Effect of Fe2O3 doping on the electrical properties of a SnO2 based varistor

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The effect of Fe2O3 addition on the densification and electrical properties of the (0.9895 − x)SnO2 + 0.01CoO + 0.005Nb2O5 + xFe2O3 system, where x = 0.005 or 0.01, was considered in this study. The samples were sintered at 1300 °C for 2 h. Microstructure analysis by scanning electron microscopy showed that the effect of Fe2O3 addition is to decrease the SnO2 grain size. J × E curves indicated that the system exhibit a varistor behavior and the effect of Fe2O3 is to increase both, the non-linear coefficient (α) and the breakdown voltage (Er). Considering the Schottky thermionic emission model the potential height and width were estimated. Small amount addition of Fe2O3 to the basic system increases both the potential barrier height and width. © 2002 Kluwer Academic Publishers

1. Introduction

Tin dioxide (SnO2) is a n-type wide band gap semiconductor with crystalline structure of rutile type and has low densification rate due to its high surface diffusion at low temperature and high SnO2 partial pressure at high temperatures [1–3]. Recently, CoO addition to the SnO2 was observed to lead to 98.5% of theoretical density and made possible the application of these systems in the preparation of varistors [4]. The introduction of either Nb2O5 or Ta2O5 to the SnO2-CoO system decreases the grain resistance, making possible the measurement of breakdown electrical field of these systems [4–7]. The non-linearity of SnO2 based varistor is strongly influenced by the additions of transition metal oxides such as Cr2O3, Bi2O3 and MnO2 [7, 8].

2. Experimental procedure

Analytical grades of SnO2 (Merck), CoO (Riedel), Nb2O5 (Aldrich), and Fe2O3 (Merck), were used as precursors for processing SnO2 based ceramics. Varistor compositions powders were prepared by weighing the oxide precursors and using ball mill to mix the oxides. The powders were uniaxial pressed in pellet shapes using a pressure of 75 MPa. The pellets were then isostatically pressed using a pressure of 200 MPa. The samples were then sintered in ambient atmosphere at 1300 °C during 2 hours and then were slow cooling down (3 °C/min) until ambient temperature. Apparent bulk densities were determined by weighting the samples and measuring the volume by geometric dimensions.

Microstructures were characterized by using a scanning electron microscopy (SEM) (Jeol Model JSM T330A). The samples were ground, polished and thermally etched at 1250 °C during 15 min for microstructure revealing. Grain sizes were measured based on the method proposed by Mendelson [11]. The crystalline phases were determined by X-ray diffraction (XRD) using a θ–2θ goniometer (Siemens Model D-5000). The lattice parameters were determined using X-ray diffraction data through the least squares refinement using a computing program.

The samples were ground to reach 1 mm thick with parallel faces and silver electrodes were deposited in these faces for electrical characterization. The electrical voltage as function of electrical current was determined using a voltage source (Tectrol model TCH 3000-2) and measuring the electrical current and voltage by two
digital multimeters (Fluke 8050 A). Then the electric field \( (E = V/d) \) and current density \( (J = I/A) \), where \( d \) is the sample thickness and \( A \) is the sample electrode area, were determined for several applied voltages. The non-linear coefficient \( (\alpha) \) was determined by linear regression of the \( \ln E \) versus \( \ln J \) curve from 1 mA/cm\(^2\) and the electric field breakdown was determined at this electrical current density.

### 3. Results and discussions

Fig. 1 show the XRD patterns for the SnO\(_2\) - CoO - Nb\(_2\)O\(_5\) system with addition of 0.05 or 0.1 mol% of Fe\(_2\)O\(_3\). Lattice parameters were determined from these patterns and are listed in Table I and compared with the undoped basic SnO\(_2\) system. Lattice parameters decreased with increasing amount of Fe\(_2\)O\(_3\) which imply the formation of solid solution. Both lattice parameters, \( a \) and \( c \), decreased due to substitution of Sn\(^{4+}\) (ionic radius 0.64 Å) by Fe\(^{3+}\) (ionic radius 0.71 Å). XRD patterns of both systems indicated only the SnO\(_2\) crystalline phase indicating solid solution. However dopants concentration used were well bellow the detection limit of XRD.

