Research Article

Preparation of Ultrahigh Potential Gradient of ZnO Varistors by Rare-Earth Doping and Low-Temperature Sintering

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The effects of rare-earth doping and low-temperature sintering on electrical properties of ZnO varistors were investigated. The potential gradient (E_{1mA}) of the ZnO varistors increased significantly to 2247.2 V/mm after doping 0.08 mol% of Y_2O_3 and sintering at 800°C for 2 h. The notable decrease of the grain size with the given experimental conditions was the origin for the increase in E_{1mA} . During the process of high-temperature sintering, both the oxygen at the grain boundary interface and the neutralisation of the ions on the depletion layer were directly reduced, which caused the weight loss and the internal derangement of double Schottky barriers.

1. Introduction

ZnO-based varistors are ceramic resistor devices, which have been widely used in voltage stabilization, transient surge protection in electronic circuits and electrical power systems. They exhibit excellent nonlinear current-voltage (I - V) characteristics described by the relation $J = KE^\alpha$, where J is the electrical current density, E is the potential gradient, α is the nonlinear coefficient, and K is a constant that depends on the microstructure [1, 2].

Numerous researchers have studied the effects of processing and microstructure on electrical conduction in ZnO varistors [3–5]. The nonlinear current-voltage characteristic results from the formation of double Schottky type electrostatic barriers at the grain boundaries with characteristic voltage drops of 2–3 V per grain boundary [6]. The increase in conductivity has been attributed to the mechanism of depletion layer breakdown or electron tunneling, which is due to the lowering of the electrostatic barriers [7].

Most previous work on fabrication of ZnO varistors has based on traditional raw materials, which contain zinc oxide mixed with small amounts of other oxides. The samples are sintered at a high temperature about 1200°C [8, 9].

For the fabrication of high potential gradient varistors, one main method is to decrease the grain size [10]. However, the elevated temperature sintering process accelerates the growth of grain size. In order to reduce grain growth and maintain the high-field properties, rare-earth doping and low-temperature sintering are adopted. A lower temperature reduces the cost and is easier to be realized. The objective of this paper is to investigate the electrical properties of samples produced by this process, especially the potential gradient.

2. Experimental

Reagent-grade raw materials were used in proportions of (96.5 – X) mol% ZnO + 0.7 mol% Bi_2O_3 + 1.0 mol% Sb_2O_3 + 0.5 mol% Cr_2O_3 + 0.8 mol% Co_2O_3 + 0.5 mol% MnO_2 + X mol% Y_2O_3 , with X equal to 0 or 0.08. Instead of grinding for more hours with a conventional ball milling, raw materials were mixed by high-energy ball milling with stainless steel balls and ethanol in a nylon bottle for 5 h at 500 rpm. The mixture was dried at 120°C for 2 h and pulverized using an agate mortar/pestle. The powder samples were mixed with few drops of a binder addition of 2 wt% polyvinyl alcohol (PVA) and uniaxially pressed into discs of 10 mm in diameter

TABLE 1: Relative density of samples with different doping concentrations and sintering temperatures.

Groups	Doping concentration of Y_2O_3 (mol%)	Sintering temperature ($^{\circ}C$)	Relative density (%)
Sample 1	0.00	1200	96.37
Sample 2	0.08	1200	96.31
Sample 3	0.00	800	98.70
Sample 4	0.08	800	98.03

and 1 mm in thickness under 150 Mpa pressure. The green pellets were, respectively, sintered at 800 $^{\circ}C$ and 1200 $^{\circ}C$ for 2 h. The densities of the pellets were measured by Archimedes method. Silver paste was coated on both faces of the pellets and the ohmic contact of electrodes was formed by heating at 600 $^{\circ}C$ for 15 minutes. All samples were divided into four groups for investigation, as shown in Table 1.

