

Nonlinear I – V characteristics study of doped SnO_2

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Abstract. When tin oxide is doped with Sb_2O_3 and CoO , it shows highly nonlinear current (I)–voltage (V) characteristics. Addition of CoO leads to creation of oxygen vacancies and helps in sintering of SnO_2 . Antimony oxide acts as a donor and increases the conductivity. The results are nearly the same when antimony oxide is replaced by tantalum oxide. The observed nonlinear coefficient, $\alpha = 30$ and the breakdown voltage is 120 V/mm.

Keywords. Varistors; SnO_2 ; nonlinear coefficient; breakdown voltage.

1. Introduction

Varistors (voltage dependent resistors) based on polycrystalline ZnO ceramics are already commercially available to protect electrical/electronic components from transient over voltages (Gupta 1990; Clarke 1999). The important parameters that characterize a typical varistor are nonlinear coefficient (α), breakdown voltage and energy absorption. The advantages of ZnO varistor are their high nonlinear coefficients and energy absorption capability when compared to conventional Zener diodes. However, the breakdown voltage is very high (3.2 V per grain boundary) and precludes them for low voltage applications (Gupta 1990; Clarke 1999). Various techniques to grow larger grain sizes such as seed method have been adopted to overcome this drawback (Quing *et al* 2001). Simultaneously the search for varistor action in other systems has led to the discovery of nonlinear I – V characteristics in TiO_2 (Yan and Rhodes 1982), SrTiO_3 (Fujimoto *et al* 1985) and SnO_2 (Pianaro *et al* 1995; Santhosh *et al* 1997; Varela *et al* 1999; Bueno *et al* 2001; Ravi and Date 2001; Santos *et al* 2001; Dhage *et al* 2002; Dhage and Ravi 2003; Oliveira *et al* 2003). However, the α values are not as high as found in ZnO ceramics. In present investigations, we have focused our efforts to develop varistor based on doped SnO_2 . Tin oxide is an n -type semiconductor with many interesting electronic properties. Tin oxide with ~ 1 mole% antimony oxide exhibits quasi-metallic conductivity while maintaining transparency in the optical region (Cleva *et al* 1998). This optoelectronic property is exploited in optical devices and solar cells. At higher concentration of antimony oxide, the conductivity decreases due to charge compensation occurring by multiple valency of antimony oxide i.e. due to presence of Sb^{3+} , ion conductivity decreases

(Mishra *et al* 1995). Thin film of tin doped indium oxide is a degenerate wide band gap semiconducting oxide, which is commonly used in optoelectronic applications that require a transparent electrode with high optical transmissivity of visible light and reasonable conductivity (Cleva *et al* 1998). The other major application is its property of gas sensing ability due to its poor sinterability in air in pure form even at high temperatures (Pianaro *et al* 1995). The aim of the present work is to study the nonlinear I – V characteristics of doped tin oxide ceramics.

2. Experimental

SnO_2 containing additives were prepared by both wet chemical method and standard ceramic technique. The SnO_2 , along with dopants such as CoO and Sb_2O_5 or Ta_2O_5 in the stoichiometric ratio were mixed and ground well and calcined at 1473 K for 24 h. The calcined powders were again ground and fired at 1473 K for another 24 h. The compositional formula for the series was $\text{Co}_{0.01}\text{Sb}_{0.0005}\text{Sn}_{0.9895}\text{O}_2$ or $\text{Co}_{0.01}\text{Ta}_{0.0005}\text{Sn}_{0.9895}\text{O}_2$. In case of chemical method, SnCl_4 was diluted using ice-cold distilled water and the required quantity of $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, SbCl_5 or TaF_5 was mixed with it. The standard ammonia solution was then added dropwise to the above solution with constant stirring until $\text{pH} \sim 10$. The precipitate was filtered, washed free of anions and dried in an 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 (12 mm dia, 1 mm thick) at 2–3 tons. The pellets were sintered at 1573 K for 2 h. 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 using Philip 1730 X-ray diffractometer. The microstructure of the sintered pellets was observed using a Leica Cambridge 440 microscope.

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The I - V characteristics were measured by using 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 relation of a varistor is given by the equation

$$J = (E/C)^a, \quad (1)$$

where J is the current density, E the applied field, C the proportionality constant and a the nonlinear coefficient. The current-voltage curves were plotted on log-log scale from which the slope of the curve gives the value of a . The important parameter, E_b breakdown voltage is taken as the field applied when current flowing through the varistor is 1 mA.

