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Research Article

Microstructure and Nonohmic Properties of SnO_2-Ta_2O_5-ZnO System Doped with ZrO_2

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The microstructure and nonohmic properties of SnO_2-Ta_2O_5-ZnO varistor system doped with different amounts of ZrO_2 (0–2.0 mol%) were investigated. The proposed samples were sintered at 1400°C for 2 h with conventional ceramic processing method. By X-ray diffraction, SnO_2 cassiterite phase was found in all the samples, and no extra phases were identified in the detection limit. The doping of ZrO_2 would degrade the densification of the varistor ceramics but inhibit the growth of SnO_2 grains. In the designed range, varistors with 1.0 mol% ZrO_2 presented the maximum nonlinear exponent of 15.9 and lowest leakage current of 110 $\mu A/cm^2$, but the varistor voltage increased monotonously with the doping amount of ZrO_2.

1. Introduction

SnO_2 varistors are semiconducting ceramic devices, which possess nonlinear voltage-current characteristics due to their grain boundary effects formed commonly by sintering SnO_2 powder with minor additives (impurity). Due to their excellent energy handling capabilities, they can be applied extensively to protect electronic circuits, various semiconductor devices, and electric power systems from dangerous abnormal transient overload [1, 2].

The first impurity-doped SnO_2 varistor was reported by Glot and Zlobin [3], and Pianaro et al. also made great contributions to the knowledge of varistor behavior of impurity-doped SnO_2 ceramics [4]. Through a series of studies on SnO_2-based varistors for decades, it is well known that an excellent SnO_2 varistor system consists of three kinds of dopants: resistance reducers (varistor forming oxide, VFO), densifiers, and modifiers, respectively [5]. To date, the commonly applied VFOs are Nb^{5+} [6–8] or Ta^{5+} [9–11], which possesses high chemical valence and is soluble in SnO_2 grains to decrease the grain resistivity; the densifier is insoluble ion of low chemical valence that will segregate at SnO_2 grain boundary regions to promote the densification by producing oxygen vacancies, for example, Co^{2+} [4, 6, 7, 9, 11], Mn^{2+} [12, 13], and Zn^{2+} [8, 14], and the modifiers can effectively improve the electrical properties of the varistors, such as Cr^{3+}, Fe^{3+}, Cu^{2+}, and rare earth elements [6–9, 15, 16].

Moreover, during modern ceramics processing, high energy attrition milling and ZrO_2 grinding media were often applied. As a result, Zr^{4+} contamination in ceramic samples is a common phenomenon. However, up to now, no literature about the role of Zr^{4+} ion (ZrO_2) in SnO_2-based varistors has been reported.

Recently, we optimized a SnO_2-Ta_2O_5-ZnO varistor system, which presents varistors of good nonlinear properties but very low varistor voltage [17]. Based on it, in the present study, SnO_2-Ta_2O_5-ZnO-based varistor system was doped with ZrO_2 (0–2.0 mol%), and the effect of ZrO_2 doping on the microstructure and nonohmic properties of SnO_2-Ta_2O_5 based varistors was investigated. To our surprise, varistors with fully dense structure and high breakdown voltage could be obtained.

2. Experimental Procedure

2.1. Sample Preparation. The samples were prepared using a conventional ceramic processing method with a nominal

composition of (99.45-x) mol% SnO_2 + 0.05 mol% Ta_2O_5 + 0.5 mol% ZnO + x mol% ZrO_2 (x = 0, 0.25, 0.5, 1.0, 2.0). All the oxides were raw powders of analytical grade. At beginning, the raw powders were mixed in deionized water and ball-milled in polyethylene bottle for 24 h with 0.5 wt% of PVA as binder and highly wear-resistant ZrO_2 balls as grinding media. Subsequently, the obtained slurries were dried at 110°C in an open oven. After drying, the powder chunks were crushed into fine powders, sieved, and pressed into pellets of 6 mm in diameter and 1.5 mm in thickness under a pressure of 40 MPa. Then, the pressed pellets were sintered at 1400°C for 2 h in a Muffle oven by heating at a rate of 300°C/h and cooling naturally. To measure the electrical properties, silver electrodes were prepared on both surfaces of the sintered disks by heat treatment at 500°C for half an hour.

