Materials Science and Engineering B 151 (2008) 146–151

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Improvement of electrical properties and aging characteristics of Pr–Co–Cr–Y-modified ZnO varistors by Al_2O_3 doping

Choon-W. Nahm*

Department of Electrical Engineering, Dongeui University, Busan 614-714, Republic of Korea

ARTICLE INFO

Article history:
Received 16 March 2008
Received in revised form 17 May 2008
Accepted 27 May 2008

Keywords:
Ceramics
Doping effects
Electrical measurement
Nonlinear effects
Zinc oxide
Varistors

ABSTRACT

The dependence of the microstructure, electrical properties, and DC accelerated aging characteristics of Zn–Pr–Co–Cr–Y–Al-based varistors on the doping levels of Al_2O_3 was studied. The Al_2O_3 doping led to a small increase in the sintered density and average grain size. The breakdown field decreased in a wide range from 6396 to 338 V/cm with increasing doping levels of Al_2O_3. The nonlinear coefficient increased from 38.4 for Al_2O_3-free samples to 47.1 for Al_2O_3-doped samples up to 0.005 mol%, whereas the further doping levels caused it to decrease. Al_2O_3 acted as a donor due to the electron concentration, which increases from 0.41×10^{18} to 1.80×10^{18} cm^{-3} with increasing doping levels of Al_2O_3. The sample doped with Al_2O_3 of 0.001 mol% exhibited the highest stability, in which the variation of electric field is −0.2% and the variation of nonlinear coefficient is −5.0% under DC accelerated aging stress condition of $0.95E_B$/150 °C/24 h.

1. Introduction

ZnO varistors are semiconducting electroceramics possessing a property, which maintains a relatively small voltage change across its terminals when a large surge current flows through it. This nonlinear action allows the varistors to divert the current of a surge when connected parallel across a line and hold the voltage to a value that protects the equipment connected to that line. The basic conduction mechanism of the varistors results from semiconductor junctions at the grain boundaries of zinc oxide grains. The varistors are a multi-junction device with a number of grains acting as a series-parallel combination between the electrical terminals. The material of the varistors is primarily zinc oxide with minor additives, such as Bi_2O_3, Pr_6O_{11}, and CoO. The structure of the body consists of a matrix of conductive zinc oxide grains separated by grain boundaries, which provide p–n junction semiconductor characteristics. The varistors have been extensively used in the field of circuit overvoltage protection, with application ranging from a few volts in electronic circuits to millions of volts in electric power systems [1,2]. The majority of commercial ZnO varistors contain Bi_2O_3 as varistor-forming oxides and they exhibit excellent nonohmic properties. However, they have a few flaws due to the high volatility and reactivity of Bi_2O_3 during liquid sintering [3]. The former changes varistor characteristics due to the variation of intercomposition ratio of additives, the latter destroys the multi-layer structure of chip varistors, and it generates an insulating spinel phase, deteriorating surge-absorption capabilities.

To overcome these problems, the varistors containing Pr_6O_{11} as varistor-forming oxides have been actively studied [4–10]. In previous works, Pr_6O_{11}-based ZnO varistors with a rare earth oxide were revealed to possess a high electrical nonlinearity and a stability for DC accelerated aging stress [5–9]. It is very important to comprehend the influence of dopants on nonlinear properties. Al_2O_3 is often added to Bi_2O_3-based varistors to improve the performance [11–14]. However, their experimental results showed apparent differences with a part of the experimental data obtained for this paper. Thus, it is desirable to understand the role of Al_2O_3 dopant on Pr_6O_{11}-based ZnO varistors.

In this work, the influence of Al doping on the microstructure, *V–I* and *C–V* properties, and DC accelerated aging characteristics of Zn–Pr–Co–Cr–Y-based varistors was addressed.

2. Experimental procedure

2.1. Sample preparation

Reagent-grade raw materials were used in proportions of $(97.5 - x)$ mol% ZnO, 0.5 mol% Pr_6O_{11}, 1.0 mol% CoO, 0.5 mol% Cr_2O_3, 0.5 mol% Y_2O_3, and x mol% Al_2O_3 (x = 0.0, 0.001, 0.005, 0.01, and 0.1). Raw materials were mixed by ball milling with zirconia balls and acetone in a polypropylene bottle for 24 h. The mixture was dried at 120 °C for 12 h and calcined in air at 750 °C for 2 h. The

* Tel.: +82 51 890 1669; fax: +82 51 890 1664.
E-mail address: cwnahm@deu.ac.kr.