The crystalline phases were identified by an X-ray diffraction (XRD, D/max 2550V) using a CuK_{α} radiation. The surface microstructure was examined by a scanning electron microscope (SEM, JSM-5610LV). The average grain size (D) was determined by the measurement on the micrographs with the linear intercept method using the following expression [11, 12]:

$$D = \frac{1.56L}{MN}, \quad (1)$$

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. The electrical properties of varistors were measured using a DC parameter instrument (CJ1001). The breakdown voltage (U_{1mA}) was measured at the current density of 1.0 mA/cm 2 and the potential gradient (E_{1mA}) was obtained by $E_{1mA} = U_{1mA}/d$, where d is the thickness of sample. The leakage current (I_L) was measured at the electrical field of 0.75 U_{1mA} and the nonlinear coefficient (α) was determined in the range of 1.0 mA/cm 2 to 10 mA/cm 2 in current density, according to the expression of $\alpha = 1/(\log E_{10mA} - \log E_{1mA})$. It also contained a built-in 1400 kV DC power supply so as to describe the I - V property.

3. Discussion of Results

Figure 1 shows the phase composition of four samples. It is observed that ZnO is the main phase and $Zn_7Sb_2O_{12}$ is the secondary phase in all the systems. However, one can also observe the presence of bismuth-rich phase for Sample 3 and Sample 4, and Y_2O_3 phase for Sample 4 only. This indicates that the additive Y_2O_3 after sintering at 1200 $^{\circ}C$ is forming a solid solution with ZnO according to the following equation:

As indicated in (2), the formation of solid solution in the ZnO lattices should increase the zinc vacancy concentration.

FIGURE 1: XRD data of the four samples.

These defects restrain the diffusion of electron through the lattices, decreasing α of the ceramic in a certain extent. The disappearance of bismuth-rich phase indicates that the Bi_2O_3 phase is bounded into other phases or volatilized badly at the sintering temperature of 1200 $^{\circ}C$, which is unfavorable to the nonlinearity. The decrease of relative density results also from the volatilization of Bi_2O_3 (see Table 1).

Microstructural observations show a significant influence of Y_2O_3 doping and sintering temperatures on the morphology of the ZnO grains and the distribution of the grain size. The ZnO grain size has an obvious decrease from 1.602 μm to 1.145 μm with Y_2O_3 doping (see Figures 2(c) and 2(d)) and from 3.377 μm to 1.145 μm with low-temperature sintering (see Figures 2(b) and 2(d)). Comparing with the conventional ZnO varistors [2, 8], the grain size of Sample 4 has been reduced by at least 50%. The temperature at which the liquid phase occurs is about 740 $^{\circ}C$. Much higher above this temperature, such as 1200 $^{\circ}C$, exaggerated grain growth occurs. Exaggerated grain growth results in a bimodal grain size distribution, with the small grains among the huge ones. Due to the exaggerated grain growth and the volatilization of Bi_2O_3 , Y_2O_3 doping nearly makes no difference on the microstructure of ZnO varistors during the high sinter temperature (see Figures 2(a) and 2(b)). The micrographs in Figure 2 also witness that the obtained Sample 4 is nanograined and contains the very developed free surfaces as well as grain boundaries. It has been demonstrated recently that the physical properties of nanograined ZnO, especially doped one, strongly depend on the presence of defects like grain boundaries and on the presence of amorphous surficial and intergranular layers [13, 14]. The crystalline ZnO grains of Sample 4 do not directly contact each other and are completely surrounded by a thin layer of material such as amorphous intergranular phase. It forms a kind of continuous foam-like network, where the amorphous intergranular

FIGURE 2: SEM images for (a) Sample 1, (b) Sample 2, (c) Sample 3, and (d) Sample 4.

TABLE 2: I_L , E_{1mA} , and α for the four samples.

Groups	I_L (μA)	E_{1mA} (V/mm)	α
Sample 1	396	114.7	3.0
Sample 2	355	193.7	3.6
Sample 3	16.4	1626.1	13.8
Sample 4	9.1	2247.2	23.0

phase amount could be increased by the decrease in grain size.

The electrical characterization of these samples normalized in potential gradient E (V/mm) as a function of current density J ($\mu A/mm^2$) is shown in Figure 3. The values of I_L , E_{1mA} , and α are presented in Table 2. Comparing with the other three samples, Sample 4 has the highest E_{1mA} (2247.2 V/mm) and α (23.0). The E_{1mA} value of most of the existing commercial ZnO varistors is below 2000 V/mm [3]. The potential gradient of Sample 4 has been increased at least 12%. Increasing the sintering temperature causes the grains to grow, and the electrical active grain boundaries decrease with the volatilization of Bi_2O_3 . A sharp rise in I_L , after sintering at 1200°C, is attributed to the lowering of the grain boundary barrier height with the disappear of bismuth-rich phase.

