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Journal

Effect of Seed Addition on SnO_2-Based Varistors for Low Voltage Application

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The effect of seed addition on the microstructure and non-ohmic properties of the SnO_2 + 1%CoO + 0.05%Nb_2O_5 ceramic-based system was analyzed. Two classes of seeds were prepared: 99% SnO_2 + 1%CuO and 99% SnO_2 + 1%CoO (mol%); both classes were added to the ceramic-based system in the amount of 1%, 5%, and 10%. The two systems containing 1% of seeds resulted in a larger grain size and a lower breakdown voltage. The addition of 1% copper seeds produces a breakdown voltage (V_b) of ~ 37 V and a leakage current (f_{ic}) of 29 μA. On the other hand, the addition of 1% cobalt seeds produced a breakdown voltage of 57 V and a leakage current of 70 μA. Both systems are of great technological interest for low voltage varistor applications, by means of appropriate strategies to reduce the leakage current. Using larger amounts of seeds was not effective since the values of breakdown voltage in both cases are close to a system without seeds. To our knowledge, there are no reports in the literature regarding the use of seeds in the SnO_2 system for low voltage applications. A potential barrier model which illustrates the formation of oxygen species ($O'_{2(ads)}$, O'_{ads}, and O''_{ads}) at the expense of clusters near the interface between grains is proposed.

I. Introduction

To date, electronic systems are being manufactured in even smaller sizes and are highly susceptible to voltage transients (over-voltage) or electrostatic discharge.[1,2] Therefore, it is imperative to develop varistors to protect these low-voltage electronic devices. SnO_2-based varistors are semiconductor solid-state devices which are formed from the normal sintering of SnO_2 particles with addition of other oxides such as CoO or MnO as densifying agents and Cr_2O_3 and Nb_2O_5 as potential barrier-forming agents.[3] These varistors are switching devices, which operate at level of voltages whose resistance decreases drastically when the voltage is increased up to a breakdown voltage.[4]

The application of a ceramic varistor in circuits with high, medium or low voltage is related to the number of effective potential barriers between electrodes. The number of these barriers can be controlled during the sintering process by the rate of grain growth and/or by adding metal oxides as dopants, which segregate or precipitate at grain boundaries and inhibit grain growth.[5]

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The SnO_2-based ceramic varistors doped with 1% of Co + 0.05% of Nb_2O_5 + 0.05% of Cr_2O_3 have an average grain size between 2.5 and 5.5 μm with a breakdown electric field between 4000 and 6000 V/cm.[6,7] The impedance spectroscopy calculation of the potential barrier height shows values around 1.0 eV for this system.

The SnO_2-based varistors for low voltage applications must have an average grain size >20 μm to produce a small number of effective barriers per unit of length. One way to achieve grain growth is dependent upon a time increase and/or the sintering temperature of the ceramic system. However, in most cases, the increase in temperature and/or sintering time cause degradation of the non-ohmic properties due not only the volatilization of the dopants but also the metal oxide of the matrix. Santos *et al.*[8] studied the influence of sintering time on the electrical and microstructural behavior of SnO_2-based varistors and observed that the potential per barrier varies with the sintering time. Sintering at 1300°C for 1 h was insufficient for the formation of barriers. Also, sintering at 1350°C for 12 h has been exaggerated which reduces electrical properties of the material due to volatilization of the SnO_2 oxide matrix and its dopants.

Another way to obtain grain growth without employing longer times and/or higher sintering temperatures is through the addition of seed, which promotes grain growth.[9] Eda *et al.*[10] added 10% ZnO seeds doped with 0.5 mol% of BaO and a particle size in the range of 63–105 μm to the traditional ZnO varistor system and obtained grains up to 500 μm in size and a breakdown voltage of 60 V.

Zhou and Yang[11] studied the variation in the amount of seeds (5% of seeds with a particle size in the range of 20–100 μm) added to the traditional-based ZnO varistor doped with Bi, Sb, Co, Mn and Cr and obtained a breakdown electric field of 260 V/cm. Souza *et al.*[12] investigated changes in the seed concentration on electrical properties of a ZnO-based varistor and concluded that the addition of 10% seeds generates a breakdown electric field of 400 V/cm with a nonlinearity coefficient of 13.

