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Original Article

A novel economical grain boundary engineered ultra-high performance ZnO varistor with lesser dopants

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ABSTRACT

A varistor having ultra-high performance was developed from doped ZnO nanopowders using a novel composition consisting of only three (Bi, Ca and Co oxides) dopants. Improved varistor properties were obtained (breakdown field (E_b) 27.5 ± 5 kVcm^{-1}, coefficient of nonlinearity (α) 72 ± 3 and leakage current density (L_c) 1.5 ± 0.06 μAcm^{-2}) which are attributed to the small grain size and grain boundary engineering by phases such as $Ca_4Bi_6O_{13}$ and $Ca_{0.89}Bi_{3.11}O_{5.56}$ along with Co^{+2} doping in the ZnO lattice. Complex impedance data indicated three relaxations at 25 °C and two relaxations at high temperature (> 100 °C). The complex impedance data were fitted into two parallel RC model to extract electrical properties. Two stages of activation energy for DC conductivity were observed in these varistor samples where region I (< 150 °C) is found to be due to shallow traps and region II (< 225 °C) is due to deep traps. The novel composition is useful for commercial exploitation in wide range of surge protection applications.

1. Introduction

ZnO varistor is a polycrystalline over-voltage protection device whose primary role is to realize and suppress transient voltage surges. Ever since the ZnO-Bi_2O_3 based varistors doped with transition metal oxides was reported by Mastuoka in 1969 [1], several industries around the world have been manufacturing the same commercially [1–3].They are widely used for several industrial and domestic applications due to their high non-ohmic response in wide range of voltage-current (V-I). ZnO varistor is reported to find application in load sensors as well [4]. Commercial varistors generally contain more than five oxide dopants from the metals Bi, Sb, Cr, Mn, Ni, Fe, Si, Co to name a few [2]. They also require high sintering temperature > 1200 °C, particularly in Sb_2O_3 based compositions, to have the liquid phase of Bi_2O_3 spread along the ZnO grain boundaries. The grain growth of ZnO in a varistor is controlled by the spinel ($ZnSb_2O_7$) phase present around the grain boundaries [5]. Research is being carried out to develop a high performance ZnO varistor having a simple composition with less number of dopants to enable easy processing and low cost [6–10]. Efforts are also being made to prepare Sb_2O_3 free varistors having lower sintering temperature and a simple microstructure [11–13]. However, in Sb_2O_3 free ZnO varistors, the coefficient of nonlinearity (α) greater than 55 has not yet being achieved. The nonlinear property of a varistor is due to the fact that the electrical insulating grain boundary materials cover the successive conducting ZnO grains resulting in double Schottky barriers (DSB) across the grain boundaries [1,2]. To improve the energy handling capability and α of a varistor, one needs to avoid secondary phases like pyrochlore ($Zn_2Bi_3Sb_3O_{14}$) and spinel in the grains and increase the number of homo-junctions (effective ZnO grains contact). In fact, there is no direct correlation of secondary phases like pyrochlore and spinel contributing to varistor properties. Again, by reducing the amount of raw materials per unit volume of a varistor a considerable cost of production could be reduced [7]. Influence of Co_3O_4 doping on ZnO varistor has been studied extensively because it improves the α at lower current region, reduces the residual voltage and also reduces the bismuth evaporation besides retarding grain growth [14–18].

In the field of electronics, miniaturization of devices is an indication of advancement of technology, which indirectly improves the performance and reduces the cost. Similar is the case with varistors where high breakdown field (E_b) enables the miniaturization of the varistor device and size reduction with less number of dopants make the device low cost [19]. It is well documented that using nanopowders as starting materials offer lots of advantages in fabrication of high performance varistors [20–22]. The breakdown voltage is inversely relationship to the grain size of a varistor [1]. In recent past, extensive efforts have been made to develop high performance varistors using nanopowders

