Analysis of the admittance-frequency and capacitance–voltage of dense SnO₂·CoO-based varistor ceramics

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This article describes the admittance-frequency feature of a class of SnO₂·CoO-based polycrystalline ceramics with high nonlinear current–voltage characteristics (nonlinear coefficients above 50). Broad relaxation peaks caused by the presence of deep trap states were characterized based on the admittance response of different systems doped with La₂O₃, Pr₂O₃, and CeO₂. The calculation of the energy of this deep trap level revealed not only that all the compositions share the same value but also that this value could be attributed to an oxygen vacancy or to Co₃Sn-like defects. The values of barrier height and density of states obtained from a capacitance–voltage analysis are in good agreement with the nonlinear coefficients. The highest nonlinear coefficients are found in compositions with greater barrier height values and higher density of deep trap states at the grain boundary interface. © 2002 American Institute of Physics. [DOI: 10.1063/1.1455685]

I. INTRODUCTION

Tin oxides are known to display low densification during sintering, a characteristic that renders this typical n-type semiconductor appropriate for use in highly porous devices such as gas sensors, which can detect a variety of inflammable and oxidizing gases.1–3 It has been proven that negatively charged oxygen adsorbates, such as O⁻, O²⁻, etc., on the surface of SnO₂ grain boundaries (and/or of grains), play an important role in detecting inflammable gases.1–4 Hence, oxygen vacancies and electronic states on SnO₂ surfaces have been studied in great detail.4,5 The most commonly accepted model for the operation of an n-type semiconductor gas sensor is based on the variation in the potential barrier height at the grain boundary, induced by the change in the amount of oxygen adsorbates by reaction with an inflammable gas. However, nonlinear current–voltage (I–V) characteristics in porous SnO₂ ceramics are observed only above 250°C, because such high temperatures favor oxygen adsorbates, forming a Schottky-like barrier between grains.

On the other hand, the addition of CoO and MnO₂ to SnO₂ produces high densification,6–8 allowing for the development of other electronic devices, such as varistors.7,9–20 at room temperature. Although most nonlinear electric behaviors of SnO₂ ceramics have appeared in SnO₂·CoO-based systems,7,9–12,14–18 non-ohmic properties have also been reported in other systems.13,20 Yongjun et al.19 demonstrated that ZnO can substitute CoO without significantly altering the nonlinear coefficient (α) compared to the previous SnO₂·CoO-based system, the first of such SnO₂-based systems reported on in the literature.7 Yongjun et al.19 also obtained non-ohmic properties in SnO₂·Bi₂O₃-based systems.20 Castro and Aldao13 showed how dopants such as CoO, CuO, MnO₂, Bi₂O₃, and Sb₂O₃ can influence the dielectric properties, microstructure, and densification of SnO₂-based ceramics. Other authors reported that dense SnO₂ ceramics doped with CoO and small concentrations of Nb₂O₅ and Cr₂O₃ display highly non-ohmic I–V characteristics7,9–12,14–18 at room temperature, with electrical characteristics similar to commercial metal–oxide varistors, which are also highly dense polycrystalline ceramics composed predominantly of ZnO, with additions of Bi₂O₃, Sb₂O₃, and other oxide constituents.

It has recently been found that the nature of potential barriers in SnO₂-based varistors is Schottky like, as is that observed in ZnO-based systems. Furthermore, as discussed in earlier reports,7,9–12,14–18 dense SnO₂-based systems present values of nonlinear coefficient α, breakdown voltage E_b, and barrier voltage per grain v_b equivalent to those of the traditional ZnO varistor. However, non-ohmic ZnO systems have a complex microstructure consisting of several crystalline phases, such as the Bi₂O₃-rich phases, spinel (nominally Zn₉Sb₂O₁₂) and pyrochlore (nominally Zn₂Bi₂Sb₂O₁₄). The presence of these crystalline phases in these systems is easily verified by x-ray diffraction (XRD) patterns and scanning electronic microscopy (SEM).21 Unlike the ZnO·Bi₂O₃-based system, a secondary phase is not detectable by XRD in SnO₂·CoO. This technique only allows for the detection of the SnO₂ cassiterite phase in SnO₂-based varistor systems. SEM analyses show that non-ohmic SnO₂·CoO⁷,9–12,14–18 polycrystalline systems have a simpler homogeneous microstructure than that of ZnO·Bi₂O₃.21

