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Microstructure–property relationship in textured ZnO-based varistors

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Abstract

The relationship between microstructure texturing and electrical characteristics of a ZnO-based varistor system was investigated in comparison with a varistor system having the same chemical composition but conventional microstructure. Highly textured ZnO-based varistors were produced via the templated grain growth (TGG) technique. Stereological analysis, electron back-scattered diffractometry (EBSD) and X-ray diffractometry (XRD) were conducted to analyze texture development and orientation distribution. The degree of orientation, r, calculated from the (0 0 0 1) EBSD pole figure, was 0.34; the texture fraction, f (Lotgering factor), calculated from the XRD data, was 0.98 for the samples produced via TGG. The threshold voltages were found to be anisotropic, consistent with the observed morphological texture. The non-linear coefficients, α, did not exhibit a significant difference as a function of direction, even in the highly textured samples. However, different types of grain boundary characteristics depending on the direction were identified with 0.42, 0.69 and 1.14 eV Schottky barrier heights.

Keywords: Zinc oxide; Texture; Electrical properties; Electron backscattering diffraction

1. Introduction

Zinc-oxide-based varistors meet the demand for over-voltage protection for electronic and electrical equipment, due to their highly non-linear current–voltage (I–V) characteristics and high energy absorption capability [1,2]. Commercial zinc-oxide-based varistors are produced by sintering of ZnO powder with small amounts of dopants such as Bi_2O_3, Sb_2O_3, CoO, Cr_2O_3, Mn_3O_4 and NiO [3]. Distribution of these dopants during sintering and consequent cooling processes is responsible for the development of non-linear behavior. Segregation of bismuth ions at the grain boundaries provides acceptor-type interface states. These interface states trap the conduction electrons and leave positively charge depletion layers on each side of the grains. This phenomenon results in the formation of electrostatic potential barrier (double Schottky barrier) at the grain boundary which restricts the current flow below a threshold voltage [4–7]. As the voltage exceeds the threshold limit, electrostatic barriers collapse and a non-linear I–V characteristic is observed where the varistor conducts an increasingly large amount of current for a small increase in voltage. Hence, the varistor behavior originates from the electronic structure at the grain boundaries. As a result, controlling the microstructure and manipulating the grain boundaries may enable one to control the electrical performance of the varistor.

According to previous reports, grain boundary misorientation and resulting interfacial electronic structure in undoped ZnO systems are not adequate to induce non-linear I–V characteristics [8,9]. These studies reveal that dangling bonds or the difference in coordination numbers at the grain boundaries do not cause deep enough electronic states in the band gap. However, it was reported that electronic structure of the doped ZnO grain boundaries may change significantly as a function of grain boundary misorientation. Leach [10,11] analyzed a number of different grain boundaries in the ZnO–Bi_2O_3–Sb_2O_3 system by

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utilizing an electron beam induced current (EBIC) technique and observed variations in electronic structure in different boundary orientations. Sato et al. [9] used Pr-doped ZnO bicrystals joined together in predefined rotations to show the grain boundary orientation and non-linear behavior relationship. They pointed out that the available segregation sites for Pr increase as the boundary coherency decreases. Since Pr has a role for promoting the formation of acceptor-type states as Bi, non-linear $I–V$ coefficient (α) varies depending on the Pr concentration. Thus, α was reported to be increased as the grain boundary coherency decreased.

Segregation of dopants is also strongly related to the type of grain boundary plane (i.e. basal or prismatic plane) as well as grain boundary misorientation. Clarke [12] showed the preferential formation of continuous intergranular phase along the grain boundary formed by the basal plane of one of the adjacent ZnO grains. Elfwing et al. [13] pointed out that the polarity of the ZnO crystal structure may influence the equilibrium dihedral angle between the ZnO grains and bismuth-rich phases. Luo and Chiang [14] observed anisotropic surface amorphous film (SAF) formation on Bi_2O_3-doped ZnO powders. Although there was no film on the {1 −1 0 0} surfaces of ZnO, almost every {1 1 −2 0} surface was observed to have Bi_2O_3-rich films. In another study, they correlated the anisotropic wetting of Bi_2O_3-rich liquid on the same prismatic planes of ZnO single crystals with the anisotropic formation of SAFs [15]. Although a three-dimensional network of a Bi_2O_3 layer between the ZnO grains was shown to be indispensible for the non-linear behavior [12,16], wetting degree of Bi_2O_3 plays an important role in the electrical characteristics beside the fact that Bi_2O_3 liquid phase affects the distribution of other varistor dopants [1]. Thus, controlling the type of ZnO||ZnO interfaces may affect the electrical properties due to anisotropic wetting of Bi_2O_3.

