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Ge-added TiO_2–Ta_2O_5–$CaCO_3$ varistor ceramics

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Abstract

The influence of doping with Ge on the nonlinear coefficient α and the breakdown electric field E_B of TiO_2–Ta_2O_5–$CaCO_3$ varistor ceramics was investigated. In this study, TiO_2–Ta_2O_5–$CaCO_3$ varistor ceramics added with Ge was successfully prepared using the traditional method of ball milling–molding–sintering. The electrical performance, including the nonlinear coefficient α, the breakdown electric field E_B, and the leakage current J_L, are tested using a varistor direct current parameter instrument. The average barrier height Φ_B of each sample is calculated using the relevant formula. X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and scanning transmission electronic microscopy analyses demonstrated that Ge doping notably changed the microstructure of TiO_2–Ta_2O_5–$CaCO_3$ ceramics, thereby increasing α and decreasing E_B. When the doping contents of Ta_2O_5 and $CaCO_3$ were 0.2 and 0.4 mol%, respectively, the optimum doping content of 0.9 mol% Ge exhibited high α (10.2), low E_B (14.1 V mm^{-1}), and high Φ_B (0.95 eV). These results are superior to previous findings. In addition, Ge as sintering aid reduced the sintering temperature caused by the low melting point. The optimal sintering temperature was 1300 °C for the TiO_2–Ta_2O_5–$CaCO_3$ ceramics doped with Ge.

Keywords: TiO_2 varistor; Liquid-phase sintering; Nonlinear coefficient; Breakdown voltage; Ge

1. Introduction

A varistor is a typical electronic device fabricated from ceramics with nonlinear electrical property; this device is widely used for over-voltage protection, high-voltage stabilization, and high-energy surge absorption [1]. Varistor ceramics are characterized by nonlinear current–voltage (J–V), which can be expressed as follows:

$$J = (kE)^{\alpha} \quad (1)$$

where k is a dimensionless constant that depends on the microstructure and α is the nonlinear coefficient obtained by using the following formula:

$$\alpha = \log(I_2/I_1)/\log(V_2/V_1) = 1/\log(V_{1mA}/V_{0.1mA}) \quad (2)$$

where V_1 and V_2 are the voltage values at current values I_1 and I_2, respectively. Higher α value indicates better nonlinear material property. The nonlinear property of a given varistor depends on the potential barriers between crystalline grains of the polycrystalline ceramic [2]. Compared with ZnO- and SnO_2-based varistors, TiO_2-based varistors offer higher capacitance, lower breakdown electric field (E_B), and relatively simpler preparation process [3–6]. Thus, TiO_2-based varistors are suitable for protection of miniature circuits and high-density integrated circuits, as well as present favorable potential [7–10]. However, the practical applications of these varistors are limited by their low α values. Since the discovery of TiO_2-based varistors in Bell Labs in 1982 [11], researchers have expended much effort to improve α. Yan and Rhodes

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[12] first reported that (Nb, Ba)-doped TiO_2 ceramics exhibit useful varistor properties, with low α values of 3–4 and an oxidizing atmosphere requirement during cooling. Wu and Lai [13] found that adding PbO to Nb-doped TiO_2 varistors creates an effective grain boundary barrier (Φ_B) of approximately 0.70 eV and yields a maximum α of 7.6. Yang and Wu [14] studied the effect of Nb_2O_5 on a (Ba, Bi, Nb)-added TiO_2 ceramic varistor. Adding both Ba and Bi on Nb-doped TiO_2 ceramics at 1350 °C creates an efficient grain boundary barrier layer with $\alpha=9.5$, $V_{gb}=0.8$ V, and $\Phi_B=0.42$ eV. Li et al. [15] studied the effect of sintering temperature on the electrical properties of TiO_2-based capacitor varistors. The varistor with a 99.30% $TiO_2 \cdot 0.60\%$ $Y_2O_3 \cdot 0.10\%$ Nb_2O_5 composite sintered at 1400 °C exhibits a maximal α of 7.8. Su et al. [16] investigated the nonlinear electrical behavior and dielectric properties of TiO_2-based ceramics with various WO_3 contents. Their results showed that a 0.25% $WO_3 \cdot 99.75\%$ TiO_2 composite exhibits an optimal α of 9.6 and E_B of 44.5 V mm^{-1}. Sousa et al. [17] recently obtained a maximum α of 5.6 from (Ta, Co, Pr)-doped TiO_2-based varistor ceramics through conventional oxide mixing and sintering at 1400 °C. Ghafouri et al. [18] studied the effect of Si content on the electrophysical properties of Si-polymer composite varistors. They reported that adding 70% Si produces a varistor with $\alpha=10.45$, $\Phi_B=0.133$ eV, and $E_B=60$ V mm^{-1}. Zhao et al. [19] studied the influence of Ta_2O_5 doping and microwave sintering on TiO_2-based varistor properties. Their findings showed that microwave sintering increases α from 6.45 to 8.89 as the doping content increases from 0.05% to 0.075%; subsequently, α decreases to 4.87 as the doping content further increases to 0.15%. In the present study, Ge doping was adopted to improve the a and decrease the E_B of a TiO_2-based varistor. The effects of doping with Ge on the α and E_B values of TiO_2–Ta_2O_5–$CaCO_3$ varistors were investigated.