CoO in a SnO₂ matrix forms a solid solution by substituting Sn⁺₂ ions for Co⁺³ ions, as reported and discussed in previous articles.6–8 A CoSnO₃-precipitated
phase (or SnO₂–CoO-precipitated phase) at the grain boundary has only been detected by high resolution, Scanning tunneling electron microscopy, and using energy dispersive spectroscopy (EDS) electron diffraction.  

CoO is one of the components responsible for barrier formation in SnO₂-based varistors. The influence of cooling rates on the nonlinear electric behavior is attributed to CoO oxidation during cooling (oxidation of Co atoms of the SnO₂–CoO-precipitated phase). Cobalt valence states change according to the reactions represented by Eqs. (1)–(3)

\[ \begin{align*}
2\text{CoO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{Co}_3\text{O}_4, \\
\text{Co}_3\text{O}_4 + \text{CoO} & \rightarrow 3\text{CoO} + \frac{1}{2}\text{O}_2. 
\end{align*} \]

Cobalt atoms can, thus, affect the trapping state at the grain boundary and modify the potential barrier, depending on the cooling rate and atmosphere employed during sintering of the material, as reported in Refs. 12, 14, and 22. Therefore, the amounts of cobalt atoms segregated or else precipitated in the grain boundary depend on the cooling rate. This segregation or else the precipitate can become richer in oxygen through oxidation of the Co atom (e.g., CoO to Co₂O₃) below 1000 °C, thereby affecting the trapping state at the interface of the grain boundary region and, hence, the nonlinear electrical behavior of SnO₂-based varistors.

The main goal of this work is to discuss the admittance-frequency and capacitance–voltage (C–V) response of highly dense non-ohmic SnO₂ polycrystalline ceramics so as to gain a better understanding of the nature of trap states and the electrical characteristics of this new class of non-ohmic polycrystalline ceramics. This article also aims to identify the electrical characteristics of this new class of non-ohmic SnO₂-based varistors.

II. EXPERIMENTAL PROCEDURE

A. Preparation and I–V electrical characterization

The ceramic samples used in this study were prepared by the ball milling process in an alcohol medium. The oxides used were SnO₂ (Merck), CoO (Riedel), Nb₂O₅ (CBMM), Cr₂O₃ (Vetec), La₂O₃ (Aldrich), Pr₂O₃ (Aldrich), and CeO₂ (Nuclemon). The molar composition of the systems was 98.95% SnO₂ + 1.0% CoO + 0.035% Nb₂O₅ + 0.25% Cr₂O₃ + 0.25% X (SCNCr-X), with X equal to 0.25% of La₂O₃, Pr₂O₃, or CeO₂.

A chemical analysis of SnO₂ revealed that the main impurities were Pb (<<0.01%), Fe (<<0.01%), Ge (<<0.005%), and Cu (<<0.005%), all in mol%. The resulting powder was pressed into pellets (11.0 mm × 1.0 mm) by uniaxial pressure (20 MPa), followed by isostatic pressing at 210 MPa. The pellets were sintered at 1250 °C for 1 h, and cooled at a rate of 2 °C·cm⁻¹. The samples’ mean grain size was determined by analyzing the SEM micrographs (ZEISS DSM 940A) using image analysis software (PGT-IMIX). For the electrical measurements, silver contacts were deposited on the samples’ surfaces, after which the pellets were heat treated at 400 °C for 30 min.

The tetragonal structure of SnO₂ (rutile structure) was confirmed as the single phase by XRD (SIEMENS Model D-5000) on the mixed powder. I–V measurements were taken using a high voltage measuring unit (KEITHLEY Model 237).

