Low voltage varistor ceramics based on SnO$_2$

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Abstract. The nonlinear current (I)–voltage (V) characteristics of tin dioxide doped with either Nb$_2$O$_5$ and CoO or Sb$_2$O$_3$ and CoO show promising values of nonlinear coefficient (α) values (~11) with low breakdown voltages (E_B, ~40 V mm^{-1}). The pentavalent antimony or niobium acts as donor and increases the electronic conductivity. The crucial parameter for obtaining low breakdown voltage is the grain size, which depends upon sintering duration and temperature of these oxide ceramics.

Keywords. Tin oxide; electronic materials; chemical synthesis; microstructure; X-ray diffraction.

1. Introduction

Tin dioxide is an n-type semiconductor with a tetragonal crystalline structure similar to the rutile structure. It is difficult to sinter SnO$_2$ without additives to high densities and this property is exploited in gas and humidity sensor applications (Pianaro *et al* 1995). However, high densification is obtained for tin dioxide with addition of small quantities of transition metal ions (Pianaro *et al* 1995, 1997; Cerri *et al* 1996). It has already been reported (Pianaro *et al* 1997; Ravi and Date 2001) that polycrystalline dense ceramics based on SnO$_2$–CoO–Nb$_2$O$_5$–Cr$_2$O$_3$ system shows highly nonlinear I–V characteristics. The three important parameters that characterize a varistor are the nonlinear coefficient (α), breakdown voltage (E_B) and energy absorption capability. The reported α for doped tin dioxide is >20 with $E_B \sim 8000$ V cm^{-1}. Recently, Bueno *et al* (2001) compared the grain boundary barrier properties of tin dioxide with that of varistors based on ZnO ceramics. Though ZnO shows excellent varistor property, the drawback is its high breakdown voltage (Gupta 1990; Clarke 1999). Low voltage varistors based on SrTiO$_3$ (Fujimoto *et al* 1985) and SnO$_2$–TiO$_2$ systems (Yan and Rhodes 1982; Bueno *et al* 2002; Dhage *et al* 2003) have already been reported in the literature. In the case of SnO$_2$–TiO$_2$ solid solution, the samples were heated at 1723 K to obtain large grain growth (>15 μm) and α values are in the range 7–9. However, until now, there is no report on low voltage varistor based on SnO$_2$ system. Here we report the varistor characteristics of doped tin dioxide with low breakdown voltage.

2. Experimental

SnO$_2$ containing additives were prepared by the wet chemical method. The compositional formulas prepared are given in table 1. SnCl$_4$ was diluted using ice-cold distilled water and mixed with required quantities of Co(NO$_3$)$_2$·6H$_2$O and Sb$_2$O$_3$ dissolved in HCl or Nb$_2$O$_5$. The standard ammonia solution was then added dropwise to the above solution with constant stirring until pH was ~ 10. The precipitate was filtered, washed free of anions and dried in the oven. The oven dried powders were calcined at 873 K for 12 h. The calcined powders were mixed with a binder (poly vinyl alcohol, 2 wt%) and pelletized (15 mm dia, 1mm thick) at a uniform pressure of 2–3 metric tons. The pellets were sintered at 1573 K for 15 h to allow reasonable grain growth. The sintered pellets were polished and ohmic silver contacts were obtained by curing Ag-paste and annealed at 873 K for 30 min. The structure related phase determination was studied by Philip 1730 X-ray diffractometer. The microstructure of the sintered pellets was observed using a Leica Cambridge 440 microscope. The I–V characteristics were measured by using Keithley electrometer, 6517A. It also contained inbuilt 1 kV d.c. power supply so that there was no need of external power supply in the circuit. The current–voltage relation of a varistor is given by the equation

$$J = (E/C)^{\alpha}, \qquad (1)$$

where J is the current density, E the applied field, C the proportionality constant and α the nonlinear coefficient. The I–V curves were plotted on log–log scale from which the slope of the curve gave the value of α. The important parameter, E_B (breakdown voltage), was taken as the field applied when current flowing through the varistor was 1 mA. Since Schottky type grain boundary barriers

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Table 1. Characteristic parameters of doped tin dioxide ceramics.

