Research Article

Microstructure and Nonohmic Properties of SnO$_2$-Ta$_2$O$_5$-ZnO System Doped with ZrO$_2$

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The microstructure and nonohmic properties of SnO$_2$-Ta$_2$O$_5$-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 μA/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$_2$O$_5$-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$_2$O$_5$-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$_2$O$_5$ 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% SnO₂ + 0.05 mol% Ta₂O₅ + 0.5 mol% ZnO + x mol% ZrO₂ (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 ZrO₂ balls as grinding media. Subsequently, the obtained slurrys 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/max2550 HB+/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 SnO₂ grains in the samples was determined using linear intercept method from the SEM images.

A high-voltage source measurement unit (Model: CJI001) was used to record the characteristics of the applied electrical field versus current density (E-J) of the samples. The varistor voltage (Vₐ) was determined at 1 mA/cm² and the leakage current (Iₙ) was the current density at 0.75Vₐ. Then, the nonlinear coefficient (α) was obtained by the following equation:

\[ α = \frac{\log (I₂/I₁)}{\log (E₂/E₁)} = \frac{1}{\log (E₂/E₁)}, \]  

where \( E₁ \) and \( E₂ \) are the electric fields corresponding to \( I₁ = 1 \) mA/cm² and \( I₂ = 10 \) mA/cm², respectively.

3. Results and Discussion

3.1. Composition and Microstructure. Figure 1 illustrates the XRD patterns of the as-prepared SnO₂-Ta₂O₅-ZnO-based varistor ceramics doped with different amounts of ZrO₂. 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 SnO₂ 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 Sn⁴⁺ (0.071 nm) and Zr⁴⁺ (0.072 nm) ions, the doped ZrO₂ is fully soluble in SnO₂ 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 SnO₂-Ta₂O₅-ZnO based varistor ceramics also confirmed the solubility of ZrO₂ into SnO₂ lattice (please see Figure 2). The images reveal that, although doped with different amounts of ZrO₂, the typical microstructure of the samples almost has no change: almost fully dense structure of SnO₂ grains without any obvious second phases. The detailed microstructural parameters are also summarized in Table 1. With increasing doping amount of ZrO₂, the density of samples decreases in a very narrow range from 6.93 to 6.80 g/cm³ partly because the density of ZrO₂ (5.89 g/cm³) is lower than that of the matrix SnO₂ (6.95 g/cm³), 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 ZrO₂ particles in SnO₂ matrix at the designed sintering temperature because the melting point of ZrO₂ (2680°C) is much higher than that of SnO₂ (1630°C). Moreover, from these SEM images, it can be clearly seen that, with increasing ZrO₂ contents in the ceramics, the average size of SnO₂ grains decreases, which might be owing to the inhibited transportation of SnO₂ during sintering by the doped ZrO₂ with lower diffusion ability.

3.2. Electrical Properties. The E-J characteristics of the as-prepared SnO₂-Ta₂O₅-ZnO-based ceramic varistors doped with different contents of ZrO₂ 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 ZrO₂ 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 SnO₂ 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 ZrO₂ 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 ZrO₂ doping, and the varistors with 1 mol% ZrO₂ presented the lowest leakage current, 110 μA/cm², which is completely consistent with classic theory on their relationship [18]. Thus, it can be concluded that the optimum doping amount of ZrO₂ in the proposed SnO₂-Ta₂O₅-ZnO-based ceramic varistor system was 1 mol%. The varistor voltage of the samples increased monotonously with the doping amount of ZrO₂, which could be mainly attributed to the decreased SnO₂ grain size, thus increasing the number of grain boundary in unit thickness after doping.

4. Conclusions

SnO₂-Ta₂O₅-ZnO varistors doped with different amounts of ZrO₂ (0–2.0 mol%) were prepared by sintering at 1400°C
Figure 1: XRD patterns of the as-prepared SnO$_2$-Ta$_2$O$_5$-ZnO-based varistor ceramics doped with different amounts of ZrO$_2$: (a) five of the samples and (b) magnified view in 2$\theta$ region of 50–55$^\circ$.

Figure 2: Typical SEM images on fracture surfaces of the as-prepared SnO$_2$-Ta$_2$O$_5$-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$_2$O$_5$-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 ($\mu$m) | $\alpha$ | $V_B$ (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$_2$O$_5$-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 $\mu$A/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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