B. Admittance spectroscopy and capacitance–voltage analysis

The admittance spectroscopy measurements were taken using a frequency response analyzer (HP 4194 A) at frequencies ranging from 100 Hz to 15 MHz, with an amplitude voltage of 1 V. The pellets were placed in a sample holder inside a furnace and measured at temperatures ranging from 25 to 250 °C.

Admittance spectroscopy was used to characterize the bulk electron traps present in dense SnO₂ polycrystalline systems. The use of this technique with polycrystalline materials requires the presence of a double Schottky-type barrier along the grain boundaries. Admittance spectroscopy utilizes modulation of the Fermi level by an ac signal. This results in a conductance component produced by the emission and capture of electrons from deep levels within the depleted regions.

The presence of the back-to-back Schottky-type barrier is inferred from the voltage dependence of the capacitance.  

Calculations of the capacitance were made of the high frequency intercept associated with high frequency relaxation in the complex capacitance plane. The applied voltage dependence of capacitance can be approximated using the approach of Mukae et al.  

\[
\left( \frac{1}{C} \right)^2 = \frac{2}{q\varepsilon_0 N_d} (\phi_b + V) \quad (4)
\]

where q is the electron or elementary charge, \( \varepsilon_r \) is the relative permittivity (\( \varepsilon_r \) to SnO₂ grain is ~14), \( \varepsilon_0 \) is the permittivity of free space, \( N_d \) is the positive space charge density in the depleted region (free electron density), and \( \phi_b \) is the barrier height of the system. C₀ and C are the capacitance per unit area of a grain boundary biased, respectively, with zero and V volts. It is important to point out that it would be possible to refer to \( N_d \) as the donor concentration and to ignore the concentration of deep bulk traps, but that is not the case we will present here.
The density of \( N_{IS} \) states at the interface between the SnO\(_2\) grain and the intergranular layer was estimated using:

\[
N_{IS} = \left( \frac{2N_0 e\epsilon_0 \phi_b}{q} \right)^{1/2},
\]

where \( \phi_b \) is the barrier height. 

Thus, the interpretation of Alim et al.\(^{23} \) and the approach of Mukae et al.\(^{25} \) as discussed in Ref. 11, were used to infer the presence of the Schottky-like barrier and to characterize the nature of the barrier formed in a highly dense and porous SnO\(_2\)-based non-ohmic ceramic.

Because the most appropriate model to explain non-ohmic behavior in nonlinear semiconductor ceramics is based on the presence of an electrostatic potential barrier located in regions of direct grain-to-grain contact,\(^{21} \) we believe that this method, which has been successfully used in the past,\(^{11} \) is suitable to characterize the nonlinear \( I-V \) behavior.

III. RESULTS AND DISCUSSION

A. Structural and \( I-V \) characteristics

Figure 1 shows a typical SEM micrograph of the non-ohmic polycrystalline SnO\(_2\)-based ceramics studied here. The tetragonal structure of SnO\(_2\) (rutile structure) was confirmed as single phase by XRD in all the systems under study. However, based on previous reports,\(^8 \) it is likely that the grain boundary also contains a CoSnO\(_3\)-precipitated phase.

Table I presents the \( \alpha, E_b, v_b \), relative density and mean grain size values of the systems studied. As can be seen, all the systems display a highly non-ohmic behavior. Figure 2 contains the \( I-V \) plots, illustrating how the presence of La\(_2\)O\(_3\) improves the non-ohmic behavior. The systems containing La\(_2\)O\(_3\) present excellent \( I-V \) characteristics, as shown on a linear scale in Fig. 2(b).

The highest \( \alpha \) and \( E_b \) values were obtained in the SCNCr–La\(_2\)O\(_3\) and SCNCr–Pr\(_2\)O\(_3\) compositions, despite the higher porosity of these systems. These high values may result from the fact that La\(_2\)O\(_3\) and Pr\(_2\)O\(_3\) can segregate in the grain boundary, inducing electronic interfacial states that can trap charges at the SnO\(_2\)–SnO\(_2\) interface. These trap states consist mainly of oxygen species, as discussed in detail in Refs. 11, 12, and 22.