Another type of planar discontinuity, such as grain boundaries observed in the microstructure of ZnO-based varistors doped with Sb_2O_3, TiO_2, SnO_2, Fe_2O_3, In_2O_2, are inversion boundaries (IBs). Transmission electron microscope (TEM) studies showed that IBs have a head-to-head configuration of (0 0 0 1) planes where Zn^{2+} atoms face each other toward the boundary and the boundary plane is occupied by a single layer of dopant atoms [17,18]. IBs play an important role in controlling the final ZnO grain size, and hence the threshold voltage of the varistor [19–24]. In addition, Rečnik et al. [18] suggested that the IBs should improve the non-linear varistor characteristics by increasing the current–voltage barrier at the grain boundaries since they expose the oxygen terminating faces. Lee and Maier [25], studied the electrical properties of doped (0 0 0 −1)||(0 0 0 −1) and (0 0 0 1)||(0 0 0 1) joined bicrystals and observed a higher barrier effect in the former, in parallel to Rečnik's suggestion. Oba et al. [26] also stated that co-doped (0 0 0 −1)||(0 0 0 −1) bicrystals exhibit non-linear behavior. Moreover, microprobe electrical measurements of the commercial ZnO varistors conducted by Haskell et al. [27] indicated that IBs have similar non-linear $I–V$ characteristics to grain boundaries but with higher threshold voltage. Consequently, controlling the IB formation may also have benefits on altering the electronic structure of the grain boundaries beside the microstructure of the varistor.

The above studies clearly show that controlling the type of ZnO–ZnO grain boundaries and misorientation between them may enable one to tailor the electrostatic barriers and hence the electrical performance of the varistor. Texturing can be utilized as a powerful method to manipulate the grain boundary structure. In our previous study [28], it was shown that templated grain growth (TGG) technique [29,30] can be utilized to fabricate textured ZnO-based varistors. Such a textured microstructure of ZnO-based varistor may consist of uniform, coherent grain boundaries and specific grain boundary planes in certain directions as a result of the orientation of grains, anisotropic distribution of Bi_2O_3 liquid phase and aligned IBs regarding the alignment of grains. Consequently, textured microstructure can be used to analyze the influence of various types of ZnO–ZnO grain boundaries on the electrical properties and formation of uniform and specific type of grain boundaries in textured ZnO-based varistors will improve the current understanding on this subject and enhance the possibilities to control the electrical properties more precisely.

The objective of this study was to examine the effect of textured microstructure on the electrical characteristics of ZnO-based varistor ceramics. The microstructural and electrical characteristics of textured ZnO-based varistors were examined in three directions and compared with reference varistor samples of the same composition without texture.

2. Experimental procedure

2.1. Fabrication

Three sets of samples with the same varistor composition 97% ZnO, 1% Bi_2O_3, 0.5% TiO_2, 0.5% SnO_2, 0.5% Co_3O_4 and 0.5% Mn_3O_4 (each in moles) were prepared. Reagent-grade oxides were utilized as starting materials. Two sets of samples were prepared by tape-casting: template-free system (0T) and 10 vol.% anisometric ZnO template-containing system (10T). Anisometric ZnO templates were produced by hydrothermal synthesis as described by Lu and Yeh [31]. A third set of samples (R) was produced by conventional ceramic processing (i.e., dry pressing).

Aqueous suspensions of powders in the varistor composition (33 vol.% solid loading) was ball-milled for 24 h to prepare 0T and 10T systems. Ammonium polymethacrylate solution (2.1 vol.%) (25 wt.%, Darvan-C, R.T. Vanderbilt Co. Inc.) was used as dispersant. After the milling stage, the suspensions were transferred on a magnetic stirrer. For the template-containing system, templates were added at this stage and both suspensions were stirred for 5 h. Polyethylene glycol (6 vol.%) (PEG 3000, Fluka,