Effect of Ni_2O_3 Doping on the Electrical Properties and Intrinsic Defect Concentration of ZnO Varistor Ceramics

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Abstract. With the development of high voltage transmission, there is an urgent need to develop ZnO varistor ceramics with high anti-aging properties. The key is to manipulate the intrinsic defect concentration of ZnO varistor ceramics precisely. In this paper, ZnO varistor ceramics doped with different contents of Ni_2O_3 are taken to study the relationship between the microstructure and electrical properties, and the effect of ZnO varistor ceramics doped with different contents on intrinsic defect concentration is also considered. The results show that, best electrical performance is shown when the content of Ni_2O_3 is 1.2mol%, the electrical breakdown field $E_{1\text{mA}}$ is 356 V/mm, the nonlinear coefficient α reaches 32, and the leakage current I_L is 3.4 μs . While the amount of the doped Ni_2O_3 is more than 0.8mol%, a new phase of $\text{Co}_2\text{Cr}_5\text{Sb}_5\text{O}_4$ phase is observed from X-ray diffraction. The SEM micrographs showed that the average grain size decreased monotonously from 14.56 μm to 5.73 μm with the amount of the doped Ni_2O_3 increased. According to the results of dielectric spectroscopy, the intrinsic defect concentration increased with the contents of the doped Ni_2O_3 increased. The increase of Zinc interstitial is much greater than that of Oxygen vacancies, which is harmful to Long-term aging characteristics of ZnO varistor ceramics.

1 Introduction

ZnO varistor ceramics are widely used in the overvoltage protection of power systems, electronic devices and communication systems because of its excellent I-V characteristics and large energy absorption capacity[1-2]. It is generally believed that the nonlinearity of ZnO varistor ceramics results from Schottky Barrier[3]. The formation and degradation of the double Schottky barrier at the grain boundary of ZnO varistor ceramics and the barrier height, width and other important parameters are determined by the grain boundary depletion layer and the non-uniform distribution of point defects at the interface. In its dynamic process, the types of point defects include intrinsic point defects and extrinsic point defects, which together have a profound impact on the electron transport and relaxation process of the Schottky barrier. In addition, Intrinsic point defect plays a critical role in modern functional material, such as semiconductors, organic electronic devices, high-efficiency batteries and dielectric ceramics[4-7]. However, the drop in the height of the Schottky barrier at the grain boundary is the direct cause of the deterioration of the electrical properties of ZnO varistor ceramics. The main reason affecting its height is the migration of zinc interstitials and oxygen vacancies. When the zinc interstitials in the depletion layer move towards the grain boundary, the negative charge of the interface state is neutralized, resulting in a

decrease in the barrier height. Therefore, reducing the zinc interstitial concentration and increasing the oxygen vacancy concentration become critical. He[8] found that the appropriate concentration of Ni_2O_3 doping can help reduce the residual voltage ratio of ZnO varistor ceramics, and the nonlinear coefficient can reach up to 47.6. He[9] found that although Zr doping can reversely manipulate the intrinsic defect concentration, that is zinc interstitial concentration increased, the oxygen vacancy concentration reached up to the opposite direction, which resulted in bad aging performance. Moreover, there is a lack of relevant research on the effect of Ni_2O_3 doping on the intrinsic defect concentration.

In this paper, the solid-phase sintering was used to prepare ZnO- Bi_2O_3 series multi-element ceramic samples doped with different contents of Ni_2O_3 , and the effect of Ni_2O_3 doping on the microstructure, electrical properties and intrinsic defect structure of ZnO varistor ceramics was studied.

2 Experiments

In this paper, ZnO- Bi_2O_3 varistor ceramics doped with four different contents of Ni_2O_3 were prepared by solid-phase. The formulation includes ZnO, Bi_2O_3 , Co_2O_3 ,

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Sb_2O_3 , MnO_2 , Cr_2O_3 and $x\text{Ni}_2\text{O}_3$ ($x=0$ mol%, 0.4 mol%, 0.8 mol% and 1.2 mol%). First of all, put the configured powder and an appropriate amount of deionized water into a polyamides bottle and ball milling for 12 h and add a concentration of 2 wt% polyvinyl alcohol solution (PVA) and drying treatment. The powder was pressed into green discs of 14 mm in diameter and 1.3 mm in thickness. In the last, the discs were placed in the sintering furnace and sintered in the air at 1200 °C for 2 h, the heating rate was 150 °C/h, and the cooling rate is 100 °C/h ($\phi \approx 12$ mm, $d \approx 1$ mm).

The voltage source used to measure the low current I-V characteristics of the sample is WJ10001D precision linear high-voltage DC power, and the instrument used to measure the current is HP 34401A multi-meter. The electrical breakdown field of the sample is $E_{1\text{mA}} = U_{1\text{mA}}/d$, where $U_{1\text{mA}}$ is the voltage when the current is 1 mA, d is the thickness of the sample, and the nonlinear coefficient is defined as:

$$\alpha = \frac{\log I_2 - \log I_1}{\log U_2 - \log U_1} \quad (1)$$

In the formula, U_1 and U_2 are the voltage values when the current is at I_1 and I_2 respectively, $I_1=0.1$ mA, $I_2=1.0$ mA.

