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Short communication

The influence of surfactant on ZnO varistors

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Abstract

ZnO varistors with and without surfactant such as sodium dodecyl sulphate (SDS) are prepared by nitrate-combustion process. The samples were identically heat treated and sintered at 1000 °C for 12 h to study the influence of the surfactant on the nonlinear electrical properties of polycrystalline ZnO. It is observed that the nonlinear coefficient decreases marginally ($\alpha = 35$) for samples prepared with surfactant, whereas breakdown field ($E_B = 130$ V/mm) decreased significantly. The corresponding parameters for the samples synthesized without surfactant are $\alpha = 45$ and $E_B = 400$ V/mm. Hence, this method can be used for the manufacture of varistors with low to moderate breakdown fields.

Keywords: B. X-ray methods; D. ZnO; Semiconductors; Chemical synthesis

1. Introduction

Mesoporous materials have attracted much interest due to their large surface areas and narrow pore size distributions, which make them ideal candidates for catalysts, molecular sieves and electrodes in solid-state ionic devices [1]. Since the discovery of the ordered mesoporous silica M41S, a number of mesoporous materials have been synthesized by various molecular templates [2]. Varistors are electroceramic devices that show nonlinear electrical property [3–5]. They are widely used to protect electrical and electronic equipment against transient overvoltages. Their current (I)–voltage (V) characteristics can be expressed by $J = (E/C)^{\alpha}$, where J is current density, E is applied field strength, C is the proportionality constant and α is the nonlinear coefficient. The most commonly used commercial varistors are ZnO-based compositions [3,4]. It had been already well established that the electrical nonlinearity in polycrystalline ZnO ceramics arises from grain boundary phenomenon. Hence, controlled pore distribution during diffusion of additives in polycrystalline-sintered ceramics is expected to produce unusual electrical properties. We have attempted to study the influence of the mesoporous structure formed due to addition of surfactant on nonlinear electrical properties of ZnO varistors. Final densification during sintering for the samples with and without mesoporous structure will be different because of difference in the microstructure. Here, we present the details of our investigations on nonlinear electrical properties of ZnO ceramics on this aspect.

2. Experimental

Varistor compositions in the following stoichiometric formula ($Zn(NO_3)_2 \cdot 6H_2O$:Bi_2O_3:$Co(NO_3)_2 \cdot 6H_2O$:Sb:Mn: 0.965:0.01:0.01:0.01:0.005 (in at.%) are prepared by glycine nitrate process [6]. The metal salts are dissolved in nitric acid and 1 mol of glycine is mixed and heated on a hot plate. Combustion starts spontaneously after the evaporation of the solvent. The beaker was covered with fine mesh sieve to prevent the loss of fine particles during burning of the mixture. In one batch of samples, 10 wt.% of aqueous surfactant, such as SDS ($C_{12}H_{25}NaSO_4$) solution is mixed with them before keeping on the hot plate. The weight ratio of surfactant to ZnO is 0.1:1. All the powders are calcined at 700 °C for 12 h. It is to be noted that surfactant will leave the system at this temperature and pore structure also will be collapsed. The advantage of using surfactant is to modify the additive distribution at the grain boundaries in ZnO varistors. The powder samples are mixed with few drops of a binder (poly vinyl alcohol, 1 wt.% solution) and pelletized (15 mm diameter, 2 mm thickness). The green pellets were sintered at 1000 °C for 12 h. The density of the pellets were measured by Archimedes method

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and they are >93%. The sintered pellets were polished and low-temperature curing silver paint is applied on its surfaces. The pellets were cured at 600 °C for 30 min. The *I–V* curves are measured using a Keithley electrometer 6517 A. It also contains a built-in 1-kV d.c. power supply, so that there is no need of external power supply in the circuit. The current–voltage curves were plotted on log–log scale and the slope of the curve gives the value of α. The important parameter, E_B, breakdown field strength is taken as the field applied when current flowing through the varistor is 1 mA/cm^2. Since Schottky-type grain boundary barriers are present in the present samples, the barrier height (Φ_B) is calculated using the equation given in Ref. [5].

3. Results and discussion

Fig. 1 shows the low-angle XRD recorded for the samples prepared with SDS before annealing at 700 °C. The broad peak at low angles indicates the formation of mesoporous structure. The ordered pore structure leads low-angle peak as explained in the Refs. [1,2]. This peak disappears after calcining at 700 °C as mesoporous structure collapses. The residual carbon analysis revealed that whole surfactant has decomposed and no trace of carbon was present. However, diffusion of additives will be different for samples prepared with and without SDS. Fig. 2 depicts the *I–V* characteristics for the samples prepared with and without SDS. It can be seen that the nonlinear coefficient decreases marginally for samples prepared with SDS, whereas decrease in the breakdown voltage is very significant. For the present samples, E_B decreases from 400 to 130 V/mm as illustrated in Fig. 2. The observed breakdown field for the samples prepared with SDS is much lower than normally reported values in the literature [3,4]. Generally, seed method [7] is employed to produce ZnO varistors to decrease the breakdown field by way of forming larger grains. But present samples do not exhibit larger grains as compared to samples prepared without SDS. This can be explained only by the role of surfactant in producing the pore structure. Even though