According to the literature, dopants such as CoO and CuO favor grain growth in SnO_2-based ceramics. Fayat and Castro[13] observed a grain size of ~ 20 μm for SnO_2-based systems containing 0.34 mol% of Co_2O_3 probably due to the formation of oxygen vacancies, which facilitates diffusion mechanisms in the solid state. Lalande *et al.*[14] observed an average grain size of ~ 10 μm in SnO_2-based ceramics doped with 7.5 mol% of CuO sintered at 1400°C. The higher growth was attributed to the formation of a liquid phase during sintering.

Few studies in the literature report the use of seeds to promote grain growth and consequently to obtain low voltage varistors, but ZnO-based varistors are employed in these studies. Therefore, adding seeds to the SnO_2-based varistor is a topic not yet explored in the literature and therefore is the main goal of this work. In this research, we evaluated the main changes on the amount and composition of 99% SnO_2 + 1% CoO and 99% SnO_2 + 1% CuO seeds on the SnO_2 + 1% CoO + 0.05% Nb_2O_5-based ceramic system to obtain a varistor with low breakdown voltage.

II. Experimental Procedure

Powders were prepared by the conventional mixed oxide method using zirconia balls in an isopropyl alcohol medium. Oxides of analytical grade such as SnO_2 (Aldrich 99.9%, Saint Louis, MO), CuO (Sigma Aldrich 99+, Saint Louis, MO), CoO (Aldrich 99.99%) and Nb_2O_5 (Aldrich 99.99%) were used to prepare the SnO_2-based ceramic compositions. The composition of the SnO_2-based varistor was 99.95% SnO_2 + 1.0% CoO + 0.05% Nb_2O_5, and the seed compositions were 99.0% SnO_2 + 1.0% CuO and 99.0% SnO_2 + 1% CoO with all compositions in mol percent.

The seed compositions were pressed into pellets of 25 mm in diameter and 2 mm in thickness and were sintered at 1400°C during 4 h in a water vapor atmosphere. Then, the seeds were crushed, ground, sieved (<25 μm) and added in proportions of 1%, 5%, and 10% in weight relative to the basic system.

The mixture of the matrix and seed powders was homogenized and pressed into disks of 12 mm in diameter and 1.5 mm in thickness followed by isostatic pressing at 210 MPa. Because these conditions favor grain growth, these disks were sintered at 1350°C for 4 h in a water vapor atmosphere[15] and cooled at 5C°/min to room temperature (see Table I for systems nomenclature).

X-ray diffraction values for sintered samples were obtained by the Rigaku–Rint 2000 (Tokyo, Honshu, Japan) diffractometer with Cu$K\alpha$ radiation (λ = 1.5406 Å) in the 2θ range from 20 to 80° with 0.2° $\min^{-1}$. The relative densities were determined using the Archimedes method. The morphology was observed using scanning electron microscopy (SEM) (Topcon - SM 300, Anderson Materials Evaluation, Inc., San Jose, CA), and the average grain size was determined using the intercept method. For electrical measurements, the samples were polished by leaving the faces parallel; gold electrodes were deposited by DC sputtering. The current-voltage characteristics were obtained with the aid of a stabilized voltage source (Keithley Model 237, Tecktronix Company, Cleveland, OH). The nonlinear coefficient (α) was determined in the current range of 1 to10 mA/cm^2 through linear regression. The electric field breakdown was extracted when the current density in the varistor was 1 mA/cm^2 and the leakage current was calculated at 70% of the electric field breakdown. The breakdown voltage (V_b) is defined by the average number of electric barriers n with the value V_{gb} formed in series between the electrodes of the material:

$$V_b = nV_{gb}; n = \frac{e}{L} \tag{1}$$

where e is the thickness and L is the average grain size of the sample, thus

$$V_b = \left(\frac{e}{L}\right)V_{gb}; V_{gb} = E_b \cdot L \tag{2}$$

where E_b is the breakdown electric field.

To achieve high densities of electric current and irreversible breakdown, current pulses of 8/20 μs were used. After the initial DC measurements, pulses were used with increasing voltage until the rupture of the sample. The values obtained were ~ 10^3 A/cm^2 up to rupture, on samples of diameter of 1 cm, thickness of 0.1 cm, and area of the gold electrodes of 0.385 cm^2. Grain resistivities were determined by the slope of J versus E curve in region III.

Impedance spectroscopy measurements were obtained with a frequency response analyzer (HP 4194A, Agilent Company, Santa Rosa, CA) from 40 to 110 MHz with a voltage amplitude of 5 mV and 2 V of bias voltage in the range of 0–38 V.