The role of each dopant is summarized by the solid-state reactions represented below in Eqs. (6)–(9):

\[
\begin{align}
\text{La}_2\text{O}_3 \rightarrow 2\text{La}^{3+}_{\text{Sn}} + \text{V}_{\text{O}}^{\text{**}} + 3\text{O}_0^\text{r}, \\
\text{Pr}_2\text{O}_3 \rightarrow 2\text{Pr}^{3+}_{\text{Sn}} + \text{V}_{\text{O}}^{\text{**}} + 3\text{O}_0^\text{r}, \\
\text{Ce}_2\text{O}_3 \rightarrow 2\text{Ce}^{\text{x}}_{\text{Sn}} + 2\text{O}_0^\text{r}, \\
\text{Ce}_2\text{O}_3 \rightarrow 2\text{Ce}^{\text{+}}_{\text{Sn}} + \text{V}_{\text{O}}^{\text{**}} + 3\text{O}_0^\text{r}.
\end{align}
\]
As a dopant, the CeO\textsubscript{2} does not strongly influence the electrical nonlinearity of the SnO\textsubscript{2}, CoO\textsubscript{2}, CeO\textsubscript{2}, NbO\textsubscript{2}, CrO\textsubscript{3} system,\textsuperscript{7} as in the case of La\textsubscript{2}O\textsubscript{3} and Pr\textsubscript{2}O\textsubscript{3}, nor does it alter the system’s porosity, as illustrated in Table I and Fig. 1. Instead, it is believed to form a solid-state solution with the system’s porosity, as illustrated in Table I and Fig. 1. Instead, it is believed to form a solid-state solution with the system’s porosity, as illustrated in Table I and Fig. 1.

**B. Admittance spectroscopy results**

Figure 3 presents the imaginary part of the complex capacitance \( C''(\omega) = G(\omega)/\omega \), where \( G \) is the conductance) measured in the SCNCr–La\textsubscript{2}O\textsubscript{3} system. The other systems present a behavior similar to that illustrated in Fig. 3. The high frequency region of the spectrum indicates the presence of an electrode inductance response, while a dc conductivity component is visible in the low frequency region. The dc conductivity component increases with increased temperatures, as expected. Clearly well-defined loss peaks are visible at intermediate frequencies and lower temperatures. The relaxation processes observed in all the samples causes relaxation when the angular frequency of the ac signal becomes equal to the emission rate \( \omega_p \) of the electrons in a trapping state, as shown in Fig. 3. The general theory of semiconductor junctions, which yields Debye-like relationships, assures displacements of the loss peak \( [C''(\omega) \text{ spectra}] \) as temperature is increased. The \( e_n \) (which is equivalent to \( \tau^{-1} \), the time dependence of the electron transition) depends on the temperature, according to the relationship

\[
e_n = \omega_p = \tau^{-1} = \sigma_n v_\text{th} N_d e^{-[(E_c - E_t)/kT]},
\]

where \( \omega_p \) is equivalent to the \( e_n \), \( \sigma_n \) is the capture cross section of the trap state, \( v_\text{th} \) is the free-electron thermal velocity, \( N_d \) represents the donor concentration as previously defined, and \( E_c - E_t \) is the energy difference between the conduction band and the trapping level. The values of \( E_c - E_t \) obtained for each sample are given in Table II. The values are the same for all the samples and are relatively close to those obtained with the standard ZnO-based varistor systems, which range from 0.30 to 0.39 eV.\textsuperscript{23,24,26} The origin of this trap in the region of the bulk depletion layer is likely to be intrinsic to the ZnO-based varistor system. Of the two possible intrinsic origins, i.e., interstitial Zn atoms and oxygen vacancies, it is suggested that this trap is associated with the ionized oxygen vacancy, \( V_\text{O}^- \), in the ZnO-based varistor ceramic.