2.2. Materials Characterization. The density of the samples was measured by Archimedes method according to international standard (ISO18754). Their crystalline phases were identified by X-ray diffractometer (XRD, D/max2550HB+/PC, Cu Kα, and λ = 1.5418 Å) through a continuous scan mode with speed of 8°/min. The microstructure was examined on the fresh fracture surfaces of the samples via a scanning electron microscope (SEM, Tescan XM5136). And the average size of SnO_2 grains in the samples was determined using linear intercept method from the SEM images.

A high-voltage source measurement unit (Model: CJ1001) was used to record the characteristics of the applied electrical field versus current density (E-J) of the samples. The varistor voltage (V_B) was determined at 1 mA/cm^2 and the leakage current (I_L) was the current density at 0.75V_B. Then, the nonlinear coefficient (α) was obtained by the following equation:

$$\alpha = \frac{\log\left(J_2/J_1\right)}{\log\left(E_2/E_1\right)} = \frac{1}{\log\left(E_2/E_1\right)}, \quad (1)$$

where E_1 and E_2 are the electric fields corresponding to J_1 = 1 mA/cm^2 and J_2 = 10 mA/cm^2, respectively.

3. Results and Discussion

3.1. Composition and Microstructure. Figure 1 illustrates the XRD patterns of the as-prepared SnO_2-Ta_2O_5-ZnO-based varistor ceramics doped with different amounts of ZrO_2. All the sharp diffraction peaks were assigned, corresponding to the (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202), and (321) reflections of SnO_2 cassiterite phase (JCPDS card no. 77-0451). No extra phases were identified, possibly because the doping levels of the additives were too low to be detected in XRD limits. And, because of the same ionic valence and almost no radius difference between Sn^{4+} (0.071 nm) and Zr^{4+} (0.072 nm) ions, the doped ZrO_2 is fully soluble in SnO_2 lattice, which can be seen from almost the same positions of XRD diffraction peaks of the prepared samples as shown in Figure 1(b) in a close view to the patterns in 2θ from 50 to 55°. As for the splitting of the XRD peaks in the figure, it might be due to the peak doublet of K-alpha 1 and K-alpha 2.

SEM images of the as-prepared SnO_2-Ta_2O_5-ZnO based varistor ceramics also confirmed the solubility of ZrO_2 into SnO_2 lattice (please see Figure 2). The images reveal that, although doped with different amounts of ZrO_2, the typical microstructure of the samples almost has no change: almost fully dense structure of SnO_2 grains without any obvious second phases. The detailed microstructural parameters are also summarized in Table 1. With increasing doping amount of ZrO_2, the density of samples decreases in a very narrow range from 6.93 to 6.80 g/cm^3 partly because the density of ZrO_2 (5.89 g/cm^3) is lower than that of the matrix SnO_2 (6.95 g/cm^3), but the relative density of the samples also decreases although also in a very narrow range from 99.8% to 98.2%, which indicates a decreased sample densification and could be attributed to the lower diffusion ability of solid ZrO_2 particles in SnO_2 matrix at the designed sintering temperature because the melting point of ZrO_2 (2680°C) is much higher than that of SnO_2 (1630°C). Moreover, from these SEM images, it can be clearly seen that, with increasing ZrO_2 contents in the ceramics, the average size of SnO_2 grains decreases, which might be owing to the inhibited transportation of SnO_2 during sintering by the doped ZrO_2 with lower diffusion ability.

3.2. Electrical Properties. The E-J characteristics of the as-prepared SnO_2-Ta_2O_5-ZnO-based ceramic varistors doped with different contents of ZrO_2 are illustrated in Figure 3, and their corresponding detailed electrical parameters calculated from the E-J curves are listed in Table 1.