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having $E_b > 20\,kVcm^{-1}$ with high $\alpha > 70$ [20,23–25]. These varistors are either found to have a very high leakage current 7.7 μAcm^{-2} [25] or the values are not reported at all [20,22–24]. In this work, a novel composition to make ultra-high performance varistors was designed using CaO, Bi_2O_3 and Co_3O_4 such that CaO and Bi_2O_3 act as grain growth inhibitors as well as oxygen generator at grain boundary and Co_3O_4 act as a donor dopant. The base composition used for this study is 94 wt% ZnO, 5 wt% Bi_2O_3 and 1 wt % CaO (ZBC) in which Co_3O_4 is doped in different concentrations (X = 0.00, 0.25, 1.00, 1.50, 1.75 and 2.50). The doped ZnO nanopowders were synthesized by Solution Combustion Synthesis (SCS) and calcined at 750 °C for 1 h followed by consolidation into disc, and their morphology, microstructure, phase, density and electrical properties were studied and are reported here.

2. Experimental section

2.1. Synthesis and consolidation

Zn $(NO_3)_2\ 6H_2O$ (99%, Alfa Asear), Ca $(NO_3)_2\ 4H_2O$ (99.9%, Alfa Asear) and Co $(NO_3)_2.6H_2O$ (99%, Sigma) were dissolved in de-mineralized H_2O. The solution was heated to 50–100 °C to make a homogeneous [Solution 1]. Bi $(NO_3)_3\ 5H_2O$ (99%, Sigma) was dissolved in dilute HNO_3 (99.99, SD Fine) [Solution 2]. The solution 2 was added to solution 1 and stoichiometric amount of sucrose was added to the final solution as fuel and heated to 200 °C and stirred until the solution caught fire followed by calcinations at 750 °C for 1 h. Different concentration of Co_3O_4 (0.00, 0.25, 1.00, 1.50, 1.75, 2.50 wt %) doped ZBC powders were synthesized to improve the α of the varistor. The powders were blended by pot milling (powder to ball ratio, 1:4) in PVA binder (3.5 wt % PVA in water) for 4 h. The slurry mix was dried in an oven at 150 °C for 6 h. The dry powders were crushed using mortar and pestle followed by consolidation into discs of 10 mm diameter at 160 MPa using a stainless steel die. Green discs of ∼55% of the theoretical density were debinded at 600 °C for 3 h (heating rate 1 °C min^{-1}). Undoped and Co_3O_4 doped 94ZnO-5Bi_2O_3-1CaO (ZBC) green discs were sintered by two step sintering: heated to 900 °C and held for 0.5 h, then cooled to 825 °C and held for 4 h (S-1), heated to 1000 °C and held for 0.5 h, then cooled to 825 °C and held for 4 h (S-2), heated to 1100 °C and held for 0.5 h, then cooled to 825 °C and held for 4 h (S-3) in air. The heating/cooling rates at 2 °C min^{-1} were retained for all the samples till 725 °C followed by furnace cooling [26].

2.2. Phase and microstructure characterization

Phase composition of the powder samples was analysed by XRD (Regaku Rapid-II D/MAX, 4000) using Cu Kα radiation. The crystallite size (d) of the powders was estimated by using Scherrer equation: $d = 0.94\lambda\ /\ B\ Cos\theta$, where B is the full width at half maximum (FWHM), λ is the X-ray wavelength and θ is the Bragg angle. Composition of the powders was analysed by ICP-OES (Varian, Liberty Series II). Surface chemistry of the powders was studied using XPS (Omicron, Nano Technology, UK). Morphology of the powders was analysed by TEM (TECNAI, 200 KV, FEI, Netherlands). Powder was dispersed in ethanol solvent by sonication around 15 min A few drops of the slurry containing dispersed nanopowders were taken on a copper grid for TEM analysis. The average particle size of the powders was estimated from bright field TEM images. The density of the green compacts was estimated using dimensional analysis. Porosity and density of sintered samples were estimated by ASTM-C373-88. The phase of sintered samples was analysed by high intensity X-ray diffractometer. Microstructure of the polished and thermally etched sintered samples was analysed by SEM (S-3400 N, Hitchi, Japan). Dimple of 3 mm size for TEM sample was prepared from sintered samples which was cut into two pieces by Isomet and then thinned down to 200 μm by polishing with emery papers of different grades (600 and 1000 no.). The 3 mm diameter dimpling was made by cutting with an ultrasonic cutter (GATAN, Model 601) and then thinned down to 50–60 μm by polishing with an emery paper (2000 no.). The sample was put into ion milling (GATAN, Model No # 691) for 8–10 h, keeping both the gun energy at 4 KeV (current 11 μA) and angle at 11° till a hole formed. The final sample was cleaned with 1.5 KeV energy for 15 min before putting into TEM for analysis. Elemental phase analysis of sintered samples were carried out by Energy-dispersive X-ray spectroscopy (EDS) attached to TEM (EDAX, USA). The average grain size was measured by linear intercept technique [27].

