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Synthesis and current–voltage characterization of tin dioxide varistors

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An overview of the steady state electrical properties of tin dioxide varistors is presented. The varistors are manufactured in two ways: (1) a ceramic route by mixing and compaction of tin dioxide powder with various dopants and (2) a sol-gel method, where dopants are dispersed in their aqueous solutions. For a quantitative agreement with the experimental data, the electronic defect states in the bulk of the tin dioxide grains and at the grain boundary interfaces are studied. Scanning electron microscope and x-ray diffraction are employed to study the morphological and structural aspects of tin dioxide varistors. The effect of various sintering temperatures on their nonohmic or nonlinear characteristics was also investigated. The varistors prepared by the sol-gel method showed high nonlinearity, high density, and high threshold voltage properties than the ones produced by the ceramic route. This is probably due to a finer grain structure and a better densification of dopants along the grain boundaries. © 1999 American Vacuum Society. [S0734-2101(99)10804-2]

I. INTRODUCTION

Tin dioxide varistors are novel semiconducting ceramics with interesting nonlinear current–voltage characteristics.^{1–5} They are widely used in consumer and military electronics, industrial protection systems, communications, transportation, data processing, power transmission, and various other applications like medical devices.^{2–4} A varistor is a device, which protects the electronic circuits from power fluctuations. Zinc oxide varistors are widely used on commercial basis to control voltage fluctuations and power surges and are proved to be successful.⁶ However, development of varistors with superior properties and cost reduction are encouraged and thus needs an alternative material to substitute zinc oxide varistors. Tin dioxide varistors have contributed a great deal to answer this question. In this article, we report the synthesis of a novel tin dioxide varistor, which shows superior nonlinear properties at lower sintering temperatures than those for ZnO.

In order to characterize a varistors nonlinear behavior, it is desirable to determine the I – V curve, which indicates all three regions of the varistor [Fig. 1(a)]. The three most important regions⁷ that control the varistor properties are as follows:

(1) Low-current linear region ($<10^{-4}$ A/cm²) or prebreakdown (linear) region in which the current–voltage characteristics have a linear relation. The current–voltage characteristics of this linear region are controlled by the resistance of the grain boundary.

(2) Intermediate nonlinear region is the heart of the varistor. In this region, the device conducts an increasingly large

amount of current for a small increase in voltage.

(3) High-current linear region (currents $>10^3$ A/cm²), in which the current–voltage characteristics are linear, similar to that in the low-current prebreakdown region, with the voltage rising faster with current than in the non-linear region.

Among the three regions mentioned above, the nonlinear intermediate region is the most important part because it forms the base of the non-linear current voltage characteristics. Functionally, the varistor acts as a near insulator (resistor) prior to reaching a voltage known as the non-linear voltage or threshold voltage, and it acts as a conductor thereafter. The important parameters of the varistor are the nonlinear coefficient (α) and the nonlinear voltage (E_b). The present work explains both the processing and the electrical characterization of tin dioxide varistors.

II. EXPERIMENT

A. Materials

Pure tin dioxide (99.99%) is a nonstoichiometric semiconductor material with a linear I – V behavior. It exhibits a rutile type structure. The rutile structure of SnO₂ provides an open lattice structure, which accommodates the dopants or additives that are responsible to obtain the nonlinear behavior. The dopants added to tin dioxide are Nb⁵⁺ in the form of Nb₂O₅, Al³⁺ in the form of Al₂O₃ and Cu²⁺ in the form of CuO. Both CuO and Al₂O₃ are added as densifying agents to ensure proper mixing. Since Nb⁵⁺ ionic radii (0.65 Å), Al³⁺ ionic radii (0.535 Å), and Cu²⁺ ionic radii (0.65 Å) are similar to Sn⁴⁺ ionic radii (0.69 Å) their probability of substituting Sn⁴⁺ is large.

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FIG. 1. (a) I - V curves for an ideal varistor. (b) Experimental setup for I - V characteristic measurement.