0921-5107/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2008.05.023

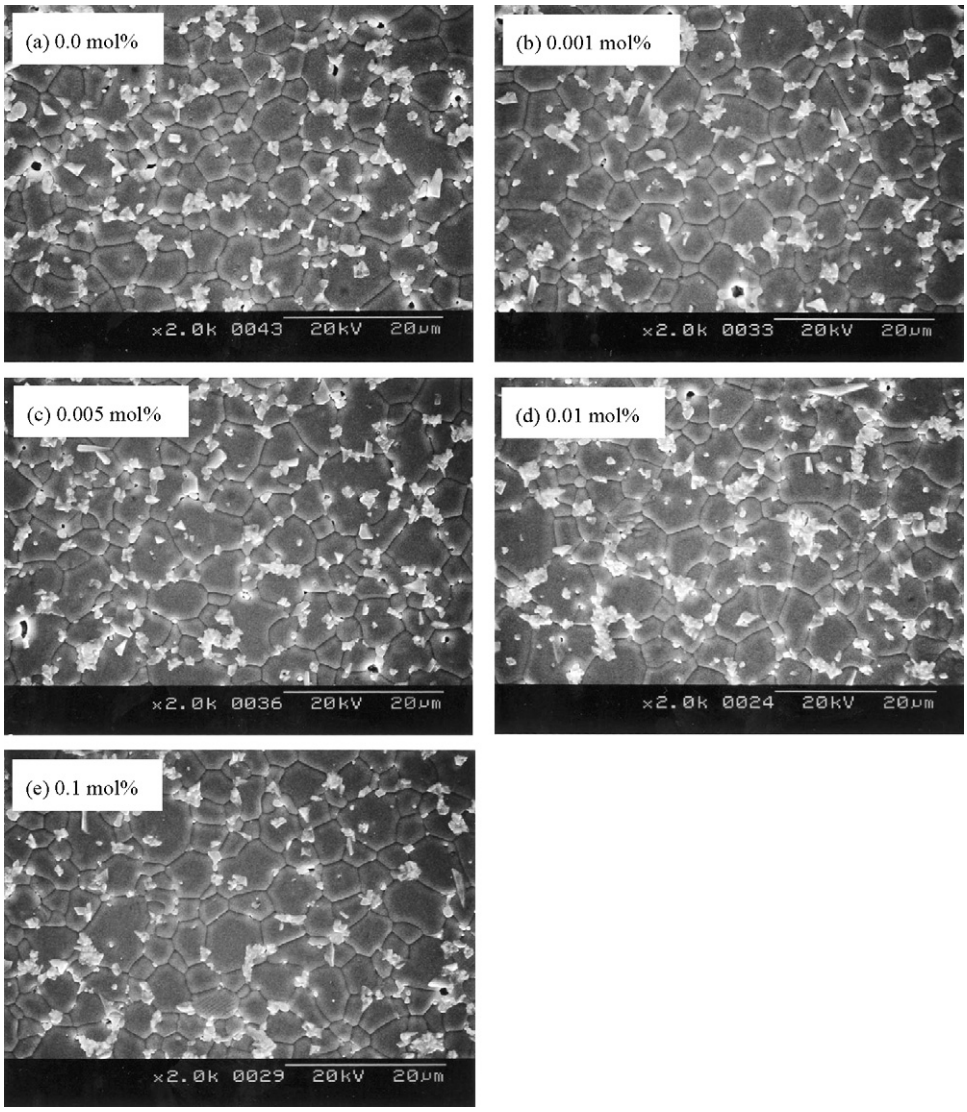

Fig. 1. SEM micrographs of the samples for different doping levels of Al_2O_3.

calcined mixture was pulverized using an agate mortar/pestle and after 2 wt% polyvinyl alcohol (PVA) binder addition, granulated by sieving through a 100-mesh screen to produce the starting power. The power was pressed into 10 mm in diameter and 2 mm in thickness at a pressure of 80 MPa. The discs were sintered at sintering temperatures of 1300 °C in air for 1 h and furnace cooled to room temperature. The heating and cooling rates were 4 °C/min. The sintered samples were lapped and polished to 1.0 mm in thickness. The final samples were about 8 mm in diameter and 1.0 mm in thickness. Silver paste was coated on both faces of the samples and the electrodes were formed by heating at 600 °C for 10 min. The electrodes were 5 mm in diameter.

2.2. Microstructure measurement

Both surfaces of the samples were lapped and ground with SiC paper and polished with 0.3-μm Al_2O_3 powder to a mirror-like surface. The polished samples were thermally etched at 1100 °C for 30 min. The surface of the samples was metallized with a thin coating of Au to reduce charging effects and to improve the resolution of the image. The surface microstructure was examined by a scanning electron microscope (SEM, Hitachi S2400, Japan). The average grain size (d) was determined by the lineal intercept method by the following expression [15]:

$$d = \frac{1.56L}{MN} \quad (1)$$

where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines. The compositional analysis of the selected areas was determined by an attached energy dispersion X-ray analysis (EDX) system. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2100, Japan) using a Cu Kα radiation. The sintered density (ρ) of varistor ceramics was measured by the Archimedes method.

2.3. Electrical measurement

The electric field–current density (E–J) characteristics were measured using an I–V source/measure unit (Keithley 237). The breakdown field (E_B) was measured at 1.0 mA/cm^2 and the leakage current density (J_L) was measured at 80% of the breakdown field. In addition, the nonlinear coefficient (α) is defined by the empirical law, $J = KE^{\alpha}$, where J is the current density, E is the applied electric