Some early researches about ZnO-based varistors report that the best nonlinear behavior is achieved between 1200°C and 1300°C. However, in the specific case of our varistors, the change in α with the sintering temperature, as shown

FIGURE 3: Partial I - V characteristics for the four samples.

in Figure 4, is related to the microstructural modifications associated with the reactions that occur during the liquid phase sintering. Higher sintering temperature makes the reactions more adequately, except the largely evaporation process of Bi_2O_3 . In the present varistor systems where no bismuth-rich phase is observed in Sample 1 and Sample 2,

FIGURE 4: Evolution of the nonlinear coefficient α as a function of sintering temperature.

this dependence would be related to the high-energy ball milling in the early period of experiment and the pinning effect of Y_2O_3 during the sintering process. High-energy ball milling induces the grain refinement, and the deliquescent Y_2O_3 particles between ZnO grains restrain the grain growth. Both of these realize the wetting of smaller grains at a relative lower temperature.

On the other hand, the ionic radius of Y^{3+} ($0.89\text{\AA}$) is larger than the ionic radius of Zn^{2+} ($0.74\text{\AA}$). It is difficult for Y^{3+} ions to solid dissolve into the grains at a lower temperature (800°C). Y^{3+} ions dissolve at the grain boundaries and exist in the forms of Y_2O_3 and/or other two crystal phases of Bi_3YO_6 and $Bi_{19}YO_{30}$ [15]. The equilibrium reactions occurred at the grain boundaries can be written (not observed in our experiment) as

The dissolved Y^{3+} ions have no effect on the lattice structure of ZnO. They form small particles at the edge of the grains and as a result pin the grains to restrict their growth. The decrease of the grain size directly induces the increase in the amount of grain boundaries, subsequently in E_{1mA} and α . At a higher temperature (1200°C), with the volatilization of Bi_2O_3 , the above-mentioned reaction processes do not occur, however, being substituted by the solid solution reaction according to (2). High sinter temperature makes the solid solution reaction occur easily. Y^{3+} ions act as acceptor ions, which make the resistance of grains rise, with the given experimental conditions of high-energy ball milling and low-temperature sintering. Additional vacancies (V_{Zn}'') are created with Y^{3+} ions solid dissolved into the ZnO grains. The volatilization of Bi_2O_3 causes the resistance of

grain boundaries to decrease. The reduction of differences in resistance between the grain boundaries and the grains accelerates the degeneration in nonlinear of the varistors (see Table 2).

With (2) proceed during the sintering process, more V_{Zn}'' and oxygen appear. The oxygen migrates away along the grain boundaries, which causes a significant rightward progress of (2). The shortage of oxygen makes the reaction occur during the cooling process as follows:

where O_{ad} is the adsorbed oxygen at the grain boundaries.

According to the model proposed by Gupta and Carlson [16], $V_O^{\cdot}$, V_O'' , $Zn_i^{\cdot}$, and Zn_i'' are the primary defects on the depletion layer. The donor levels of $V_O^{\cdot}$ and V_O'' are at 0.5 and $\sim 2\text{ eV}$ below the conduction band edge of ZnO, it is too large for O_{ad}'' to enter into the lattices of varistors to form O_O'' . Instead, a charge transfer occurs between the positively charged oxygen vacancy and the negatively charged adsorbed oxygen at the interface:

The reactions described above only contain the doubly charged ions, and a similar analogy can be written for the singly charged ions as well. With the loss of oxygen, the neutralisation of the ions on the depletion layer reduces the barrier height of double Schottky barrier and finally decreases the potential gradient of the varistors.

4. Conclusions

The ZnO varistors with ultrahigh potential gradient are prepared by rare-earth doping and low-temperature sintering. The origin for this is the great decrease of grain size. The experimental results indicate that the deliquescent Y_2O_3 particles between ZnO grains during the low-temperature sintering process restrain the grain growth and promote the electrical nonlinear. At a higher temperature, the decrease of potential gradient can be explained by the solid solution of Y^{3+} ions and the volatilization of Bi_2O_3 . The adsorbed O_{ad}'' ions at the grain boundaries induce the neutralisation of ions on the depletion layer and cause the barrier lowering, which also have an effect on the electrical properties of the varistors.

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