Sample identity	Composition	α	E_B (V mm^{-1})	Φ_B (eV)	Relative density (%)	Average grain size (μm)
SCA-1	(98·99)%SnO$_2$ + 1%CoO + 0·01%Sb$_2$O$_3$/2	10	41	0·30	96·2	10
SCA-2	(98·95)%SnO$_2$ + 1%CoO + 0·05%Sb$_2$O$_3$/2	6	26	0·29	94·8	12
SCA-3	(98·9)%SnO$_2$ + 1%CoO + 0·1%Sb$_2$O$_3$/2	8	41	0·34	95·9	11
SCN-3	(98·9)%SnO$_2$ + 1%CoO + 0·1%Nb$_2$O$_5$/2	7	23	0·31	95·6	11
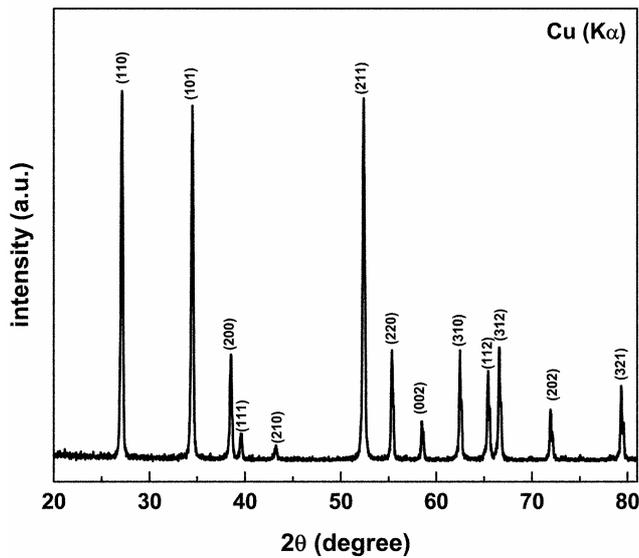
Figure 1. XRD of doped tin dioxide.
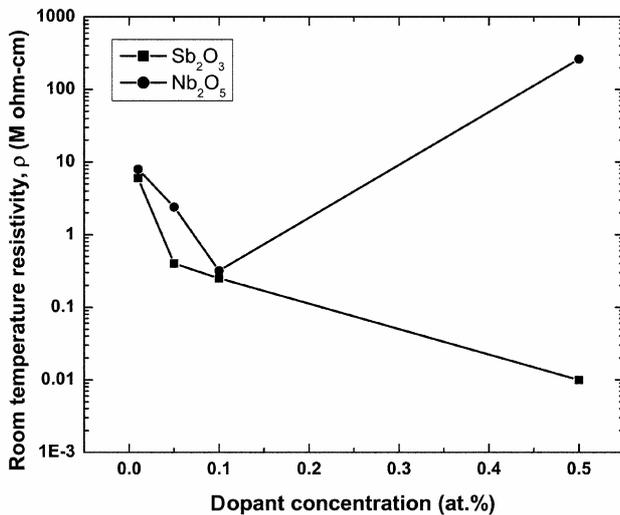
Figure 2. Variation of room temperature resistivity with donor content for CoO doped tin dioxide.

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

where $A = 4\rho emk^2/h^3$, is Richardson's constant, e the electron charge, m the electron mass, k the Boltzmann constant, h the plank constant, Φ_B the interface barrier height, and β a constant related to the relationship given in the equation

$$\beta \alpha 1/(r \times \omega), \tag{3}$$

where r is the grain number per unit length and ω the barrier width, making the current density in ohmic region and keeping the temperature of the tested varistor constant. For two different applied fields, the following equations are used.

$$J_1 = AT^2\exp[(\beta E_1^{1/2} - \Phi_B)/kT], \tag{4}$$

$$J_2 = AT^2\exp[(\beta E_2^{1/2} - \Phi_B)/kT], \tag{5}$$

The values of Φ_B and β can be calculated from the above equations.

3. Results and discussion

Figure 1 shows the X-ray diffractogram (XRD) recorded for the present sample. No second phases are found and all the lines are corresponding to SnO$_2$ tetragonal rutile type phase. It is also to be noted that the concentrations of dopants added are too small to be detected by X-rays. The variation of room temperature resistivity with donor content is depicted in figure 2. The resistivity decreases continuously for antimony doped sample whereas it increases after a minimum value for niobium doped specimens. For identical conditions of processing, low voltage varistor action is observed over a range of antimony doping whereas low breakdown voltage is found at a specific concentration (0·1 at%) of niobium only. This is evident from the resistivity–donor content relations for these ceramics. The obtained values of barrier height, breakdown voltage, nonlinear coefficient, relative sinter density and grain size are given in table 1. The *I–V* curves for the samples containing Sb and Nb are illustrated in figure 3. The calculated α value for Sb and Co doped SnO$_2$ is 11 and for Nb and Co doped SnO$_2$ is 7 and their breakdown voltages are in the range of 40–20 V mm^{-1} as shown in table 1. The microstructure of Sb and Nb doped samples are shown in figures 4(a) and (b), the grain size is ~ 12 μm

were present in the present samples, the current density in ohmic region of varistor was related to the electric field and the temperature given by the equation (Pianaro *et al* 1997)

and ~ 11 μm, respectively. No second phases were found at grain boundaries supporting XRD results.