B. Ceramic process

High purity metal oxide powders (SnO_2 , Nb_2O_5 , CuO , and Al_2O_3) were mixed in suitable proportions using ethyl alcohol as a mixing medium and polyvinyl alcohol as a binder. Function of the binder is to impart sufficient green strength and proper coalition of powder particles. The homogeneously mixed powders were dried for 8–10 h at room temperature and subsequently pressed into pellets. The green pellets were sintered in a muffle furnace (heating rate $200^\circ\text{C}/\text{h}$) at temperatures ranging between 1200 and 1350°C . The rate of heating was reduced to $100^\circ\text{C}/\text{h}$ between 700 and 900°C in order to prevent any possible thermal stresses in the pellets due to shrinkage. After heating, the samples were cooled to room temperature.

C. Chemical process

An enhancement in the performance parameters of the varistors has been noted when prepared by various chemical routes like sol-gel, microemulsions, liquid mix, etc.⁸ As the electronic properties of these materials are highly microstructure dependent, a preferable microstructure consisting of uniformly packed particles with a narrow size distribution is necessary. This article reports a liquid mixing technique for homogeneous synthesis of tin dioxide with Cu, Nb, and Al as dopants. A solution containing $\text{CuO}\cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was prepared in 1000 mℓ distilled water.

SnCl_2 was hydrolyzed in 600 mℓ distilled water and was added to the above solution. The whole solution was continuously stirred. Nb_2O_5 was added to the stirring solution along with 18 mℓ of ammonia. Ammonia was added to make the mixture alkaline ($\text{pH } 9$). Alkaline mixture is the indication of presence of all the cation hydroxide, e.g., copper hydroxide. Stirring was continued for 3 h and the solution was then allowed to settle down by itself. The solution was then dried in a water bath to avoid the possible loss of any dopants during filtration. The dried powder was calcined at 800°C for 3 h. The calcined powder was grounded (avoid agglomeration), pelletized, and sintered at temperatures in the range of 1200 – 1350°C . The sintered samples were lapped to the required thickness for further measurements.

D. Physical and chemical characterization

For electrical property measurements, it is necessary to make provision for electrical contact because ceramic oxides are highly nonconducting. The lapped pellets were coated uniformly on both sides by a silver paint. The coated pellets were dried in a furnace at 600°C to ensure the evaporation of other organic compounds and the retention of pure silver on the surfaces. The room temperature direct current (dc) current-voltage (I - V) characteristics for the sintered samples (both for physical and chemical synthesis) were measured using a Keithley Electrometer (Model 610C) and Aplab stabilized dc power supplies (Model 7161 & 7323). The experimental setup is shown in Fig. 1(b). The samples were then sintered at different temperatures 1200 , 1250 , 1300°C for 15–18 h.^{9,10} These temperatures were chosen based on our past experiments on sintering previous varistor samples at various temperature/time intervals.¹¹

III. RESULTS AND DISCUSSION

A. Scanning electron microscopy

The microstructural changes^{12,13} of the varistor samples produced by physical and chemical synthesis are studied using scanning electron microscopy (SEM) to understand the grain-grain boundary microstructure pattern. The pellets were fractured and the fractured surface was analyzed using SEM after coating the surface with gold. The scanning electron micrographs of the samples sintered at 1200 , 1250 , 1300°C (ceramic route), and 1250°C (chemical route) are shown in Fig. 2. The grain sizes obtained for each sample are listed in Table I. It is to be noted that the grain size increases with increasing sintering temperatures.

