Effects of Aluminum Doping on the Microstructure and Electrical Properties of ZnO-Pr$_6$O$_{11}$-Co$_3$O$_4$-MnCO$_3$-Y$_2$O$_3$ Varistor Ceramics

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Abstract: The effect of Al$_2$O$_3$ doping on the microstructure and electrical properties of the ZnO-Pr$_6$O$_{11}$-Co$_3$O$_4$-MnCO$_3$-Y$_2$O$_3$ system was investigated in the range of 0.0-0.1mol%. The results reveal that Al$_2$O$_3$ doping has slight influence on the densification process. The microstructure of the ceramics comprises of ZnO phase, ZnAl$_2$O$_4$ spine phase and Pr-rich phases. The addition of Al$_2$O$_3$ greatly affects the electrical properties. The varistor voltage ($E_{1mA/cm^2}$) of ZPCMYAl samples decreases over a wide range from 5530 V/cm to 1844 V/cm with the increasing Al$_2$O$_3$ content. The nonlinear exponent ($\alpha$) increases with the increasing Al$_2$O$_3$ content to 0.01mol%, whereas it is decreased by the further doping. The ZPCMYAl-based varistor ceramics with 0.01mol% Al$_2$O$_3$ exhibit the best electrical properties, with the nonlinear exponent ($\alpha$) attaining the highest value of 33.4 and the lowest leakage current of 2.7$\mu$A. The capacitance-voltage (C-V) measurement shows that the donor density ($N_d$) at the grain boundaries increase from $1.58\times10^{18}$ to $3.15\times10^{18}$ cm$^{-3}$, the barrier height ($\phi_b$) increases from 1.60 to 2.36 eV, and the depletion layer width ($t_d$) decreases from 24.9 to 21.6 nm.

Key words: microstructure; electrical properties; Al$_2$O$_3$ doping; varistors

1 Introduction

ZnO varistors doped with only a small amount of oxides of Bi, Pr, Co, Cr, Mn and others possess exceptional nonlinearity in their voltage ($E$)-current ($J$) characteristics and the ability to absorb large amounts of energy. For this reason varistors have been used as surge absorber in electronic circuits, devices and electrical power systems to protect from transitory overvoltage$^{[1,2]}$. Three significant parameters characterize the varistors including the nonlinear exponent $\alpha$, the varistor voltage $E_{1mA}$ and the leakage current $J_L$. The characteristics of varistor ceramics are closely related to their microstructure, which is characterized as follows: the ZnO grain size and the grain size distribution; the grain boundaries; secondary phases; the distribution of secondary phases along the grain boundaries; and the presence of porosity$^{[3]}$. Each of the dopants plays a distinctive role in the subtle tuning of the final nonlinear characteristics of the varistor ceramics, and can not be omitted. In such materials small amounts of oxide are added to control the electrical characteristics of the ZnO grain boundaries, and to optimize the varistor behavior. In very small amounts aluminum is a potential dopant for increasing the conductivity of the ZnO grains and enhancing the varistor’s performance at high currents$^{[4-7]}$. The doping behaviors of Al as well as some other minor dopants and their influence on the current-voltage characteristics of ZnO were thoroughly investigated and reported by Gupta$^{[8]}$.

In recent years, Pr$_6$O$_{11}$-based ZnO varistors added various of rare-earth oxides (REO), such as Er$_2$O$_3$ and Dy$_2$O$_3$, are being very actively studied aiming to find a substitution for Bi$_2$O$_3$-based ZnO varistors, which have a few drawbacks due to Bi$_2$O$_3$ having high volatility and reactivity$^{[9-11]}$. It is very important to comprehend the influence of additives on varistor properties. Al$_2$O$_3$ is often added to ZnO-Bi$_2$O$_3$-based varistors to improve the performance$^{[12-14]}$. Thus, it is desirable to understand the role of Al$_2$O$_3$ doping on ZnO-Pr$_6$O$_{11}$- based varistors. In this paper, the effect of Al$_2$O$_3$ doping on the microstructure and electrical properties of the ZnO-Pr$_6$O$_{11}$-Co$_3$O$_4$-MnCO$_3$-Y$_2$O$_3$(in short, ZPCMYAl)
system was investigated.