The results indicate that, with increasing doping content of ZrO_2 up to 1.0 mol%, the nonlinear coefficient of the samples increased up to 15.9, possibly owing to the increased carrier concentration in the varistors, decreased electrical resistivity of SnO_2 grains and thus enhanced barrier height by doping, and higher number of voltage barriers due to the decrease in grain size, but it would drop down with more ZrO_2 doped, due to the corresponding less dense sample structure, degraded effective grain boundary, destroyed depletion layer structure, and thus decreased barrier height. The leakage current of the samples presented an opposite trend to that of nonlinear coefficient with ZrO_2 doping, and the varistors with 1 mol% ZrO_2 presented the lowest leakage current, 110 μA/cm^2, which is completely consistent with classic theory on their relationship [18]. Thus, it can be concluded that the optimum doping amount of ZrO_2 in the proposed SnO_2-Ta_2O_5-ZnO-based ceramic varistor system was 1 mol%. The varistor voltage of the samples increased monotonously with the doping amount of ZrO_2, which could be mainly attributed to the decreased SnO_2 grain size, thus increasing the number of grain boundary in unit thickness after doping.

4. Conclusions

SnO_2-Ta_2O_5-ZnO varistors doped with different amounts of ZrO_2 (0–2.0 mol%) were prepared by sintering at 1400°C

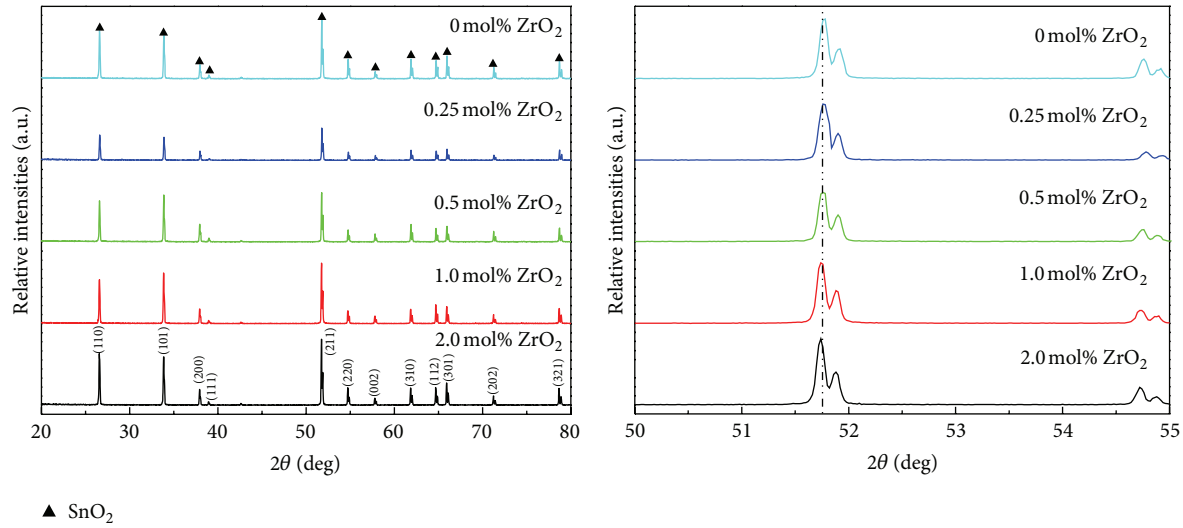

Figure 1: XRD patterns of the as-prepared SnO_2-Ta_2O_5-ZnO-based varistor ceramics doped with different amounts of ZrO_2: (a) five of the samples and (b) magnified view in 2θ region of 50–55°.