For the samples sintered at 1200°C (ceramic route), the average grain size is $2\text{ }\mu\text{m}$. As the temperature is increased to 1250°C , grain size also increases to $3\text{ }\mu\text{m}$. A further increase in grain size ($5\text{ }\mu\text{m}$) is observed when the temperature is increased to 1300°C . This increase in the grain size has a definite impact¹⁴ on the current-voltage characteristics of the varistor, i.e., on its nonlinear properties and its level of nonohmic behavior. The SEM micrograph of the fractured surfaces of the sol-gel synthesized sample sintered at 1250°C shows a uniform and smaller grain size ($1\text{ }\mu\text{m}$) distribution

FIG. 2. SEM micrographs of samples sintered at various temperatures by ceramic and chemical routes.

as compared to the sample prepared by the ceramic route. In the chemical synthesis, grains are well defined and the voids are considerably reduced due to proper mixing. This results in a greater dopant segregation around the grain boundaries of tin dioxide due to larger grain boundary area. Since grain boundaries are more resistive than grainbody, the varistor effectively exhibits better nonlinear behavior and can be related to the avalanche or the zener effect.⁷

B. Structure determination

The x-ray diffraction (XRD) studies of the sample sintered at 1250°C by the ceramic route (Fig. 4) indicates diffraction peaks corresponding to tin dioxide rutile structure. The typical XRD peak positions, their relative intensities and (hkl) parameters are shown in the Table II. The relative intensities of the peaks compared to the rutile structure available in the literature differ slightly since the XRD measurements were performed on pellets.

In the pellets, orientation of planes can occur during sample processing. The calculated lattice parameters of our

TABLE I. Grain sizes of samples obtained from scanning electron microscope.

Ceramic route	
Sintering temperature (°C)	Grain size (μm) (± 0.5)
1200	2
1250	3
1300	5
Chemical route	
1250	1

TABLE II. X-ray diffraction data of rutile SnO_2 .

d values ($\text{\AA}$)	2θ (°)	(hkl)	Intensity (arb units)
3.351	26.578	110	93
2.644	33.875	101	100
2.369	37.949	200	32
2.309	38.975	111	8
2.120	42.611	210	3
1.765	51.751	211	72
1.675	54.757	220	25
1.593	57.834	002	14

sample are, $a = b = 4.752 \text{ \AA}$, and $c = 3.183 \text{ \AA}$. The XRD patterns of the sample do not show any additional peaks corresponding to the secondary phases which are expected to develop during the sintering process. Also the concentration of dopants is too small to form a secondary phase to be detected by XRD. In addition, the ionic sizes of the dopants [$\text{Al}^{3+}(0.535 \text{ \AA})$, $\text{Nb}^{5+}(0.65 \text{ \AA})$, and $\text{Cu}^{2+}(0.65 \text{ \AA})$], are smaller than $\text{Sn}^{4+}(0.69 \text{ \AA})$ and hence these ions occupy the lattice position by substitution.

C. Current–voltage characteristics

The varistor is characterized by a voltage,¹⁵ which marks the transition from linear to nonlinear mode. The voltage at the onset of this nonlinearity, just above the “knee” of the I – V curve, is the nonlinear voltage, which determines the voltage rating of the device. To calculate the varistor parameters, the convention followed is to plot current density (A/cm^2) versus voltage (V/mm) on a log–log scale. The current voltage relation of a varistor in the nonlinear region can be empirically expressed as

$$I = K(V)^\alpha.$$

The voltage corresponding to 1 mA as calculated from the I – V curve is the nonlinear voltage.

The most important parameter of the tin dioxide varistor is the nonlinear coefficient (α),¹⁵ which is the reciprocal of

FIG. 3. Current–voltage characterization of sintered tin dioxide doped samples prepared by ceramic and chemical routes.