Table I. Composition and Nomenclature Employed in this study

Systems	Nomenclature
SnO_2+1.00%CoO + 0.05% Nb_2O_5	SCN
SCN + 1% Co seeds	SCNCo1
SCN + 5% Co seeds	SCNCo5
SCN + 10% Co seeds	SCNCo10
SCN + 1% Cu seeds	SCNCu1
SCN + 5% Cu seeds	SCNCu5
SCN + 10% Cu seeds	SCNCu10

III. Results and Discussion

X-ray diffraction values for sintered samples are shown in Fig. 1. X-ray data for both seed compositions show identical behavior and exhibit the cassiterite tin oxide structure. No secondary phases relative to the added seeds were observed, which indicates that all dopants are below the detection limit of the equipment.

Densities of the sintered samples were around 97.5%–99.8% of the theoretical density. The addition of 1% cobalt or copper seeds reveals a density at around 99.7% of the

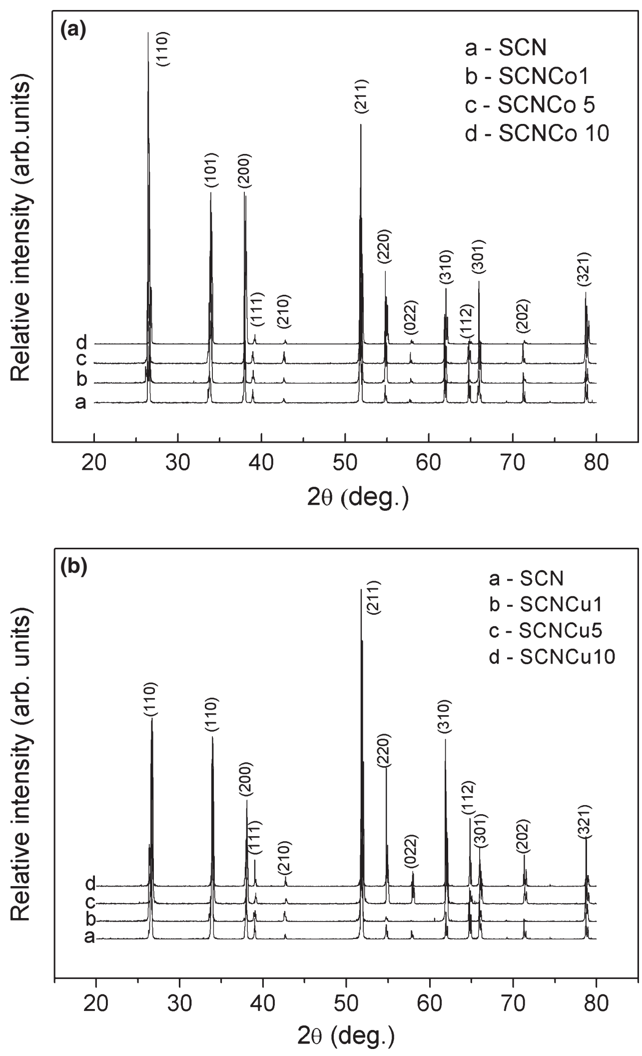

Fig. 1. X-ray patterns of samples sintered at 1350°C/4 h showing: (a) cobalt seeds and (b) copper seeds.

Table II. Relative Density (ρ_R), Average Grain Size (L), Nonlinear Coefficient (α), Breakdown Electric Field (E_b), Breakdown Voltage (V_b), Breakdown Voltage of Grain (V_{gb}), Leakage Current (f_{ic}), and Resistivity of the Grain (ρ) for Systems Sintered at 1350°C/4 h

Systems	ρ_R (%)	L (μm)	α	E_b (V/cm)	V_b(V)	V_{gb}(V)	f_{ic} (μA)	ρ (Ω.cm)
SCN	99.8	23	10.5	579	72	1.3	32	1.6
SCNCo1	99.7	32	8.1	437	57	1.4	70	1.6
SCNCo5	98.3	29	7.9	476	62	1.4	40	1.3
SCNCo10	97.7	27	6.2	487	63	1.3	80	1.3
SCNCu1	99.8	32	7.0	284	37	0.9	29	1.6
SCNCu5	98.9	26	6.0	492	65	1.3	80	1.6
SCNCu10	97.5	26	6.0	481	61	1.3	85	1.3

theoretical density, which is almost equal to the system without seeds. By increasing the amount of seeds, the density decreased, which is probably due to intergranular and intragranular pores. According to Wang *et al.*[16] the maximum densification of SnO_2 occurs with ($x < 0.5\%$) mol of CuO and decreases rapidly for quantities ($x > 0.5\%$). Table II shows the percentage of relative density for all studied systems.

