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Grain growth kinetics and electrical properties of CuO doped SnO_2-based varistors

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ABSTRACT

Up to now, attempts for developing coarse-grained SnO_2-based varistors which exhibit high nonlinearity property at lower voltage have become a challenge without any prominent result because of its unknown grain growth mechanism. In this study, the effect of CuO addition to SnO_2-based varistors as a grain growth enhancer additive on microstructural development, grain growth kinetics, and electrical properties was investigated. The characterization of grain growth kinetics showed that CuO addition encouraged grain growth and enhanced the grains size as it could be seen in the activation energy which decreased from 594 kJ/mol to 364 kJ/mol. In the samples with a low amount of CuO, the solute drag force is the controlling mechanism of grain growth. By further addition, the mechanism changed to the Sn^{4+} solution-precipitation in CuO-rich liquid phase. Also, the electrical properties of CuO doped samples showed that they are so promising for low voltage applications.

1. Introduction

Due to excellent non-ohmic property, metal oxide varistors have long been used as protective devices against over-voltages and electrical noises in electric and electronic systems such as high-voltage transmission and low-voltage electronic circuits [1–3]. SnO_2-based varistors have become technologically important because of their superior microstructural and electrical features [4]. Because of predomination of non-densifying mechanism during sintering process such as surface diffusion at low temperature and evaporation-condensation at high temperature, SnO_2 is known as a non-densified composition [5]. Thereupon, several improvements are needed to make the SnO_2 system feasible in varistor applications. Pianaro et al. presented a SnO_2-based varistor with the addition of small quantities of other metal oxides including CoO as a densifier, Nb_2O_5 as a grain electrical resistance reducer and Cr_2O_3 as an electrical modifier (SCNCr). SCNCr system presents high nonlinear coefficient ($\alpha = 41$) and electrical breakdown field ($E_B = 4$ kV/cm); which are extremely attractive properties for high-voltage applications [4]. Worth to be noted, E_B of a varistor is directly dependent on the grain size and grain boundary properties [6]. Many failed attempts for obtaining a coarse-grained microstructure in SnO_2-based varistors suitable for low voltage applications can be seen by reviewing the literature and seemingly it is attributed to the unidentified grain growth mechanism in SnO_2-based varistors. Therefore, it is important to fundamentally comprehend the microstructural development and grain growth mechanisms of SnO_2–based varistors.

Up to now, vast principle approaches have been used to attain a low-voltage SnO_2-based varistor with a similar aim: making a maximized grain size of SnO_2 and subsequently reducing E_B [7–9]. The simplest way to reduce E_B seems to be the increase in sintering time or sintering temperature in the fabrication process stage. In the work of Santos et al., it was observed that although grain size increases from 5.6 μm (at 1300 °C for 1 h) to 12.2 μm (at 1350 °C for 12 h), the electrical properties of the varistor made at 1350 °C for 12 h were totally deteriorated [10]. In another effort, Mesteghin et al. introduced 1D SnO_2 nanobelt to the Pianaro system and as a consequence E_B decreases to 0.8 kV/cm [8]. Seed addition to the SnO_2-CoO-Nb_2O_5 system (SCN) was a further effort to make a low-voltage SnO_2-based varistor conducted by Cilense et al. and it was shown that seed addition could decrease E_B of SCN system to 0.24 kV/cm [7].

Notwithstanding the respectable electrical properties, however, these methods are not practical for industrial production. Instead, an effective way to enhance the grain size of the SnO_2-based varistors is the use of grain growth enhancing additives such as Bi_2O_3,

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and CuO. Maleki Shahraki et al. obtained the best electrical varistor properties for low-voltage applications by adding Bi_2O_3 to the varistor system of CoO, Nb_2O_5, Cr_2O_3, and Y_2O_3 doped SnO_2. The optimum sample of this research has acceptable E_B and α equal to 0.5 kV/cm and 22, respectively [9]. Although the Bi_2O_3 doped SnO_2-based varistor is suitable for low voltage applications, the other improvements are needed to increase the performance of this system [11].

The effect of copper oxide on the SnO_2-based varistors has been widely investigated and it has been concluded that the CuO addition results in the acceleration of grain growth [12–14]. Recently, low-voltage SnO_2-based varistors have been made by adding CuO [15,16]. These kind of varistors possess commendable electrical properties and also coarse-grained microstructure [15]. With all commentaries, despite numerous studies in the field of investigation into the effect of different additives, little information exists in the literature in the fields of grain growth mechanisms study, the kinetics study of grain growth and the controlling growth process, in order to create an analytical look for a deeper understanding of growth behavior in SnO_2 varistors. There is just a report of Safaee et al. which studies the grain growth kinetics of SnO_2-based varistors with the addition of Pr_6O_{11} [17].

It is the stimulus of the present study to provide further information on the grain growth kinetics in SnO_2-based varistors with addition of various amount of copper oxide. Also, the electrical properties of prepared varistor pellets for low voltage application is examined.

