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Varistor and dielectric properties of Cr_2O_3 doped SnO_2–Zn_2SnO_4 composite ceramics

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ABSTRACT

Cr_2O_3 doped SnO_2–Zn_2SnO_4 composite ceramics were prepared by traditional ceramic processing and the varistor, dielectric properties were investigated. With increasing Cr_2O_3 content, the breakdown electrical field E_B increases from 11 to 92 V/mm and the relative dielectric constant ε_r measured at 1 kHz, 50 °C decreases from 11,028 to 3412, respectively. The barrier height ϕ_B about 0.8–0.84 eV and the decreasing of SnO_2 grain size suggest that the varistor behavior with high ε_r is originated from SnO_2–SnO_2 or SnO_2–Zn_2SnO_4 grain boundary. In the dielectric spectra lower than 1 kHz, a dielectric peak is presented and depressed with increasing bias voltage. Similarly, at high temperature, the dielectric constant also presents a dielectric peak in the temperature spectra and the peak becomes faint with increasing frequency. The exhibition of the dielectric peak is thought to be attributed to the conduction of grain boundary since it is accompanied by the sharp increase of dielectric loss. In addition, a dielectric relaxation with the activation energy about 0.4–0.5 eV was observed in the temperature range of 20–100 °C. Based on the results, the formation mechanism of Schottky barriers at grain boundaries and the varistor behavior with high dielectric constant are well understood.

1. Introduction

A varistor is a voltage-dependent resistor whose primary function is to sense and limit transient-voltage surges and hence, protect sensitive-state components. With the miniaturization and integration of electronic devices, varistor materials of multiple properties have attracted much attention for both scientific understanding and their numerous technological applications. For example, varistors with low breakdown voltage and high permittivity can be used as protectors to absorb the sparks in electrical micro-machines. Such typical and widely studied varistor materials are $SrTiO_3$ and TiO_2 ceramics [1–6]. In 2005, we discovered that without any doping, the composite SnO_2–ZnO ceramics have electrical properties similar to $SrTiO_3$ and TiO_2 varistors [7]. Further study revealed that the varistor behavior is also a grain boundary barrier effect and ZnO has synthesized with SnO_2 during sintering, virtually, the composite ceramics are composed of SnO_2, Zn_2SnO_4 [8]. Recently, we found that the oxygen vacancies are the key factor to the formation of grain boundary barriers [9]. However, the electrical properties of SnO_2 and Zn_2SnO_4 grains, the original mechanisms of the varistor and high permittivity behavior are not clearly understood up to now. For SnO_2 and ZnO ceramics, the varistor properties can be greatly improved by doping Cr_2O_3 [10–13] and in this paper, the varistor and dielectric properties of Cr_2O_3 doped SnO_2–Zn_2SnO_4 composite ceramics were investigated.

2. Experimental procedure

The ceramic samples with the compositions 0.8 mol SnO_2 + 0.2 mol Zn_2SnO_4 + x mol% Cr_2O_3 (x = 0, 0.02, 0.04, 0.06, 0.08) were prepared using analytical grades of SnO_2, ZnO and Cr_2O_3. Zn_2SnO_4 was synthesized using SnO_2 and ZnO powders at 1000 °C for 1 h. The chemicals were mixed in a nylon bottle for 12 h using ZrO_2 milling media in distilled water. The dried powders were mixed with 6% weight of polyvinyl alcohol (PVA) binder and pressed into 15 mm diameter disks with 1.5 mm thickness at 200 MPa. After burning out the PVA binder at 650 °C for 2 h, the disks were sintered at 1400 °C for 1 h. To measure the electrical

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properties, silver electrodes were made on both surfaces of the sintered disks.

The microstructure of the sample surfaces was analyzed by scanning electron microscopy (SEM) (JSM-5900). For the measurement of electrical characterization of current density versus applied electrical field, Source Meter (Keithley 2410) was used. The permittivity spectra were measured from 40 Hz to 1 MHz with a bias voltage varied from 0 to 40 V by the impedance analyzer (Agilent 4294A). The temperature spectra of the dielectric properties were measured during the temperature range of 18–350 °C from 10^2 to $10^{5.5}$ Hz (316 kHz).

3. Results and discussion

Fig. 1 shows the SEM micrographs for the samples of $x = 0$, 0.02, 0.04, 0.06. Besides dense structure, it can be observed that the size of the smooth-faced grains decreases apparently with increasing Cr_2O_3 content, whereas, the small angular grains (as indicated by the ellipses) change slightly. It has been validated that the smooth-faced and small angular grains are composed of SnO_2 and Zn_2SnO_4, respectively [8]. That is, the SnO_2 grain growth is hindered by doping Cr_2O_3. The radius of Cr^{3+} is 0.063 nm, which is smaller than that of Sn^{4+} (0.071 nm) ions. As a result, some Cr^{3+} substituting Sn^{4+} brings lattice distortion; the remanent ions may accumulate in the grain boundary and the both factors are disadvantageous for the growth of grains.

