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The control of abnormal grain growth in low-voltage SnO_2 varistors by microseed addition

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ABSTRACT

In this research, the addition effects of three different quantities of micron-sized seeds (microseeds) to a SnO_2 varistor prepared from nanomaterials on the microstructure and electrical properties were studied. Moreover, surge-withstanding capability of low-voltage SnO_2 varistors was investigated. The X-ray diffraction pattern disclosed a single phase SnO_2 for microseed grains. The morphological features of samples were characterized using scanning electron microscopy. The abnormal distribution of grain size with elongated grains of SnO_2 in fine grains matrix was observed in sintered samples without microseeds. The low content of microseed addition (0.3 wt%) had not controlled abnormal grain growth, however, it increased mean grain size to 37 µm. Although the high content of microseeds (7.5 wt%) stopped abnormal grain growth, it had a negative effect on relative density and mean grain size. The normal grain size distribution with maximum mean grain size (45 µm) was obtained in samples containing 1.5 wt% microseeds. These samples showed the lowest breakdown field (240 V/cm) and the highest surge-withstanding capability (1.5 kA/cm^2). Furthermore, the standard deviation of the electrical parameters of these samples was improved due to normal grain-size distribution.

1. Introduction

Metal oxide varistors (MOVs) are widely used for protection of electrical and electronic components from transient power surges due to their nonohmic properties [1]. The MOVs are characterized by their nonlinear current density–electric field (*J–E*) characteristics. The breakdown electric field (E_b), nonlinear coefficient (α), and surge-withstanding current are the most important parameters of varistors [2]. A high value of α is required for a MOV, but more importantly, it should be capable of withstanding a current surge [3]. The breakdown field, determining the MOV application, depends on the metal oxide grain size. Small average metal oxide grain size (< 10 µm) is required for high-voltage applications, whereas the average grain size needs to be larger (> 30 µm) for low-voltage applications [4]. ZnO-based varistors are commercially used as surge arresters and surge absorbers in high- and low-voltage applications, respectively, due to their excellent nonohmic properties and high energy-handling capability. However, due to the degradation of ZnO-based varistors, especially in low-voltage applications, development of new MOVs is still required [5].

Among various new MOVs, metal oxides such as TiO_2 [6] and SnO_2 [7] are the favored candidates for low-voltage applications. The latter appears to be the most promising due to its nonlinear exponent. Initially, SnO_2-based varistors were introduced for high-voltage applications [8]. Compared with the ZnO-based varistors, the SnO_2-based varistors have several distinct advantages, such as a limited number of additives, simple microstructure, high nonlinear coefficient, and superior resistance to degradation [9,10]. Recently, developing a coarse-grained SnO_2-basedvaristor that presents a low breakdown field and high nonlinear coefficient has become an important challenge [11–13]. Seed addition and use of grain-growth-enhancing additives are two ways applied for lowering the breakdown field in SnO_2 varistors [14,15]. Cilense et al. [15] have used micron-sized seeds (microseeds) to decrease the breakdown field of the SnO_2–CoO–Nb_2O_5 system. This system showed a low nonlinear coefficient (8) and low breakdown field (230 V/cm). Using nanosized seed (nanobelt) in a (Co,Nb,Cr)-doped SnO_2-based varistor, the nonlinear coefficient was improved to 19, while the breakdown field was still relatively high (2280 V/cm) [16]. These strategies were not successful for preparation of low-voltage

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SnO_2-based varistors with suitable electrical properties. Recently, the authors [17] have presented a low-voltage SnO_2-based varistor with coarse-grained microstructure by Bi_2O_3 addition to a (Co, Nb, Cr, Y)-doped SnO_2-based varistor (SCNCrY) prepared from nanopowders. The breakdown field decreased from 1400 to 500 V/cm by addition of 0.3 mol% Bi_2O_3. Therefore, it seems that Bi_2O_3 is an effective grain-growth-enhancing additive in SnO_2-based varistors. However, when the SCNCrY ceramic system was doped with a large amount of Bi_2O_3, a broad range of grain size was obtained due to the discontinuous grain growth. It forms a few enormous grains appearing in a fine-grained matrix of SnO_2. It has been shown that high local currents are caused by very large grains, which give rise to rapid degradation of the MOV in electrical pulse operation. Hennings has used microseed addition in low-voltage ZnO-based varistors to overcome the duplex microstructure [18]. Addition of microseed grains to the duplex microstructure of a ZnO-based varistor prevents the growth of single large grains, making a more homogeneous microstructure and better electrical properties than a seed-free sample.

Therefore, in this research, the effect of microseed addition on microstructure and electrical properties of (Bi, Co, Nb, Cr, and Y)-doped SnO_2 was studied. Moreover, the surge-withstanding capability of low-voltage SnO_2 varistors was investigated.