2. Experimental method

Analytical grades of SnO_2 (Us-nano), Co_3O_4 (Aldrich), Cr_2O_3 (IoLiTec), Nb_2O_5 (Merck), and CuO (Aldrich) powders were used in the preparation of four basic compositions for SnO_2-based varistors. Selected compositions are listed in Table 1. Except for Nb_2O_5, all the powders in this study were nanosized materials (50–200 nm). A high-energy mill (SPEX-8000) was applied to obtain nanocrystalline Nb_2O_5 separately. The specific surface area of the high-energy milled Nb_2O_5 was about 15 m^2/g. The particles size after milling was less than 100 nm which is in accordance with the $D(paricle\ size) = \frac{6}{BET * density}$ formula [18]. By inserting the values in the formula (density of Nb_2O_5 is 4.6 gr/cm^3), the average particle size attained by this formula is 86 nm.

The powders were mixed and milled in ethanol by a shaker mill (SPEX 8000 M) using a zirconia container (3 cm diameter barrel) and milling media (0.5 and 1.0-cm diameter balls) for 2 h. After drying, the slurry was dried and then it was granulated in a 200 mesh sieve. Afterward, the green bodies were uniaxially pressed at 250 MPa. The green-pressed pellets were sintered in air at 1250, 1300, and 1350 °C for 1, 2.5, 5 and 10 h using a heating rate of 5 °C/min and were naturally cooled in a Carbolite RHF 17/6S Furnace.

The density of the sintered samples was measured by using the Archimedes method in water. The weight loss data was determined by weighing the annealed green-pressed pellets at 700 °C before and after heating at 1300° C and 5 h by employing the same heating and cooling rate used in sintering process. The X-ray diffraction analyses were accomplished on a Philips Xpert (3710) diffractometer with Cu k_α operating at 40 kV and 30 mA. The micrographs of the samples were obtained by using a field emission scanning electron microscope (FESEM-TESCAN). The imaging system, Image J software, was used to calculate the average grain size from the linear intercept data collected over 300 grains. The energy dispersive spectroscopy (EDS) was used to recognize the elements present in the chosen phases.

Table 1
Selected compositions (mol%).

	SnO_2	Co_3O_4	Nb_2O_5	Cr_2O_3	CuO
SCNCr	99.24	0.66	0.05	0.05	–
SCNCr-0.1Cu	99.14	0.66	0.05	0.05	0.10
SCNCr-0.25Cu	98.99	0.66	0.05	0.05	0.25
SCNCr-0.5Cu	98.74	0.66	0.05	0.05	0.50

The grain growth kinetics was determined by using the simplified following grain growth kinetics equation:

$$G^n - G_0^n = K_0 \cdot \exp\left(-\frac{Q}{RT}\right) \cdot t \quad (1)$$

G is the average grain size at time t, G_o is the initial average grain size, n is the kinetic grain growth exponent value, k_o is a constant, Q is the apparent activation energy for growth, R is the gas constant and T is the absolute temperature. Whenever the initial grain size, G_o, is significantly smaller than the grain size, G, then G_o can be neglected and Eq. (1) simplifies to

$$G^n = K_0 \cdot \exp\left(-\frac{Q}{RT}\right) \cdot t \quad (2)$$

The n value can be determined from the slope of the log (G) vs. log (t) plot constructed by the linear regression method. Also, the Q value can be calculated from the slope of log (G) vs. (T/1000) plot.

Electrical measurements were carried out by applying silver paste electrodes fixed on both faces of the samples. The electrodes were annealed at 650 °C for 15 min. The nonlinear coefficient (α) was determined from the *J–E* characteristic curve. *J-E* data were collected using a Keithly Sourcemeter (2410). The breakdown voltage (E_b) was measured as the voltage at a current of 1 mA/cm^2. The nonlinear coefficient (α) was calculated by measuring the voltages of E_2 and E_1 at correspondence currents of J_2 and J_1 (10 mA/cm^2 and 1 mA/cm^2, respectively), using the formula of:

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} \quad (3)$$

3. Result and discussion

3.1. Microstructural analysis of the samples

Fig. 1 shows the relative density of the sintered samples at 1300 °C for 5 h versus CuO content. The relative density of sintered

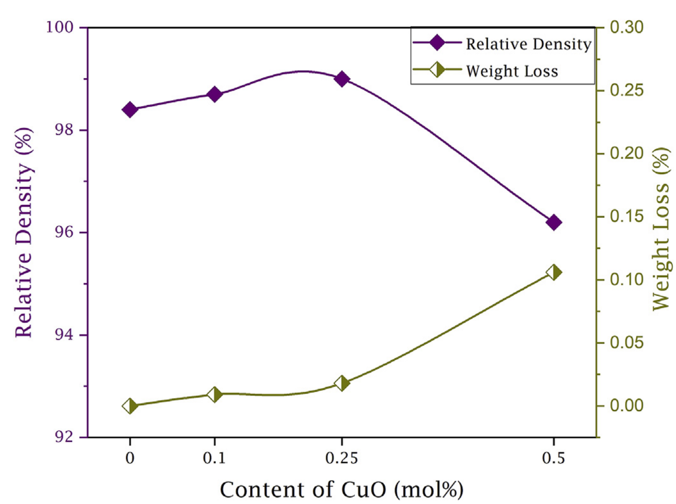

Fig. 1. Variation of relative density and weight loss as a function of CuO content in the samples sintered at 1300 °C and 5 h.