Figure 2 shows SEM of non-ohmic polycrstalline SnO_2-based ceramics. SCNCo1 and SCNCu1 systems promoted grain growth ~ 40% over the SCN based system. Each seed is a nucleous of grain growth matrix which promotes its growth at the expense of the matrix (SCN-based system). The addition of 5% and 10% seeds facilitate nuclei growth and reduces the amount of material from the matrix for grain growth and as a consequence the grain size vanishes (see Table II). A larger average grain size is observed for systems containing cobalt seeds as compared with a system without seeds because when CoO is added to the SnO_2, oxygen vacancy concentrations improve the diffusion process and mass transport and thus promotes the grain growth.[15,17,18] In the case of adding copper seed with 5% and 10%, the grain growth was negligible when compared with the SCN-based system.

According to Gaponov,[19] grain growth is feasible up to 1 mol% of copper oxide; above this value and up to ~ 8 mol%, the grain size remains constant. However, if we take into consideration the amount of nuclei added in the SCNCu5 and SCNCu10 systems which hinders growth by the deficiency of the amount of matter in the matrix near the nuclei, our results are consistent with the values obtained by Gaponov. Also, during sintering at elevated temperatures, the CuO liquid phase controls grain size.[14]

The current density (J) plot as a function of the electric field (E) is shown in Fig. 3. For systems with seed additions, a lower breakdown electric field (E_b) was reported for cobalt SCNCo1 (437 V/cm) and copper SCNCu1 (284 V/cm). The nonlinear coefficient value for the system (SCN) is α = 10,