Ge is an excellent semi-conductor with low melting point. The resultant GeO_2, which is also an excellent semi-conductor, appears in the sample during sintering. GeO_2 easily dissolves in TiO_2 lattice because of the same valence state and the slightly smaller radius of Ge^{4+} compared with Ti^{4+}. This feature improves the semiconducting degree of grains and decreases E_B. In addition, liquid-phase sintering caused by the low melting point of Ge may present certain advantages to sintering conditions and improve α value.

2. Experimental details

Table 1 shows the nominal content of the samples. Four samples were analyzed for each component, and each parameter of each component was an average of four samples with the same component. Based on the optimization results, the contents of Ta_2O_5 and $CaCO_3$ were 0.2 and 0.4 mol%, respectively. The reaction powder was obtained through the conventional ball mill mixing method using the following powder (in mol%): $(99.4-x)$ TiO_2 (99.9%), 0.2 Ta_2O_5 (99.99%), 0.4 $CaCO_3$ (99.99%), x (x=0, 0.1, 0.3, 0.6, 0.9, 1.2, 1.5) Ge (99.99%). The starting materials were mixed for 8 h in a ball mill at a mass ratio of 1:2:3 of powder to water mixed with alcohol (water:alcohol=4:1) to balls. After homogenization, each blend was oven-dried at 80 °C for 12 h and then de-agglomerated with a 420-mesh sieve. The obtained powder was isostatically pressed at 150 MPa into tablets (10 mm in diameter and 1 mm in thickness). The tablets were degummed at 600 °C for 0.5 h in a box-type resistance furnace and then sintered at 1200, 1250, 1300, 1350, or 1400 °C for 3 h in a tube furnace. Afterward, the tablets were cooled to room temperature via furnace cooling. The density and relative density of each pellet were obtained using the Archimedes method. The average grain size Dg of each sample was calculated using the scanning electron microscopy (SEM) scale. To characterize the electrical properties after slight polishing, we deposited silver electrodes on the two surfaces of sintered pellets and heat-treated at 600 °C for 15 min to ensure fixation. The varistor properties of the pellets were evaluated by measuring α, E_B, and the leakage current J_L by using a varistor direct current parameter instrument that is used to characterize the electrical performance of a varistor. The Φ_B of each sample was calculated using the following formula

Table 1
Doping contents of samples.

Sample	Doping content (mol%)		
	Ta_2O_5	$CaCO_3$	Ge
1	0.2	0.4	0
2	0.2	0.4	0.1
3	0.2	0.4	0.3
4	0.2	0.4	0.6
5	0.2	0.4	0.9
6	0.2	0.4	1.2
7	0.2	0.4	1.5

$$J = A^{*}T^{2}\exp\left[(\beta E^{1/2}-\varphi_B)/kT\right] \quad (3)$$

where A^* is the Richardson constant, K is the Boltzmann constant, T is the absolute temperature, and Φ_B is the interface barrier height. Φ_B and β were calculated by measuring the current density in the Ohmic region and maintaining the temperature of the tested varistor constant for two applied fields.

Our previous research showed that a 3 h sintering time is sufficient to complete various reactions, mass transport, and grain growth. Thus, in the present study, we sintered samples 1, 2, 3, and 4 for 3 h at different temperatures (1200–1400 °C) with a step value of 50 °C. We then measured the α and E_B of the samples to determine the optimal sintering temperature. Sample 1 presented no α value at sintering temperature <1300 °C. However, the α value of sample 2 was 6.1 at sintering temperature of 1250 °C, and those of samples 3 and 4 were 5.7 and 5.9, respectively, at sintering temperature of 1200 °C. The α value increased with increasing sintering temperature below 1300 °C for samples 2, 3, and 4. These results suggest that doping with Ge reduced the sintering temperature to obtain an α value that characterizes the nonlinear property of a varistor. Table 2 shows the variable