The varistor action observed in polycrystalline ZnO ceramics is explained by the presence of Schottky type
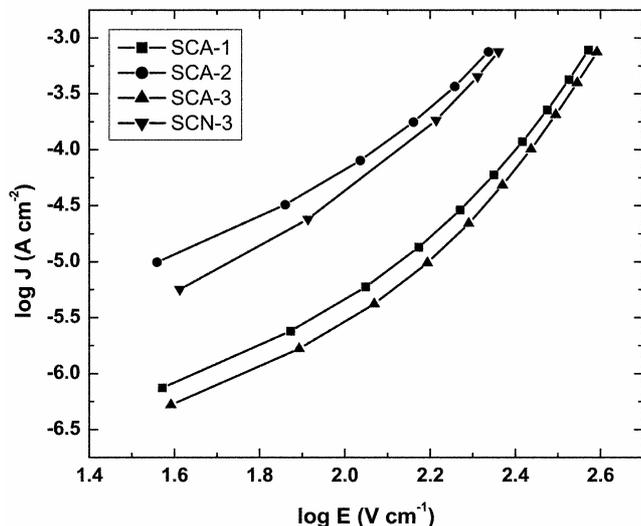

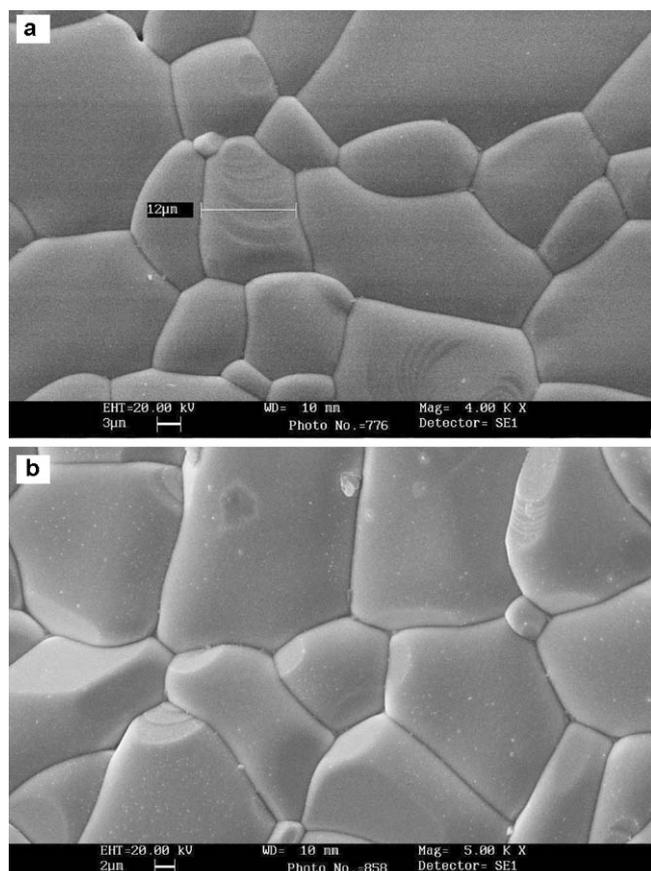**Figure 3.** *I–V* characteristics of doped tin dioxide ceramics.

Figure 4. Microstructure of doped tin dioxide ceramics: (**a**) SCA-2 and (**b**) SCN-3.

energy barrier at the grain boundaries. In the present case the acceptor like surface states formed by CoO will lead to formation of energy barrier at the grain boundaries. This is unlike other tin oxide system reported by us (Dhage *et al* 2002) wherein the presence of rare earth ion at the grain boundaries leads to formation of grain boundary defect states. There the ionic radius of La³⁺ ion being larger than Sn⁴⁺ ion, it prefers grain boundary site. This modification resulted in high α values. As mentioned in the introduction the addition of small quantities of transition metal oxides such as CoO to tin oxide helps in its densification. For example, with 1 mol % CoO, the sinter density is > 94% when sintered at 1573 K for 1 h. The Co²⁺ ion having lower valence creates oxygen vacancies in tin oxide lattice, which is rate-determining step for sintering. The reaction may be written as

$$CoO \xrightarrow{SnO_2} Co''_{Sn} + V_o^{\cdot\cdot} + O_o^x. \tag{6}$$
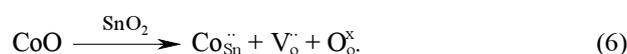
The ionic radius of cobaltous ion being similar to Sn⁴⁺ ion, it may substitutionally replace latter in tin oxide lattice. Co segregation at grain boundary is reported with the help of EDX, TEM and impedance analysis (Wang *et al* 2000; Bacelar *et al* 2002; Cassia *et al* 2005). The incorporation of either antimony oxide or niobium oxide increases electronic conductivity of tin oxide. At lower concentrations, antimony is present as pentavalent and acts as a donor. The defect reaction may be given as

$$Sb_2O_5 \xrightarrow{SnO_2} 2Sb^{\cdot}_{Sn} + 2e' + 4O_o^x + 1/2O_2. \tag{7}$$
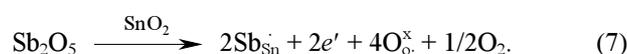
The present varistor system contains less number of additives when compared to ZnO ceramics wherein a variety of metal oxides are added in small quantities to achieve optimum properties.

4. Conclusions

Varistor with low breakdown voltages (E_B, ~ 40 V mm⁻¹) are obtained on doped tin dioxide system. The same ceramics show higher breakdown voltages when the grain size is decreased.

Acknowledgement

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