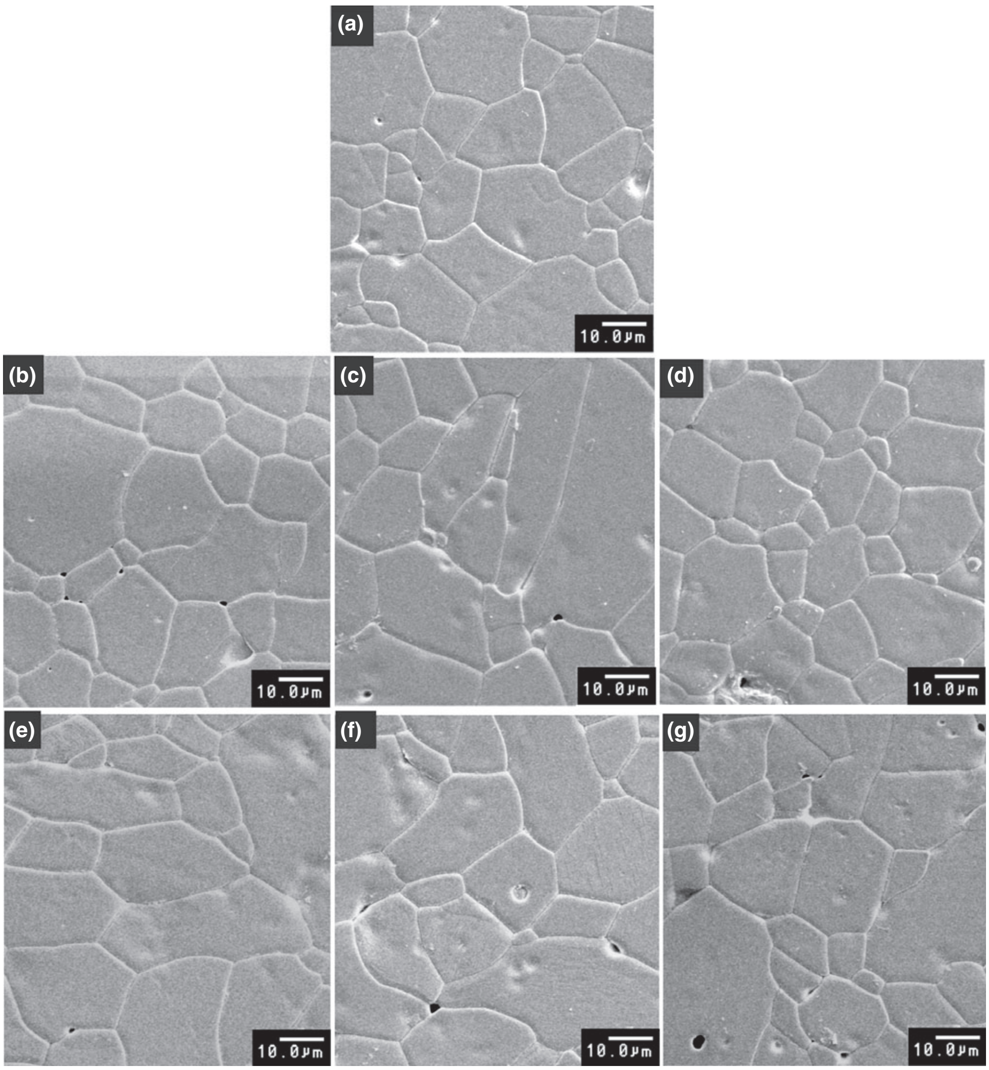

Fig. 2. Scanning electron microscopy images of the polished and etched surface of the varistor systems: (a) SCN; (b) SCNCo1; (c) SCNCo5; (d) SCNCo10; (e) SCNCu1; (f) SCNCu5, (g) SCNCu10.

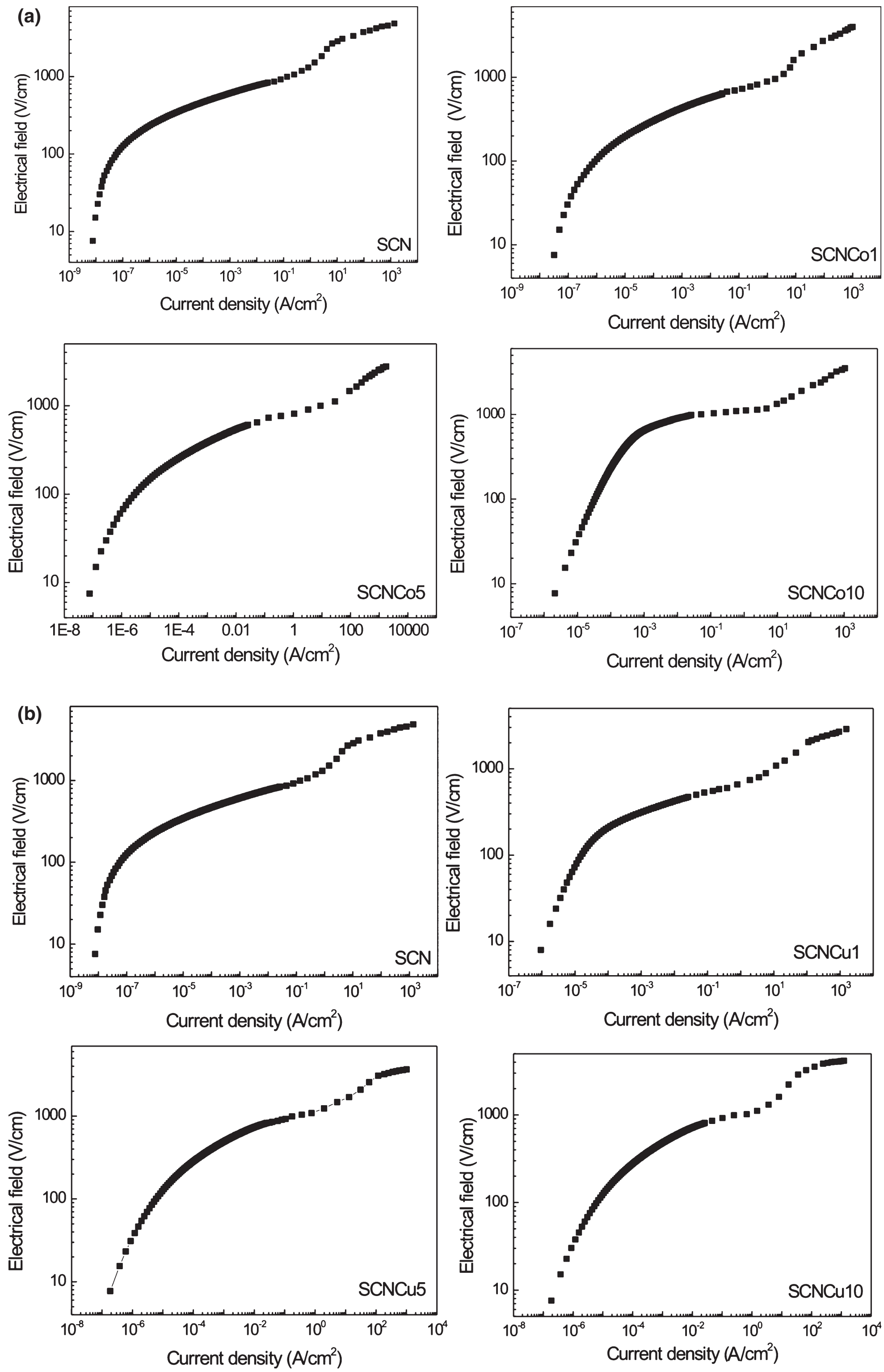

Fig. 3. Current density (J) versus electric field (E) for systems sintered at 1350°C 4 h with seeds addition: (a) cobalt; (b) copper.

