coefficient α, the nonlinear coefficient is mainly determined by effective barrier number and the barrier height. At the beginning, the effect of Nb_2O_5 content on grain growth has little impact on α. With the increase of Nb_2O_5 content, a large number of free electrons effectively promote the SnO_2 grains to become semiconducting. The increase in Sn vacancies and other defects help to establish the grain boundary barrier and the nonlinear coefficient is improved consequently. When the Nb_2O_5 content continues to increase, the reason for the decrease of nonlinear coefficient also is that the extra free electrons in turn make the grain boundary depletion layer to be weakened or disappear. The value of E_b does not change significantly at the beginning. Whereafter more Nb_2O_5 additions bring more free electrons which depresses the voltage strength of each grain boundary, and results in the depressed threshold electric field E_b. Defects caused by Nb_2O_5 addition accelerate diffusion and promote grain growth, thus help getting more complete and compact grain boundary. Therefore, the leakage current is restricted.

4 Conclusions

Based on our research, Nb_2O_5 concentration has a significant effect on the residual voltage ratio and other nonlinear electrical properties of the SnO_2-based varistors. With the change of the Nb_2O_5 content from 0.05 mol% to 0.08 mol%, the residual voltage ratio of samples first increases, then decreases, and at last increases again. In this range, the lowest residual voltage ratio of 1.86 is obtained when the Nb_2O_5 concentration is 0.07mol%, which is comparable with that of the ZnO-based varistors. It indicates that the SnO_2-based varistors' residual voltage ratio can be lowered further by optimizing the concentration of Nb_2O_5 and the SnO_2-based varistors are a kind of promising varistor materials as a potential candidate to compete with the traditional multicomponent ZnO-based varistors.

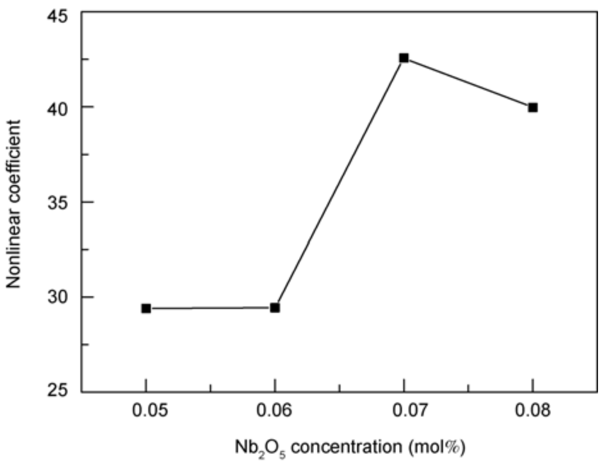

Figure 4 The nonlinear coefficient α of SnO_2 varistors doped with different Nb_2O_5 concentration.

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