The values obtained herein for the trap’s energy in the bulk depletion layer also indicate that the potential barrier of the SnO\textsubscript{2}-based varistor system is similar to that of the ZnO-based varistor, as discussed in Refs. 11 and 22. A great deal of evidence indicates that the similarities between these ceramics are associated with the amount of oxygen in the grain boundary. According to the barrier formation model for metal oxide varistor systems,\textsuperscript{11,22} the physical origin of interfacial states is not an intrinsic one caused by lattice mismatch at the boundary, but an extrinsic one resulting from metal atoms segregated at the grain boundaries. These metal atoms, being mainly transition metal oxides, generally have several oxidation states, which facilitate the chemisorption of oxygen on the grain surfaces. This mechanism enables electrons to become localized at the surface, giving rise to a

**TABLE II.** \( \phi_0, N_d, N_{IS} \), and \( \delta \) values for a back-to-back Schottky-type potential barrier of SCNCr–X varistor systems. These calculations take into consideration the average number of grains between electrodes.

<table>
<thead>
<tr>
<th>System</th>
<th>( \phi_0/\text{eV} )</th>
<th>( N_d \times 10^{23}/\text{m}^3 )</th>
<th>( N_{IS} \times 10^6/\text{m}^{-2} )</th>
<th>( \delta/\text{nm} )</th>
<th>( E_c - E_t/\text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCNCr–CeO\textsubscript{2}</td>
<td>1.10 ± 0.05</td>
<td>7.79</td>
<td>3.64</td>
<td>23.4</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>SCNCr–Pr\textsubscript{2}O\textsubscript{3}</td>
<td>1.99 ± 0.04</td>
<td>5.76</td>
<td>4.21</td>
<td>36.5</td>
<td>0.41 ± 0.03</td>
</tr>
<tr>
<td>SCNCr–La\textsubscript{2}O\textsubscript{3}</td>
<td>2.48 ± 0.06</td>
<td>4.43 \times 10^2</td>
<td>4.12 \times 10^4</td>
<td>4.65</td>
<td>0.41 ± 0.02</td>
</tr>
</tbody>
</table>
negative surface (negative interfacial states). To maintain local electrical neutrality, the charges are compensated for by the space charge formed in the depletion region adjacent to the grain boundary. As a result, electron depletion layers are formed and act as potential barriers. Details of the similarities between the grain boundaries of ZnO- and SnO$_2$-based varistor systems, including the amount of oxygen in this region, are given in Ref. 22. Therefore, because the grain boundary region of non-ohmic ceramics is richer in oxygen than the bulk\textsuperscript{11,22} (Fig. 4), the trap state at the interface responsible for barrier formation is related to the negative charge trapped by oxygen species, whose degree of coordination differs from that of the bulk oxygen. Hence, this oxygen in the grain boundary region can generate an interfacial trap state both in ZnO- and in SnO$_2$-based varistors. The interfacial states must, therefore, be formed by electrons trapped in oxygen in the grain boundary region and by ionized shallow donors plus deep traps in the depletion layer.\textsuperscript{22} One of the possible intrinsic ionized shallow donors is an ionized oxygen vacancy. Thus, it can be inferred that shallow and deep donor levels in the depletion layer balance the electrons trapped by oxygen in the grain boundary region. However, the distribution of electronic states in this region depends on the nature of segregated transition metals.

The fact that the energy of trap states in the bulk depletion layer remain unchanged with the composition of the samples may indicate that this trap state is formed by an intrinsic defect in the SnO$_2$-based varistor, such as the one believed to exist in the ZnO-based varistor. Natural SnO$_2$ cassiterite or synthetic crystals are both oxygen deficient (n-type semiconductor), leading to the formation of a shallow donor level approximately 0.1 eV below the bottom of the conduction band. This shallow donor level is ascribed to the first ionization energy of oxygen vacancies V$_{O}^{**}$.\textsuperscript{29}

Therefore, it could be argued that the 0.41 eV energy observed in all the SnO$_2$ samples studied here is not a shallow but a deep trap level associated with the second ionization energy of oxygen vacancies V$_{O}^{**}$ (intrinsic defect), or even to the Co$_{O}^{**}$, which is also common to all the compositions (an extrinsic defect). Thus, the defect that gives rise to this deep trap level can be either native to the SnO$_2$ or involve extrinsic impurities.