3. Results and discussion

The X-ray diffractogram (XRD) recorded for the present samples showed that no second phases are found and all the lines are corresponding to SnO_2 tetragonal rutile type phase (JCPDS no. 21-1250). It is also to be noted that the concentrations of dopants added are too small to be detected by X-rays. The I - V curves for the samples containing Sb or Ta are illustrated in figure 1. The calculated a value for Sb and Co doped SnO_2 is 30 and for Ta and Co doped SnO_2 is 29, the breakdown voltage is in the range 120 V/mm. The results obtained are nearly same for both the ceramic and chemical methods. The microstructure of Ta and Sb doped samples are shown in figure 2. The grain size is $\sim 5 \mu\text{m}$ in both cases. 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 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. A

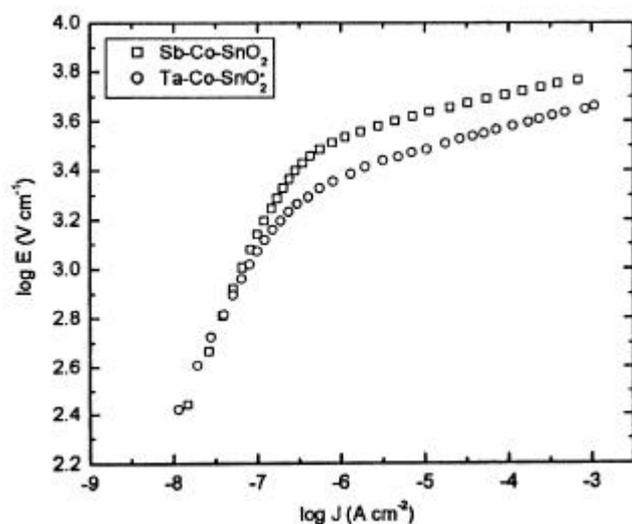


Figure 1. I - V characteristics of SnO_2 doped with CoO and Sb_2O_3 and CoO and Ta_2O_5 .

precipitate consisting of Co_2SnO_4 is observed at the grain boundaries only when the energy dispersive spectroscopy stage is attached to the high resolution transmission electron microscopy and electron diffraction is used (Varela *et al* 1999). This also explains why our attempts to detect any secondary phase at the grain boundaries using scanning electron microscopy attached with energy dispersive analyser failed. The amount of acceptor incorporated being very small in quantity is the main reason for this difference. The increase in conductivity of antimony or tantalum doped with very small quantities (0.05 at.%) also supports this fact that most of the acceptors reside 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 La^{3+} ion being larger than Sn^{4+} ion, it prefers grain boundary site. This modification resulted in high α values. The corresponding breakdown voltages are high for lanthanum doped systems (220 V/mm) in comparison to present compositions. As mentioned in the introduction the addition of small quantities of transition

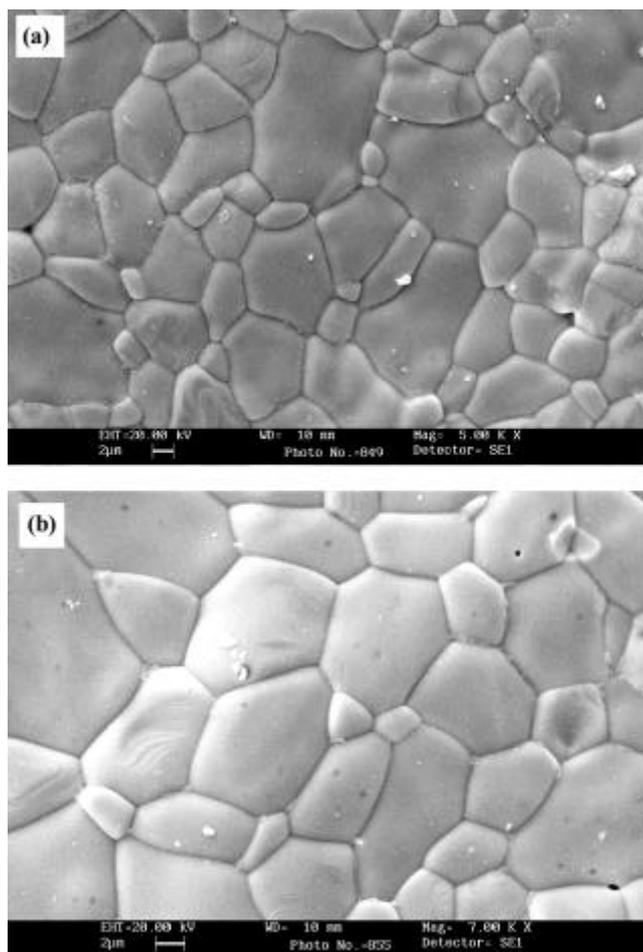
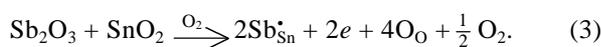


Figure 2. Microstructure of SnO_2 (a) doped with CoO and Sb_2O_3 and (b) doped with CoO and Ta_2O_5 sintered at 1573 K for 2 h (thermally etched).

metal oxides such as CoO to tin oxide helps in its densification. For example, with 1 mol% CoO, the sinter density is > 98% when sintered at 1573 K for 1 h (Cerri *et al* 1996). 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 given below,



However, addition of CoO leads to increase in the resistivity of tin oxide. The ionic radius of cobaltous ion being similar to Sn⁴⁺ ion, it may substitutionally replace the latter in tin oxide lattice, whereas the incorporation of antimony oxide increases the conductivity of tin oxide. At lower concentrations antimony is present as pentavalent and acts as donor. The defect reaction may be given as



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. Conclusion

A new varistor system based on doped SnO₂ system is prepared and it has $a = 30$ and $E_B = 120$ V/mm.

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