In order to analyze the crystalline phase of the sample, X-ray diffraction (XRD: d8 advanced 3.0) was used. The surface microstructure images were conducted by a scanning electron microscopy (SEM: VE-9800S). The broadband dielectric spectrum test system (Novocontrol) produced in Germany was used to measure the dielectric properties of the sample at a temperature of -110 °C ~ -60 °C, an interval of 10 °C, and a frequency of $10^{-1} \sim 10^7$ Hz.

3 Results and discussion

The electrical properties of the ZnO varistor ceramic samples doped with different contents of Ni_2O_3 are shown in Figure 1. With the amount of the doped Ni_2O_3 increased, the electrical breakdown field $E_{1\text{mA}}$ rises from 185 V/mm to 356 V/mm. The reason of $E_{1\text{mA}}$ increased may be related to the spinel phase formed at the grain boundaries, the spinel phase inhibits the growth rate of the crystal grains, led to a decline in the size of the grains. Therefore, the number of grain boundaries per unit thickness raises, which makes the electrical breakdown field increase; the nonlinear coefficient α first decreases and then rises, and reaches up to 32 when the content of Ni_2O_3 is 1.2 mol%; however, the leakage current I_L show an opposite trend with α .

Figure 1. Electrical properties of ZnO samples doped with different contents of Ni_2O_3 .

The XRD patterns of the ZnO varistors doped with different contents of Ni_2O_3 are shown in Figure 2. As shown in the figure, all samples include ZnO main crystalline phase and Bi_2O_3 phase, but when Ni_2O_3 doping concentration is 0.0 mol% and 0.4 mol%, the ZnO sample generates $\text{Co}_7\text{Sb}_2\text{O}_{12}$ phase, when the Ni_2O_3 doping concentration was 0.8 mol% and 1.2 mol%, the ZnO sample formed $\text{Co}_2\text{Cr}_5\text{Sb}_5\text{O}_4$ phase. And the peak intensity of the main crystalline phase of ZnO gradually decreases with the contents of doped Ni_2O_3 augmented.

Figure 2. XRD patterns of ZnO samples doped with different contents of Ni_2O_3 .

Figure 3 and figure 4 show the calculation results of the micro morphology and average grain size of the samples doped with different contents of Ni_2O_3 . We can draw conclusion that the microscopic morphology of samples mainly includes ZnO grains, pores and bismuth-rich phases. The grain size decreases from 14.56 μm to 5.73 μm with the amount of the doped Ni_2O_3 increased, indicating that Ni_2O_3 doping restrained grain growth.

Figure 3. The SEM image of ZnO samples doped with different contents of Ni_2O_3 .

Figure 5 is the dielectric spectrum of the samples doped with 0.4 mol% Ni₂O₃ at different temperatures in the frequency range of 10⁻¹~10⁷ Hz. And figure 6 is the simulation of ϵ'' spectroscopy of samples based on Cole-Cole equation at -110 °C. It can be seen from Figure 5 that there are relaxation peaks at low frequency and high frequency respectively, and the peak position moves toward the high temperature and high frequency direction, which is a typical Debye relaxation process, and after calculating the activation energy, that is 0.29 eV and 0.19 eV from low frequency to high frequency respectively, which corresponds to oxygen vacancies and zinc interstitials. And the dielectric loss rises sharply in high frequency. It can be known from the literature that the process may be caused by the Maxwell-Wager effect[10], which is closely related to the resistance of the crystal grains and grain boundaries.

Figure 7 and Figure 8 are the variation trend of the correlation coefficients of the intrinsic defect concentration with the amount of doped Ni₂O₃ increased. As the doping contents of Ni₂O₃ increases, the zinc interstitial concentration and the oxygen vacancy concentration both augment, and the rising amplitude of the zinc interstitial concentration is greater than the oxygen vacancy concentration. Therefore, K1 /K2 decreases monotonously with the amount of doped Ni₂O₃ increased.

4 Conclusion

In this paper, a solid-phase sintering was used to prepare ZnO varistors ceramics doped with different contents of Ni₂O₃. The effect of Ni₂O₃ doping on the microstructure, electrical properties and intrinsic defect concentration of ZnO varistor ceramics was studied. Studies have shown that Ni₂O₃ will inhibit the growth of grains. The most excellent electrical performance is presented when the content of Ni₂O₃ is 1.2 mol%. Dielectric spectroscopy studies have shown that ZnO samples doped with Ni₂O₃ will not affect the intrinsic defect energy level, but will increase the zinc interstitial and oxygen vacancy concentration in the same direction, and the amplitude of zinc interstitial concentration is much greater than that of the oxygen vacancy concentration, which is not conducive to the long-term stability of ZnO varistor ceramics.

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