and the seed addition decreases the nonlinear coefficient which is probably due to an increase in porosity from 5% to 10% of seeds. A cobalt and copper samples with 1% addition of seeds reduces the number of barriers due to the grain size increase, which affects the breakdown voltage.[20]

A very important variable in ceramic varistors is the leakage current which controls stability during its lifetime.[21–23] Therefore, the SCNCu1 system had the lowest leakage current as a potential candidate for low-voltage protection. Table II displays the relative density (ρ_R), average grain size (L), nonlinear coefficient (α), breakdown electric field (E_b) breakdown voltage (V_b), breakdown voltage of grain (V_{gb}), leakage current (f_{ic}), and resistivity of the grain (Ω) for systems sintered at 1350°C/4 h. No changes in the grains resistivity were observed in all investigated samples (within experimental error).

Samples were characterized using impedance spectroscopy for a better understanding of changes in conduction mechanisms (see Fig. 4). Two semicircles represent two relaxation processes: one at high frequency possibly related to space charges at grain boundaries; and the other at low frequencies associated with grain boundaries. Orlandi *et al.*[24] proposed

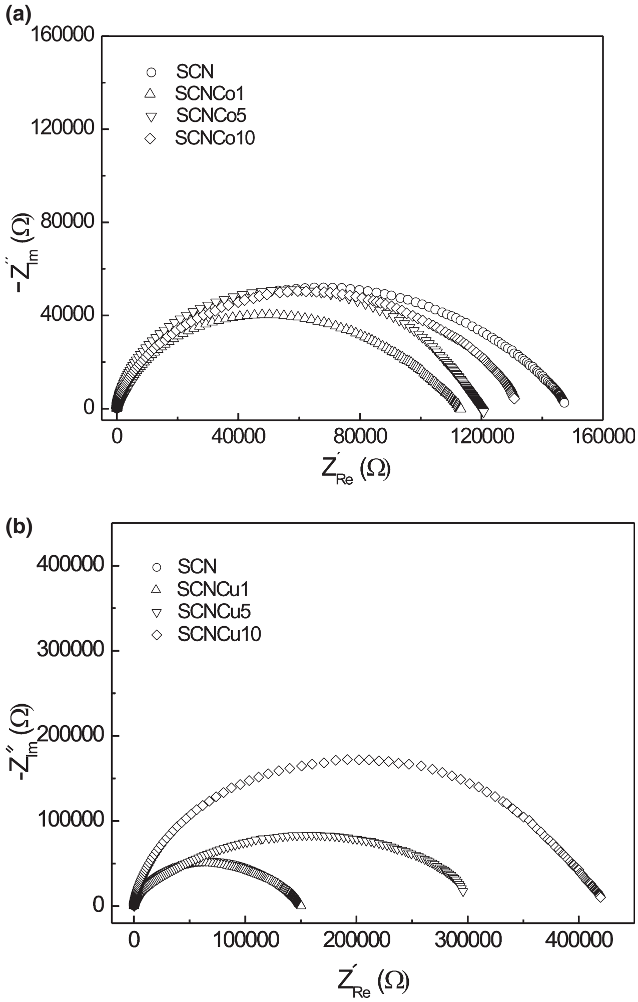

Fig. 4. Cole-Cole diagrams for varistor systems sintered at 1350°C 4 h with seeds addition: (a) cobalt; (b) copper.

an equivalent circuit representation (R [RC] C) for the different processes associated with grain boundaries and space charges or levels of electron trapping for the varistor system SnO_2-MnO with different amounts of Nb_2O_5. This relaxation process for space charges is a manifestation of the charge carriers trapped in the grain-boundary region which are balanced by the space charge regions in the adjacent grain zone as outlined by Bueno *et al.*[25]

With the cobalt seed addition, the total resistance (grains plus grain boundaries) decreases (see Table III) when compared with the SCN-based system. However, with the copper seed addition, the total resistance increases. With an increase in the grain size and the seed addition, a reduction in the number of grain boundaries per unit of length occurs, which causes a reduction in the total resistance for samples with addition of cobalt seed. The largest increase in the resistance with the copper addition could be due to a liquid phase at grain boundaries as discussed in the literature[19,20] and as shown in Fig. 5 in this study.