FIG. 4. X-ray diffraction of rutile SnO_2 .

the slope of the curve in the non-linear region. The greater the value of α , the better the device. Figure 1(a) shows that as the current increases, α values are progressively changed. The α value increases in the prebreakdown region, reaches a maximum value in the nonlinear region, and then diminishes in the upturn region. Thus it is important to determine the values of α with reference to the magnitude of currents over which the application is desired. In practice, therefore, the α value is estimated between the two desired magnitudes of currents and corresponding voltages and is expressed as:

$$\alpha = \log(I_2/I_1) / \log(V_2/V_1).$$

The I - V characteristics of samples at 1200, 1250, and 1300 °C are plotted in Fig. 3. The thickness of all the samples is 0.65 mm and the measured area of contact is 0.433 cm². The values for the nonlinear coefficients and their respective nonlinear voltages are listed in Table III. It is seen that the nonlinear coefficient (α) value for the samples prepared by the ceramic route increases, reaches a maximum value and then decreases with increase in the sintering temperature. The optimum value of α is 14 at 1250 °C, and it decreases as temperature increases to 1300 °C. Thus the optimum sintering temperature is chosen to be at 1250 °C. Figure 3 shows the I - V characteristics plotted on a logarithmic scale for various samples. The samples processed by ceramic

TABLE III. Effect of sintering temperature on I - V curves.

Ceramic route		
Sintering temperature (°C)	Nonlinear coefficient (α) (± 2)	Nonlinear voltage ($E_{1 \text{ mA}}$) V/mm (± 10)
1200	12	672
1250	14	431
1300	8	289
Chemical route		
1250	15	400

route and sintered at 1200, 1250, and 1300 °C showed a very small ($< 10^{-6}$ A/cm²) prebreakdown current (Fig. 3). The linear low-current region represents the grain boundary characteristics. The prebreakdown characteristics show that for the samples sintered at 1200, 1250, and 1300 °C, the grain boundary resistance is considerably large. From our past experiments,¹¹ it has been noted that no nonlinear behavior was observed when the samples were sintered below 1200 °C (at 1000, 1100, and 1150 °C nonlinear behavior was not observed).¹¹ Hence it is concluded that in our case, a sintering temperature of 1200 °C and above is needed for the formation of highly resistive grain boundary regions and thereby an effective energy barrier. Sintering above and below 1250 °C yielded inferior nonlinear current-voltage characteristics as observed from Fig. 3. The values of α (nonlinear coefficient) and E_b (nonlinear voltage) were calculated using empirical equations mentioned in earlier sections.

The reason for optimum properties of a varistor depends primarily on the dopant concentration^{16,17} and is related to the formation of intergranular segregation layers which in turn are responsible for the changes in the nonlinear coefficient values and hence the nonlinearity.² When the dopants are added to the parent varistor base material, they tend to segregate along the grain boundaries. This is based on the data provided by various researchers in the past.^{2,18-19,20} For example, in the case of Sb_2O_3 -doped ZnO varistors, Sb^{+3} dopant segregates along the grain boundaries as detected by detailed XRD and SEM studies.^{2,21} In the present case, the

FIG. 5. (a) Schematics of microstructure and (b) electrical characteristics of a varistor.

dopant ion concentration is low enough to be detected by XRD, as discussed earlier.

From conventional resistivity measurements, [as seen in Fig. 5(a)] the resistivity (ρ_g) of the SnO_2 grain is found to be 1–10 $\Omega \text{ cm}$. The resistivities for the grain boundary (ρ_{gb} — $1.5 \times 10^{10} \Omega \text{ cm}$) are estimated from the slopes of the $I-V$ curve shown in Fig. 3. This makes the boundary makes resistive, whereas the grainbody remains conductive. A sharp drop in the resistivity from grain boundary to grainbody occurs within a distance of ≈ 50 –100 nm, [Fig. 5(b)] known as the depletion layer.¹ Thus at each grain boundary, there exists a depletion layer on both sides of the grain boundary extending into adjacent grains. The varistor action arises as a result of this depletion layer within the grains. Since the region near the grain boundary is depleted of electrons, a voltage drop appears across the grain boundary due to an applied external voltage thus protecting the device. These resistive grain boundaries function in the nonlinear region of the varistor thus enhancing its properties.

The nonlinear voltage is decreased with increasing sintering temperature and is due to the reduction in grain size. The smaller the grain size, the greater the grain boundary area and thus more dopants can segregate along the grain boundaries. This leads to the formation of more resistive grain boundaries.