As discussed earlier, some impurities, such as Co, do not segregate or else precipitated to any great extent to form a large second phase in SnO$_2$; therefore, a great amount of Co$^{3+}$ and Co$^{2+}$ remains in the SnO$_2$ lattice\textsuperscript{6} probably forming only very shallow single donor-like levels. Thus, from the above-described potential barrier formation mechanism, it can be inferred that the defect generating these trap states in the bulk depletion layer is linked to one that is present in all the compositions and is possibly related to an intrinsic defect, such as a V$_{O}^{**}$ oxygen vacancy. The first energy ionization of oxygen vacancies is shallow and is not visible at ambient temperature or above. Hence, since the second energy ionization of oxygen vacancies requires higher energy than the first one, it can only be observed in the depletion layer region.

In the simplest scenario, therefore, the role of transition metal segregated or else precipitated at the grain boundary is that of a "grain boundary activator," supplying excess oxygen to the grain boundary interfaces from the bulk, as discussed in Ref. 22, creating an interface rich in oxygen species and a deep trap level in the bulk depletion layer that is rich in oxygen vacancies. In this scenario, the traps in the grain boundary region that generate the potential barrier are believed to be formed by

$$O^{-2} + V_{O}^{**} \rightarrow \text{‘‘trapped states at the interface’’}$$

$$+ \text{‘‘trapped states in the bulk.’’}$$

The thermodynamic equilibrium of solid-state defects at the grain boundary depend on the type and nature of the transition metals precipitated at the grain boundary and on how easily these metals oxidize.\textsuperscript{22} The mechanism proposed herein is in agreement with the reaction presented in Eqs. (1)–(3). This statement is also supported by results found in ZnO-based varistors. A relatively high oxygen content at ZnO grain interfaces\textsuperscript{22,30,31} in ZnO varistors has been confirmed experimentally by x-ray photoelectron spectroscopy. It has been proposed that the electron interface state is produced by bismuth and oxygen at ZnO interfaces,\textsuperscript{30,31} for which reason high oxygen vacancy concentrations remain inside ZnO grains.

Figure 4 shows an EDS analysis of the grain and grain boundary region of a SnO$_2$-CoO-MnO-based varistor doped with Nb$_2$O$_5$ and Cr$_2$O$_3$. As can be seen, the grain boundary region is rich in transition metal elements and oxygen species and deficient in Sn atoms, confirming the potential barrier formation mechanism proposed in Ref. 22.

It must be emphasized that the model proposed here is based mainly on segregation of transition metals at the interface or junctions of SnO$_2$–SnO$_2$. However, as evidenced, the precipitates are also presented and, for us, they are regions in which there is a higher amount of transition metal segregate, consequently acquiring a particular crystalline feature that is also richer in oxygen compared to the grain. Such a distinct region is primarily adjacent to the SnO$_2$–SnO$_2$ junction. As a result, we have noted that the oxygen enrich-

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**FIG. 4.** EDS analysis of the grain and grain boundary region of a SnO$_2$-CoO-MnO-based varistor doped with Nb$_2$O$_5$ and Cr$_2$O$_3$. The mass ratio of each element in the grain and grain boundary region was calculated based on the total amount of these components in the sample. Here is shown the amount of differences existing between grain and grain boundary for each of indicated elements and corroboration that the grain-boundary region is richer in transition metals and oxygen. In this case, the comparison of mass ratio between elements is only illustrative.
boundary region, for example. The enrichment of precipitate in the grain–boundary region, as discussed previously. Moreover, the SnO₂–SnO₂ type junction is the main one that is controlling the overall properties and, as a result, the electrical active barriers are for the most part presented in this kind of junction.