The voltage–current relations are illustrated in Fig. 2. As can be seen, all the samples have varistor properties and the breakdown electrical field E_B increases obviously with increasing Cr_2O_3 content. The variation of E_B is thought to be related to the decrease of SnO_2 grain size since it can be expressed by Equation (1):

$$E_B = n \cdot V_g. \quad (1)$$

In Equation (1), n is the average grain number per unit length, V_g is the breakdown voltage of one grain boundary. Because the composite ceramic varistor is composed of SnO_2 and Zn_2SnO_4

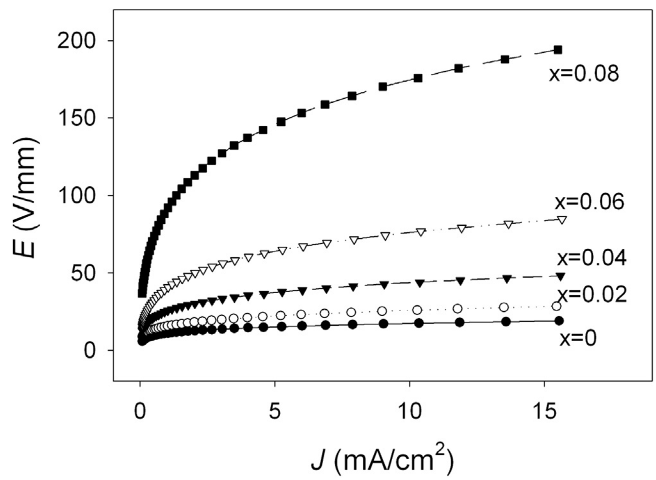

Fig. 2. E–J character of the samples doped with different Cr_2O_3 content.

grains and E_B is affected greatly by SnO_2 grain size, it is reasonable to conclude that the varistor property must be mainly originated from SnO_2–SnO_2 or SnO_2–Zn_2SnO_4 grain boundary. It is worth to note that the sample without doping has the lowest E_B value about 10 V/mm which is very important to low voltage protections. The grain size effect can also be confirmed by the dielectric spectra as shown in Fig. 3(a). At low frequency, ε_r decreases from about 13k to 6k with increasing x and it is proportional to the grain size d as described in Equation (2) [14].

$$\varepsilon_r = \varepsilon_B d / t_B. \quad (2)$$

In Equation (2), ε_B is the internal permittivity of the barrier material, t_B is the mean thickness of the insulation barrier. Usually, the origination of large permittivity for varistor materials is mainly attributed to the grain boundary layer where located the back to

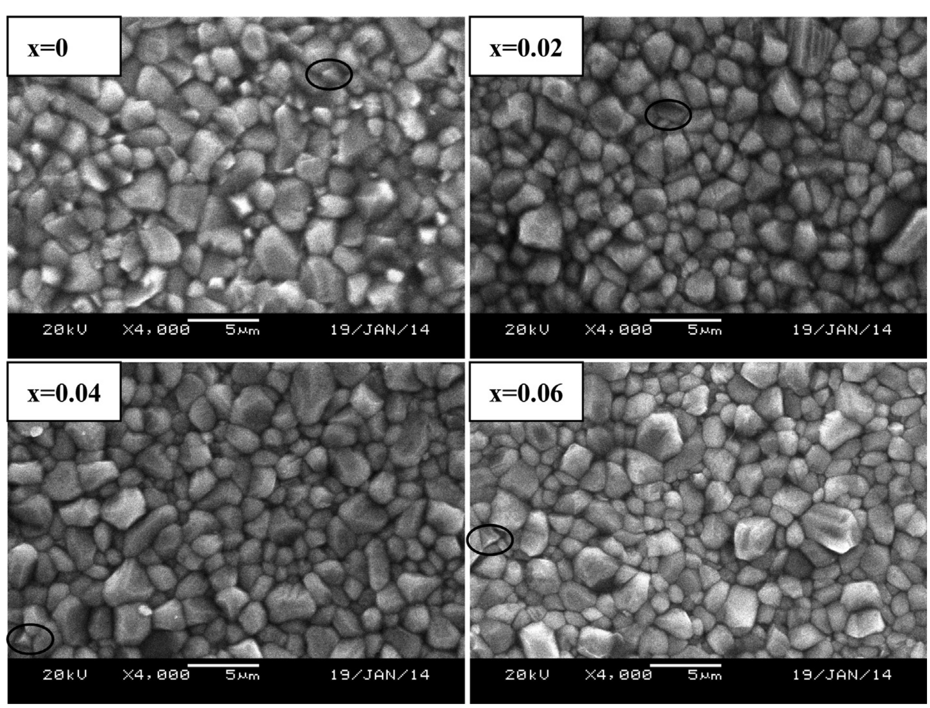

Fig. 1. SEM micrographs of SnO_2–Zn_2SnO_4 composite ceramics doped with different Cr_2O_3 content, some of the Zn_2SnO_4 grains are emphasized using the ellipse.