2.3. Electrical properties measurement

2.3.1. I-V Characteristics

The sintered discs of Φ = ∼8 mm, t = ∼1 mm were measured for varistor properties. Silver was used as contact electrode on both the faces of a disc. Varistor properties of the discs were measured by 5 kV DC breakdown voltage tester (Rectifier Electronics, India). The α was estimated by using equation: $\alpha = (\log J_2 - \log J_1)\ /\ (\log E_2 - \log E_1)$, where E_1 is the field at current density J_1 (0.1 $mAcm^{-2}$) and E_2 is field at current density J_2 (1 $mAcm^{-2}$). The E_b was estimated at a current density of 1 $mAcm^{-2}$. Assuming the voltage drop at each grain boundary is equal, the breakdown voltage drop (V_g) per grain boundary was estimated using equation: $Vg = V(d/t - 1)$, where d is the grain size, V is the total voltage drop, t is the thickness of the sample. The L_c was estimated at 75% of the $E_{b\ (1mA)}$.

The barrier height, depletion layer width, donor density and density of interface state of the varistor samples were calculated using a Schottky-type barrier model as given below [1,25]:

$$J = AT^2 \exp[\beta\ E^{1/2} - \Phi_B\ /kT] \quad (1)$$

$$\beta = [(1/\gamma\omega)\ (2e^3/4\pi\varepsilon_0\varepsilon_r]^{1/2} \quad (2)$$

$$\omega^2 = 2\Phi B\varepsilon_0\varepsilon_r/e^2N_D \quad (3)$$

$$N_S = N_D\ \omega \quad (4)$$

where A is the Richardson constant, E is the electric field, k is the Boltzmann constant (8.6173303 × 10^{-5} eVK^{-1}), ε_0 is vacuum dielectric constant (8.85 × 10^{-14} Fcm^{-1}), and ε_r is relative dielectric constant (ε_r = 8.5 for ZnO). Using room temperature current-voltage data, graphs of lnJ versus $E^{1/2}$ are plotted for the samples. The barrier height (Φ_B) was obtained from the intercept of with the lnJ axis and the constant β was calculated from slope of the plot. The depletion layer thickness (ω) was determined by Eq. (2). The donor density (N_D) was estimated from Eq. (3). The density of the interface states (N_S) at grain boundaries was calculated using Eq. (4).

2.3.2. Dielectric and impedance study

Frequency and temperature dependent AC electrical properties of the sintered discs (Φ = ∼8 mm, t = ∼1 mm) were measured with impedance analyser (Alpha-High Resolution Novocontrol, Germany) in the frequency range from 1 mHz to 1 MHz over a wide range of temperature 25–500 °C at 25 °C interval with silver as an electrode, the data were analysed by complex impedance, dielectric and modulus formalisms.

3. Results and discussion

3.1. Phase, morphology and compositional analysis of powders

To understand the effect of Co_3O_4 doping on phase formation, morphology, size and surface chemistry of the ZBC powders; the X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) characterization were carried out on the powders. Wurtzite ZnO (JCPDS No. # 13–7122) and $Ca_4Bi_6O_{13}$ (JCPDS No. # 42–1439) phases were observed in both