C. Capacitance–voltage analysis

The corresponding Mott–Schottky plot (i.e., [C_{BL}]^{-2} versus dc voltage) at room temperatures was obtained, as described above and shown in Fig. 5, for SCNbCr–X systems. A good linear correlation can be seen between the left side of Eq. (4) and the dc voltages. The value of this frequency-dependent capacitance, used in conjunction with the information on grain size, reflects the averaged Mott–Schottky response of any junction within the SnO₂ varistor device. Table II presents the ϕ_b, N_d, N_IS, and barrier width δ values from this averaged Mott–Schottky response. The δ values were calculated from the electrical neutrality condition (N_IS = 2N_dδ). A good correlation can be seen between the mean values of ϕ_b and α in Table I. The ϕ_b values are higher for compositions with higher α values. The N_d and N_IS for SCNCr–CeO₂ and SCNCr–Pr₂O₃ are similar to those obtained previously for a composition with equivalent α values. However, these values are quite different for SCNCr–La₂O₃. The N_d and N_IS values in this composition are 2 and 1 order of magnitude higher, respectively, than in the other compositions, respectively, and appear to be associated with the higher amount of La₂O₃ segregated in the grain boundary region, as discussed previously. Moreover, the δ value is lower in this system, indicating that an improved nonlinear electric behavior in SnO₂-based varistor systems is obtained with a higher ϕ_b value, in combination with a lower δ value and higher N_d and N_IS values, resulting in the behavior shown in Fig. 2(b). It should be noted that the δ value is related to the deep trap density of the grain boundary.

Assuming that the I–V characteristics are governed mainly by field emission in the voltage region above the breakdown voltage through a double Schottky-like barrier, then it is to be expected that the dependence of dc voltage on grain boundary resistance will show higher electrical nonlinearity for a grain boundary with a higher ϕ_b value and a higher density of states (N_d and N_IS) confined in a thin insulating layer (lower δ value). Thus, this grain boundary arrangement will present better α values. In other words, the degree of nonlinearity in the nonlinear region of I–V curves depends significantly on the energy distribution of grain-boundary states above the zero-bias Fermi level.

Figure 2 also shows that dc conductivities estimated in the linear (prebreakdown) region, which are related to the grain boundary conductivities (and leakage currents), are higher in the sequence SCNCr–CeO₂ > SCNCr–Pr₂O₃ > SCNCr–La₂O₃ and are in agreement with the potential barrier characteristics shown in Table II.

| Table IV. ϕ_b, N_d, N_IS, and δ values for a back-to-back Schottky-type potential barrier of the SCNCr–La₂O₃ varistor system thermally treated at 900 °C in different atmospheres. These calculations take into account the average number of grains between electrodes. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Annealing       | ϕ_b [eV]        | N_d [10²⁵/m³]   | N_IS [10¹⁵/m²]  | δ [nm]          |
| N₂-rich atmosphere | 2.27 ± 0.04   | 984 ± 0       | 1.86 ± 0.01     | 94.8 ± 0.5     |
| O₂-rich atmosphere | 2.57 ± 0.05   | 91.3 ± 0      | 19 ± 1          | 10.4 ± 0.1     |
|                  |                 | 0.41 ± 0.02   |                 | 0.43 ± 0.02    |

FIG. 5. Mott–Schottky behavior without charge transport influence (true Mott–Schottky behavior) of the SCNbCr–X varistor system. (a) Mott–Schottky behavior for: (■) SCNCr–La₂O₃, (○) SCNCr–Pr₂O₃, and (▲) SCNCr–CeO₂. (b) Detailed Mott–Schottky behavior for: (○) SCNCr–Pr₂O₃.

TABLE III. α, E_b, and ϕ_b for the SCNCr–La₂O₃ varistor system thermally treated at 900 °C in different atmospheres.

<table>
<thead>
<tr>
<th>Annealing</th>
<th>α [cm⁻¹]</th>
<th>E_b [V cm⁻¹]</th>
<th>ϕ_b [V grain⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂-rich atmosphere</td>
<td>89</td>
<td>11536</td>
<td>2.0</td>
</tr>
<tr>
<td>O₂-rich atmosphere</td>
<td>145</td>
<td>11831</td>
<td>2.3</td>
</tr>
</tbody>
</table>
SnO$_2$-based varistors are dependent on thermal treatment under different atmospheres. Figure 6 presents the $I$–$V$ characteristics after thermal treatment in different atmospheres: (■) as-sintered, (□) O$_2$-rich atmosphere, and (○) N$_2$-rich atmosphere.