Table III. Total Resistance of Systems Sintered at 1350°C/4 h

Seeds	0% (Ohm)	1% (Ohm)	5% (Ohm)	10% (Ohm)
99%Sn-1%Co	1.48×10^5	1.13×10^5	1.21×10^5	1.31×10^5
99%Sn-1%Cu	1.48×10^5	1.50×10^5	2.98×10^5	4.42×10^5

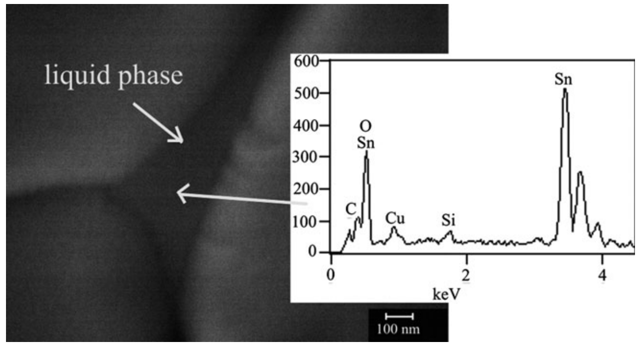

Fig. 5. Scanning electron microscopy images with EDS of the polished and etched surface of the SCNCu10 sample.

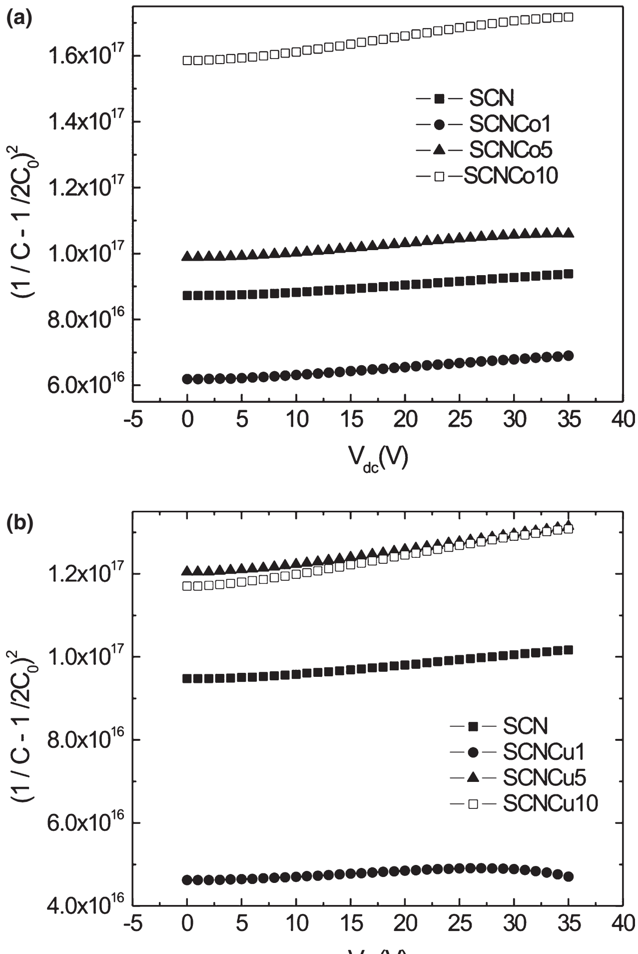

Fig. 6. Mott-Schottky behavior for varistor systems sintered at 1350°C 4 h with seeds addition: (a) cobalt; (b) copper.

The Schottky type potential barrier was deduced from the dependence between the voltage and capacitance as illustrated in Fig. 6. The values in Table IV were obtained by considering the average number of grains between electrodes. N_d and N_{IS} values are similar to values observed in the literature for low voltage (Sn, Ti)O_2-based varistors.[25] A good linear correlation can be seen between the left side of the equation $(1/C-1/2C_o)^2$ and the DC voltage, which indicates that Schotttky type barriers are formed at grain boundaries.