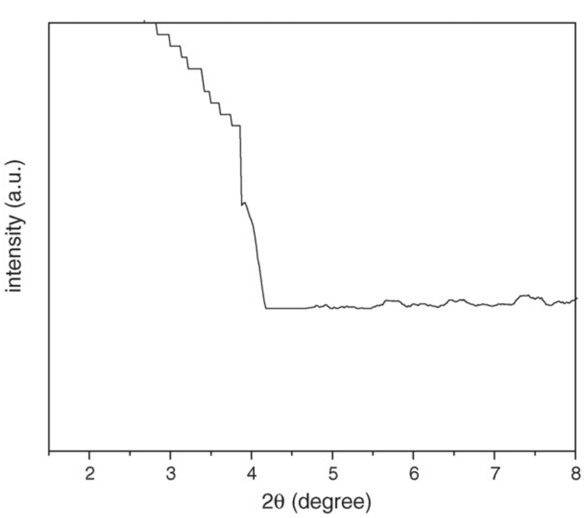

Fig. 1. Low-angle XRD for the ZnO powders with surfactant before annealing at 700 °C.

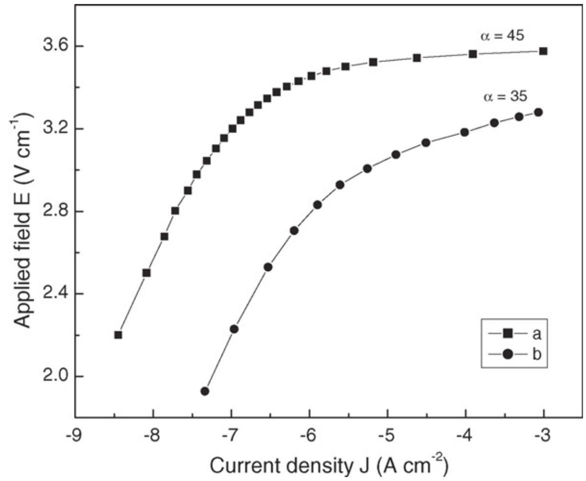

Fig. 2. *I–V* characteristics of ZnO ceramics prepared (a) without SDS and (b) with SDS.

apparent bulk compositions are the same for both ZnO varistors, the diffusion of aliovalent cations in the ZnO lattice will be microstructure-dependent. The segregation of secondary phases formed at the grain boundaries due to additives are responsible for Schottky barrier formation. Recently, Bueno et al. [8] have emphasized the importance of oxygen ion adsorbed by the transition metal ions present at the grain

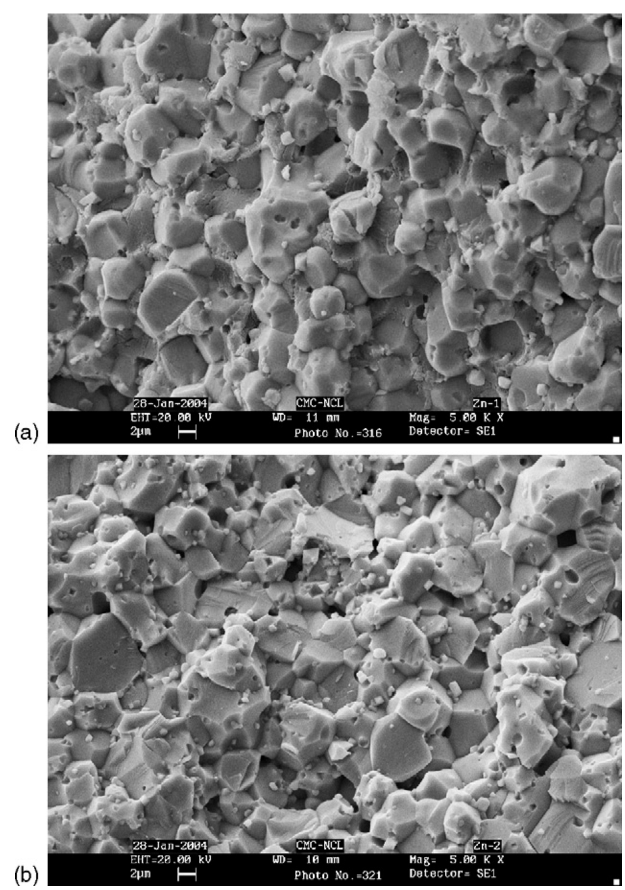

Fig. 3. SEM micrograph of samples sintered at 1000 °C and 12 h (a) prepared with and (b) without SDS.

boundaries in metal oxide varistors. Hence, present results show that the difference in the distribution of additives due to surfactant leads to changes in the *I–V* characteristics. The barrier height calculated for the samples prepared with SDS is 0.4 eV and for the specimens without SDS is 1.1 eV. The microstructure of sintered, thermally etched at 1000 °C samples are shown in Fig. 3. The average grain size is 5 μm in both cases indicating the differences in the electrical properties arises only from distribution of additives in the present samples. Further work is under progress to evaluate the compositional differences between samples at the grain boundaries.

4. Conclusions

The influence of a surfactant such as SDS on the nonlinear *I–V* characteristics of ZnO ceramics has been investigated and found to alter the electrical properties of ZnO varistors.

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