2. Experimental procedure

Analytical grades of SnO_2 (Aldrich), CoO (Usnano), Nb_2O_5 (Merck), Bi_2O_3 (Aldrich), Y_2O_3 (Aldrich), and Cr_2O_3 (IoLiTec) were used for processing SnO_2-based varistors. 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 balls to powders weight ratio and milling time were 10 and 4 h, respectively. The specific surface area of the high-energy milled Nb_2O_5 was about 15 m^2/g. The composition of the SnO_2-based varistor was 96.75 mol% SnO_2–2.50 mol% CoO–0.05 mol% Nb_2O_5–0.05 mol% Cr_2O_3–0.05 mol% Y_2O_3–0.60 mol% Bi_2O_3 and the seed composition was similar to the composition of the SnO_2-based varistor. The seed composition was pressed into pellets 25 mm in diameter and 2 mm in thickness and was sintered at 1300 °C for 4 h. Then, the sintered seed was crushed, ground, sieved (< 15 µm), and added in proportions of 0.3%, 1.5%, and 7.5% by weight relative to the SnO_2-based varistors and, labeled as MS0.3, MS1.5, and MS7.5, respectively. A sample with no seed addition was labeled MS0. The microseeds were added to nanosized precursor powders and then were wet-milled in zirconia container with ZrO_2 balls for 1 h in deionized water. The milled powders were dried, ground, and granulated with an aqueous solution containing of 0.2 wt% PVA. The granulated powders were pressed into pellets 13 mm in diameter by 1.0 mm in thickness at a pressure of 200 MPa. After burned-out of the organic binder, the samples were sintered in an electric box furnace. Initially, they were soaked for 5 h at 1300 °C and then at 1350 °C for 5 h (heating rate: 2.5 °C/min).

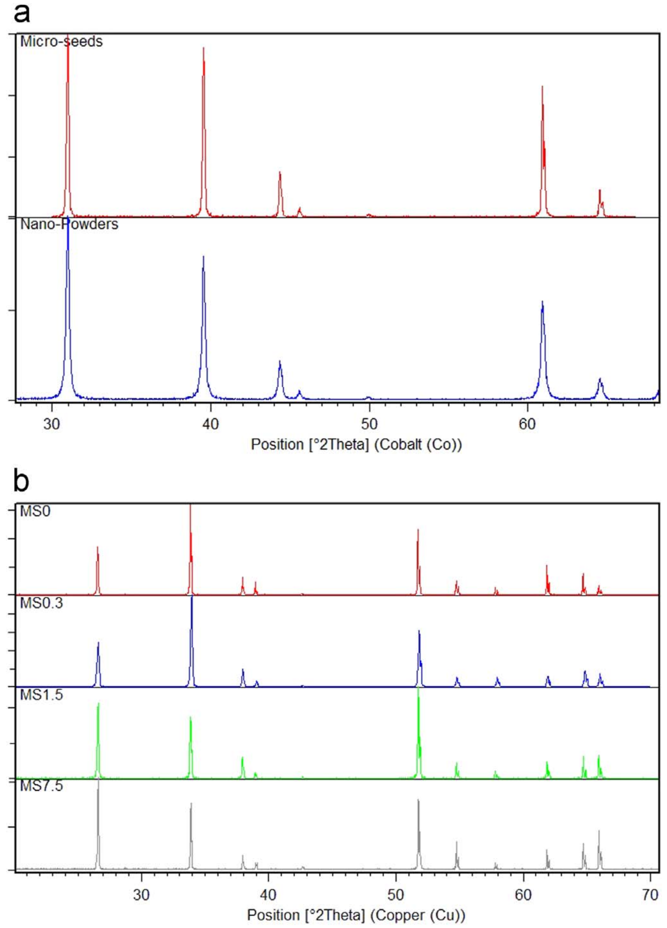

Fig. 1. XRD patterns of SnO_2 a) nanopowders and microseeds b) sintered samples with different content of microseeds.

The apparent density of the sintered samples was measured using Archimedes' method. The X-ray diffraction analyses (XRD) were carried out with Philips Xpert (3710) diffractometer. A precise XRD pattern was obtained by choosing a step size of 0.01° and the time per step of 10 s. A scanning electron microscope (SEM, Vega©TESCAN) was employed to study the micrographs of polished and thermally etched samples. The morphology of SnO_2 nanopowder was investigated using a transmission electron microscope (TEM, Philips EM208). The grain-size distribution was determined by measurement of 200–500 ZnO grains using a dedicated microstructure analysis program (Clemex software). Prior to electrical measurements, silver paste electrodes were printed on both sides of the samples and fired for 10 min at 500 °C. The current density (J) versus electric field (E) characteristics in the pre-breakdown and nonohmic region was registered with a Keithley 2430 source meter. The breakdown electric field, E_b, was determined at a current density of 1 mA/cm^2. The leakage current density, J_L, was measured at 0.8 E_{1mA/cm^2} (80% of the breakdown field). The electrical nonlinear coefficient, α, was obtained by:

$$\alpha = 1/(\mathrm{Log}\frac{E_{10mA/cm^2}}{E_{1mA/cm^2}}) \tag{1}$$

The upturn part of the J–E curves was characterized by high-current impulse tests using a current generator that delivered *8/20* µs impulse current. The SnO_2-based varistor response was registered on a Rigol DS5022M digital oscilloscope. The surge-withstanding current density, I_{max}, was defined as the maximum peak current density corresponding to a permissible variation of 10% in varistor breakdown field.

3. Results and discussion

Fig. 1a shows XRD patterns of pure SnO_2 nanopowders and microseed grains, which are, crushed SnO_2 ceramic sintered at 1300 °C. The XRD patterns of SnO_2 varistors doped with various amounts of microseeds are presented in Fig. 1b.

It is obvious that no other phase besides cassiterite (SnO_2) in the microseeds and sintered samples was observed. It shows that all dopants dissolve in SnO_2 to form a solid solution. The other possible phases might not have been detected owing to the limitations of XRD.

Fig. 2a displays the morphology and particle sizes of the pure SnO_2 nanopowders. According to the TEM image, the particles size is mostly smaller than 100 nm, although there are some agglomerations. A representative SEM micrograph of the seed grains is shown in Fig. 2b. Only Sn and O were detected during energy-dispersive X-ray spectroscopy analysis of the microseeds, which is in good agreement with the XRD results. The sizes of the seed grains are smaller than 15 µm