The sample prepared by the chemical route and sintered at 1250 °C shows an “ α ” value of 15. This indicates that some changes have taken place during the synthesis from ceramic to chemical route. This is primarily due to the homogenous distribution of the dopants around the grain boundaries and the decrease in the nonlinear voltage. In the chemical route, the dopants are in their aqueous solutions. Hence there is a greater probability of uniform mixing and segregation of dopants around the grain boundaries. As the dopant density increases around the grain boundaries, they become more resistive and as stated earlier show better nonlinear properties.

IV. CONCLUSIONS

The tin dioxide varistors, (doped with CuO , Nb_2O_5 , and Al_2O_3) prepared by ceramic route are proved to be better

voltage sensors and are comparable to ZnO varistors. A maximum nonlinear coefficient (α) as high as 15 and nonlinear voltage of 400 V/mm were obtained for the sample sintered at 1250 °C. This sample passed a very low current as shown in Fig. 3. This proves that the grain boundaries offered a very high resistance due to smaller grain size. The sintering temperature of 1250 °C seems to be the ideal temperature both in terms of nonlinearity and microstructural distribution. It is clear that the uniform distribution of dopants and grain sizes is important to get enhanced varistor characteristics, hence chemical synthesis improves the nonlinear characteristics. It is hoped that in coming years the research efforts in varistors are likely to have path breaking impact in design and development of better varistors using tin dioxide as a base material.

¹T. K. Gupta, J. Am. Ceram. Soc. **73**, 1817 (1990).

²M. Matsuoka, Jpn. J. Appl. Phys., Part 1 **10**, 736 (1971).

³W. G. Morris, J. Vac. Sci. Technol. **13**, 926 (1976).

⁴L. M. Levinson and H. R. Philipp, J. Appl. Phys. **46**, 1332 (1975).

⁵P. R. Emtage, J. Appl. Phys. **48**, 4372 (1977).

⁶L. M. Levinson, *Proceedings of the Second International Varistor Conference, Schenectady, NY, 5–6 December 1988* (American Ceramic Society, Westerville, Ohio).

⁷J. O. Levine, CRC Crit. Rev. Solid State Mater. Sci. **5**, 598 (1975).

⁸C. J. Brinker and G. W. Scherer, *The Physics and Chemistry of Sol Gel Processing* (Academic, San Diego, CA, 1990).

⁹H. R. Philipp and L. M. Levinson, J. Appl. Phys. **50**, 383 (1979).

¹⁰T. K. Gupta, M. P. Mathur, and W. G. Carlson, J. Electron. Mater. **6**, 483 (1977).

¹¹P. N. Santhosh, Ph.D. thesis, University of Pune, 1996.

¹²J. Wong, J. Appl. Phys. **46**, 1653 (1975).

¹³T. K. Gupta, *Tailoring Multiphase and Composite Ceramics* (Plenum, New York, 1986), pp. 493–507.

¹⁴T. K. Gupta, J. Mater. Res. **2**, 231 (1987).

¹⁵K. Eda, IEEE Trans. Electr. Insul. **5**, 28 (1989).

¹⁶W. G. Carlson and T. K. Gupta, J. Appl. Phys. **53**, 5746 (1982).

¹⁷T. Miyoshi, K. Maeda, K. Takahashi, and T. Yamazaki, in *Advances in Ceramics*, edited by L. M. Levinson and D. Hill (American Ceramic Society, Columbus, OH, 1981), Vol. 1, p. 309.

¹⁸D. R. Clarke, J. Appl. Phys. **49**, 2407 (1978).

¹⁹J. Wong, J. Appl. Phys. **46**, 1653 (1975).

²⁰M. Inada, Jpn. J. Appl. Phys., Part 1 **17**, 673 (1978).

²¹S. R. Sainkar, S. Badrinarayan, A. P. B. Sinha, and S. K. Date, Appl. Phys. Lett. **39**, 65 (1981).