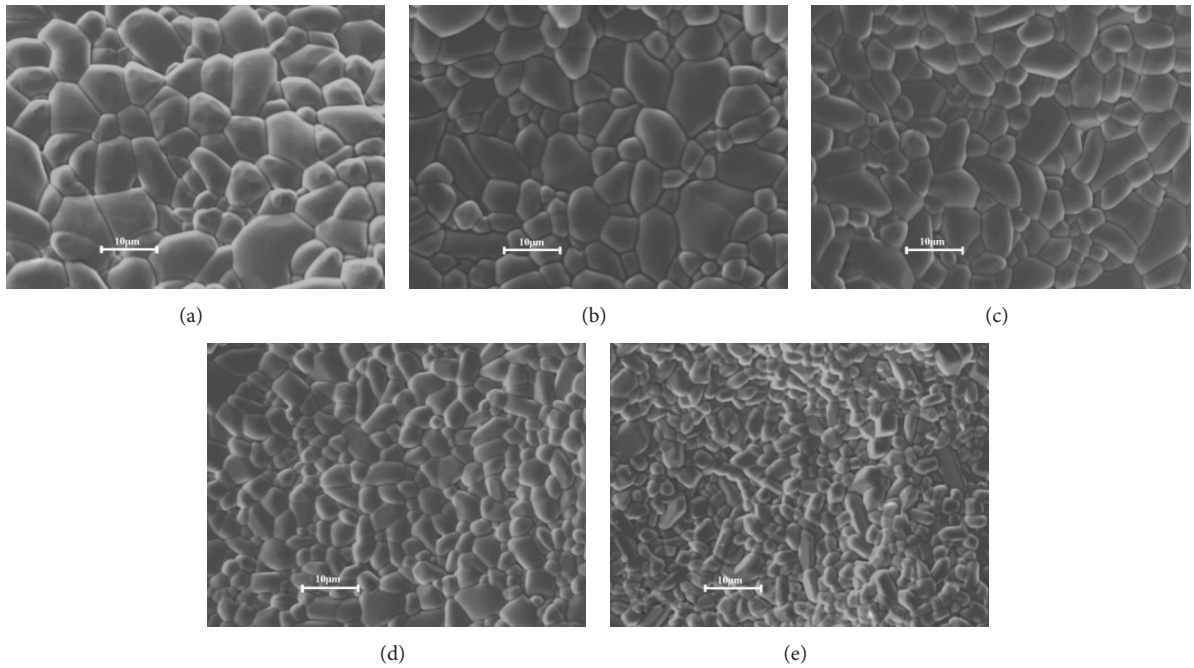

Figure 2: Typical SEM images on fracture surfaces of the as-prepared SnO_2-Ta_2O_5-ZnO-based varistor ceramics doped with different amounts of ZrO_2: (a) undoped, (b) 0.25, (c) 0.5, (d) 1.0, and (e) 2.0 mol%.

Table 1: Basic physical parameters of SnO_2-Ta_2O_5-ZnO varistor ceramics doped with different contents of ZrO_2.

Doping amount of ZrO_2 (mol)	Apparent density (g/cm^3)	Relative density (%)	SnO_2 grain size (μm)	α	V_B (V/mm)	I_L ($\mu A/cm^2$)
0	6.93	99.8	7.87	4.6	81	660
0.25	6.89	99.2	6.67	6.0	103	560
0.5	6.88	99.1	5.45	8.2	250	220
1.0	6.84	98.6	4.55	15.9	500	110
2.0	6.80	98.2	3.03	11.6	720	170

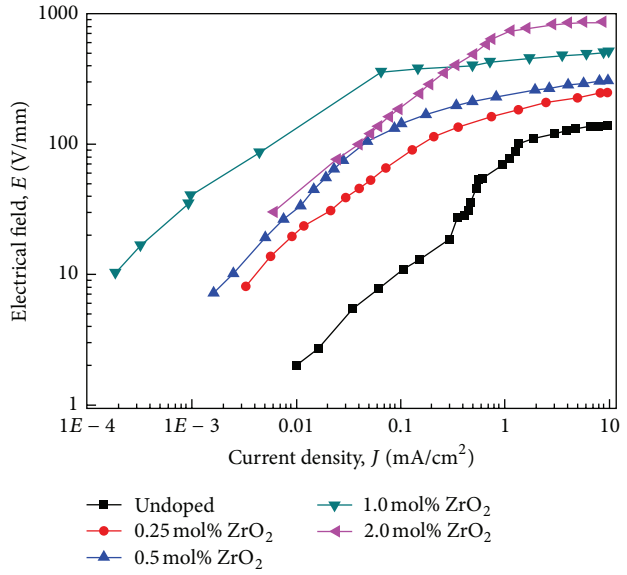

FIGURE 3: *E-J* characteristic curves on a log scale at room temperature of the as-prepared SnO_2-Ta_2O_5-ZnO-based varistors doped with different contents of ZrO_2.

for 2 h with conventional ceramic processing method. The doping of ZrO_2 would degrade the densification of the varistor ceramics, but inhibit the growth of SnO_2 grains. In the designed range, varistors with 1.0 mol% ZrO_2 presented the maximum nonlinear exponent of 15.9 and lowest leakage current of 110 μA/cm^2; but the varistor voltage increased monotonously with the doping amount of ZrO_2.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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