Capacitance-frequency values suggest Mott-Schottky behavior for the SnO_2-based varistor junctions. Table IV shows potential barrier height (Φ) values, a potential barrier width (ω), donor densities in the grain (N_d), and donor densities at the interface (N_{IS}), which were calculated according to

Table IV. Values of Potential Barrier Height, Barrier Width, Density of States in the Grain and Density of Donors at the Interface for Systems Sintered at 1350°C/4 h

Systems	ϕ (eV)	ω (nm)	N_d (m^{-3})	N_{IS} (m^{-2})
SCN	0.3	6.2	2.70×10^{24}	3.35×10^{16}
SCNCo1	0.5	5.3	6.56×10^{24}	6.94×10^{16}
SCNCo5	0.5	14.3	9.99×10^{23}	2.86×10^{16}
SCNCo10	0.4	21.6	8.89×10^{23}	2.19×10^{16}
SCNCu1	1.8	9.6	7.38×10^{24}	1.42×10^{17}
SCCNCu5	1.8	7.0	1.40×10^{25}	1.96×10^{17}
SCNCu10	1.7	11.5	5.11×10^{24}	1.17×10^{17}

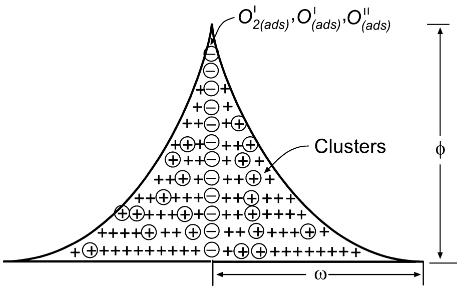

Fig. 7. Grain-boundary barrier model for a SnO_2 based varistor (adapted from Ref. [28]).

the model proposed by Mukae et. al.[26] for a Schottky double potential barrier using results obtained from impedance spectroscopy. The data show low values of barrier height to the SCN-based system and for systems with addition of cobalt seed due the lack of Cr_2O_3. However, the results reveal that copper (in addition to acting as a densifying agent for SnO_2 ceramics) promotes a potential barrier in this system.[27]

According to the potential barrier model for SnO_2-based varistor systems (see Fig. 7), the potential barrier is composed of negative defects in the grain-boundary region (notably O_2', O', and O''). These oxygen species are adsorbed by $[O_4V'_{Cu}]$ or $[O_4V'_{Co}]$ clusters located at the grain-boundary region, which donate electrons to the oxygen species. As a consequence, negative charges are stabilized by positive charge defects $[CuO_4]^{\bullet}$, $[CoO_4]^{\bullet}$ and $[NbO_5.V^{\bullet}_O]$. The equations below illustrate the cluster formation

$$[MeO_4]^x + [O_4 V^x_{Me}] \longrightarrow [MeO_4]^{\bullet} + [O_4 V'_{Me}]$$

$$[O_4 V'_{Me}] + O_{2(ads)} \longrightarrow [O_4 V'_{Me}] \ldots O_{2(ads)}$$

$$[O_4 V'_{Me}] \ldots O_{2(ads)} \longrightarrow [O_4 V^x_{Me}] \ldots O'_{2(ads)}$$

$$[O_4 V^x_{Me}] \ldots O'_{2(ads)} + [O_4 V'_{Me}] \longrightarrow 2[O_4 V^x_{Me}] \ldots O'_{(ads)}$$

$$[O_4 V^x_{Me}] \ldots O'_{(ads)} + [O_4 V'_{Me}] - \rightarrow [O_4 V^x_{Me}] \ldots O''_{(ads)} + [O_4 V^x_{Me}]$$

where Co or Cu in the complex $[O_4.V'_{Me}]$ clusters act as electron donors while the complex $[MeO_4]^{\bullet}$ acts as an electron trap.

The role of transition metals precipitated at the grain boundary is a boundary activator and supplies an excess of oxygen originating from the bulk and the atmosphere to the grain boundary creating an interface rich in oxygen species along with a layer depletion rich in oxygen vacancies.[28]

IV. Conclusions

Both seeds improved grain growth, which facilitated a larger average grain size when compared with the SnO_2-based system. SCNCo1 and SCNCu1 varistor systems have a lower breakdown electrical field, E_b (breakdown voltage, V_b) of 437 V/cm (57 V) and 284 V/cm (37 V) and a leakage current of 70 and 29 μA, respectively. Both systems can be used for low voltage devices protection being the most promising the SCNCu1 due to lower leakage current.

The oxygen is absorbed by $[O_4V'_{Cu}]$ or $[O_4V'_{Co}]$ clusters in the grain-boundary region by donating electrons to the oxygen species.

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