D. The effect of thermal treatment in oxidizing and reducing atmospheres

Experimental evidence reveals that the $\alpha$ values in SnO$_2$-based varistors are dependent on thermal treatment under different atmospheres. The $\alpha$ values decrease when the varistors are thermally treated at 900 °C for 1 h in a N$_2$-rich atmosphere, as discussed in Refs. 11, 12 and 22. The same behavior is also reported in this article in Table III for the SCNCr–La$_2$O$_3$ composition. The relative density of the system and the mean grain size value do not change with 1 h thermal treatment at 900 °C, as discussed in an earlier article. However, for the issue discussed here, the most interesting result is that the energy of the deep trap states in the depletion layer, associated with oxygen vacancies, is also not affected (Table IV) by thermal treatment in different atmospheres, indicating that the main defect (in this case, probably oxygen vacancies) responsible for this deep trap state does not change in this region with such thermal treatment. Figure 6 presents the $I$–$V$ characteristics after thermal treatment in different atmospheres. As illustrated by the figure, treatment in a N$_2$-rich atmosphere alters the flux of current through the material and increases the leakage current. At the same time, additional electrons can be trapped at the boundary, and there is a dynamic flow of trapped charges between the grains and the boundary. Thus, as expected from the results given in Table IV, a higher leakage current must be present in the varistor when it is treated in a N$_2$-rich atmosphere, as Fig. 6 confirms. Once again, a good agreement was found between barrier features and $I$–$V$ behavior of these ceramic systems.

In terms of the barrier formation mechanism proposed in a previous study, the transition metal segregated at the grain boundary becomes oxidized [Eqs. (1)–(3)] when treated in an O$_2$-rich atmosphere and that the interfacial region becomes rich in oxygen species that are trapped electrons (increasing the $N_{IS}$). The oxygen that produces oxidation of the segregates and maintains the electrostatic equilibrium of the interface comes from the atmosphere and the bulk, and increases donor concentration $N_d$ when it originates from the bulk. Therefore, the density of trap states at the interface $N_{IS}$ should increase when the grain boundary interface of the material is oxidized, giving rise to higher $\phi_b$ values. A thermal treatment in a N$_2$-rich atmosphere, on the other hand, should have the opposite effect to the one described above. This behavior appears to corroborate the proposed model for potential barrier formation illustrated in Fig. 7 and discussed in detail in Refs. 12 and 22.

Again, from the results shown in Tables III and IV, it can be concluded that the most significant electrical nonlinear features occur when the density of deep trap states in the bulk depletion layer (which is balanced by interfacial states) is high.

IV. CONCLUSIONS

A good correlation has been demonstrated between potential barrier characteristics and $\alpha$ values in a metal oxide varistor system. An atomic defect model is proposed to explain the role of extrinsic and intrinsic dopants in the non-ohmic characteristics of the polycrystalline ceramics studied. Admittance spectroscopy results showed well-defined loss peaks at intermediate frequencies and lower temperatures, which were attributed to the donor concentration found in the grain boundaries. The relaxation process of these traps presented a feature that appears to follow the Cole–Cole dielectric model. Calculation of the energy of the deep trapping level showed the same values for all the compositions studied, which were also equivalent to those obtained for the traditional ZnO-based varistor, confirming the similarities that exist in the grain boundary of SnO$_2$- and ZnO-based varistors. This deep trap level was associated to the second ionization of oxygen vacancies in the depletion layer.

The $\phi_b$, $N_d$, $N_{IS}$, and $\delta$ values obtained from the aged Mott–Schottky responses were in good agreement with $\alpha$ values, even when the ceramic material was thermally treated in N$_2$- and O$_2$-rich atmospheres or as-sintered. The greatest electrical nonlinearities are expected when there is a large density of states at the grain boundary.
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