2 Experimental

The nanocrystalline ZnO with particle sizes in the range of 20 to 100 nm was used. Other oxides were reagent grade. The ceramic samples used were composed of (98.5—x) mol% ZnO+0.5mol% Pr6O11+0.5mol% Co3O4+0.5mol%MnCO3+0.5mol% Y2O3+xmol%Al2O3(x=0.0, 0.01, 0.05, 0.1, 0.5). Raw materials were mixed for 24 hour in deionized water with zirconia balls and acetone in a polypropylene bottle. The mixture was then dried at 120 °C for 12 h and calcined in air at 750 °C for 2 h. The calcined mixture was again milled for 6 h in the deionized water after 2.5wt% polyvinyl alcohol (PVA) binder addition. After drying again, the mixture was pulverized using an agate mortar/pestle and granulated using a sieving 200-mesh screen to produce the starting powder. The powder was compacted into discs of 16.66 mm in diameter and 2 mm in thickness by employing a 30 MPa pressure in a uniaxial press. The samples were then sintered at 1 275 °C for 2 h in air, with heating and cooling rates of rate of 3 °C/min. The sintered samples were lapped and polished to 1.0 mm thickness. Silver paste was coated on both faces of samples and ohmic contact of electrodes was formed by heating at 600 °C for 15 min. The size of electrodes was 13 mm in diameter. The sintered densities (ρ) of the green samples were determined by the Archimedes method with distilled water. The reference theoretical density (TD) of pure ZnO was taken to be 5.78 g/cm³.

For microstructural observations, the either surface was lapped and ground with SiC paper and finally polished with 0.3 μm-Al2O3 powder to mirror-like surface. The polished surfaces were etched with 2% natal (2vol% nitric acid with alcohol) for about 1-2 min. The microstructure was examined by scanning electron microscopy (SEM, JSM-6360LA, Japan). The average grain size was measured directly form the micrograph, \(N\) is the number of the grain boundaries intercepted by lines. The sintered density(\(\rho\)) of ceramics was measured by the Archimedes method. The phases were identified by X-ray diffraction techniques (XRD, D/max 2500 PC, Japan) using a Cu Kα radiation.

For electrical measurements, the current-voltage (E-J) characteristics were determined at room temperature using a variable dc power supply. The varistor voltage (\(E_{\text{val}}\)) was measure at 1.0 mA/cm² and the leakage current (\(J_L\)) was defined as the current at 0.83\(E_{\text{val}}\). The nonlinear exponent (\(\alpha\)) is defined by \(\alpha = (\log J_l-\log J_1)/(\log E_2-\log E_1)\), where \(E_1\) and \(E_2\) are the electric fields responding to \(J_1=0.1\) mA/cm² and \(J_2=1\) mA/cm², respectively.

The capacitance-voltage (C-V) characteristics of the ZPCMYAl varistors were measured at 1 kHz with the variable applied bias in the pre-breakdown region of the \(V-I\) characteristics using a LRC meter.

3 Results and discussion

The scanning electron microscope(SEM) images of the ZPCMYAl samples with various Al2O3 contents are shown in Fig.1. The average grain size (\(d\)) is observed to increase from approximately 2.1 to 3.0 μm with the increasing Al2O3 content. The sintered density (\(\rho\)) increases from 5.41 to 5.53 g/cm³ corresponding to 93.6%-95.7% of theoretical density (TD=5.78 g/cm³ in ZnO). Thus, the results indicate that Al2O3 plays an important role as a prompter of ZnO grain growth due to the increase of average grain size with the increasing Al2O3 content during sintering process, while Al2O3 doping do not significantly modify the densification process. It should be noticed that the behaviors of \(d\) and \(\rho\) show the different result in comparison to ZnO-Bi2O3-based varistors [17,18]. The detailed microstructure parameters are summarized in Table 1.

The XRD patterns of the ZPCMYAl varistors samples are shown in Fig.2. The microstructures of ZPCMYAl-based varistor ceramics are composed of the ZnO phase, the spine phase and Pr-rich phases. Compared with the microstructure of the Al2O3-free sample, the spine phase is detected in the samples doped with various Al2O3 contents. The spine phase, which is only made up of single ZnAl2O4, can be formed in the ZnO-based varistor ceramics only sufficiently large additions of Al2O3, in amounts exceeding the solubility of aluminum in ZnO phase. The promotion of ZnO grain growth is attributed to the ZnAl2O4 spine phase in the Al2O3-doped ZnO-Pr2O3 systems according to the Ref.[16]. The ZnAl2O4 spine phase does not change with the increasing Al2O3 content.