The addition of Fe\(_2\)O\(_3\) in the ternary system did not change significantly the final density of the ceramics sintered in the same conditions, as shown in Table II. However grain size decreased from 8.5 \( \mu \)m in the undoped ternary system to 5.4 \( \mu \)m after doping with 0.05% of Fe\(_2\)O\(_3\), indicating that Fe\(_2\)O\(_3\) is inhibiting grain growth in this system.

Pianaro et al. [7, 8] also observed a similar behavior when the basic SnO\(_2\) varistor ceramics is doped with Cr\(_2\)O\(_3\). According to these authors, the Cr\(_2\)O\(_3\) should segregate at the grain boundaries, inhibiting then the sintering and grain growth. In the same way Fe\(_2\)O\(_3\) should segregate at the grain boundaries inhibiting grain growth during sintering, since the mean grain size decreases from 8.5 \( \mu \)m for the sintered basic ternary system to 5.4 \( \mu \)m for the Fe\(_2\)O\(_3\) doped system (Fig. 2). This segregation of iron oxide is due to the low solubility of this oxide in the SnO\(_2\) matrix [12].

As expected the addition of Fe\(_2\)O\(_3\) affects the electrical properties of the SnO\(_2\) based varistor. Due to modifications in the microstructure the breakdown electric field increases with the Fe\(_2\)O\(_3\) concentration as observed in the Fig. 3 and Table III. This behavior can be explained by the calculated values of the potential barrier per grain (\( \psi_b \)) by using the following expression [13, 14]:

\[
E_r = n \psi_b, \tag{1}
\]

being \( E_r \), the electric field breakdown and \( n \) the number of grains per unit length calculated by:

\[
n = \frac{L}{d}, \tag{2}
\]

being \( L \) the sample thickness and \( d \) the mean grain size. The calculated \( \psi_b \) values are shown in Table III and increases with increasing amount of Fe\(_2\)O\(_3\) concentration.

![Figure 1 X-ray diffractograms for the (0.9895 - x) SnO\(_2\) + 0.01 CoO + 0.0005 Nb\(_2\)O\(_5\) + x Fe\(_2\)O\(_3\) system. (a) x = 0.0005 mol%; and (b) x = 0.001 mol%.](image)
Figure 2. SEM micrograph of the 0.989 SnO$_2$ + 0.01 CoO + 0.0005 Nb$_2$O$_5$ + 0.0005 Fe$_2$O$_3$ system sintered at 1300$^\circ$C for 2 h. (b) SEM micrograph of the 0.9885 SnO$_2$ + 0.01 CoO + 0.0005 Nb$_2$O$_5$ + 0.001 Fe$_2$O$_3$ system sintered at 1300$^\circ$C for 2 h. The sample surface was thermally etched at 1250$^\circ$C for 15 min.

As proposed by Pianaro et al. [4] the electrical conduction for low applied electric field for the SnO$_2$·CoO·Nb$_2$O$_5$ system can be associated to the thermionic emission of the Schottky type. For these varistor systems containing only small additions of Fe$_2$O$_3$ the same model for the thermionic emission was considered. In this type of emission, the current density depends on the temperature, according to the following expression [15]:

\[ J = J_0 \exp \left( \frac{E_a}{kT} \right) \]  
(3)

where \( J_0 \) is a constant, \( E_a \) is the activation energy for an electron jump, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. Considering that the potential barrier are of Schottky type separated by thin film and that the conduction mechanism is by thermionic emission, the current density is related to the electric field, \( E \), by the following equation [16]:

\[ J_S = A^* T^2 \exp \left( \frac{\phi_B - \beta E^{1/2}}{kT} \right), \]  
(4)

where \( A^* \) is the Richardson constant, \( \phi_B \) is the potential barrier height at the interface, \( E \) is the applied electric field and \( \beta \) is related with the potential barrier width by the relation:

\[ \beta = \left( \frac{1}{\pi n \omega} \right)^{1/2} \left( \frac{e^3}{4\pi \varepsilon_0 \varepsilon_r} \right)^{1/2}, \]  
(5)

where \( n \) is the number of grains per unit length, \( \omega \) is the depletion layer width (potential barrier width); \( e \), \( \varepsilon_0 \) and
TABLE IV  Effect of dopant concentration on the potential barrier height (φ_B) and width (β) for the system: (98.95 − x) SnO_2 + 1.0 CoO + 0.05 Nb_2O_5 + x Fe_2O_3 (all in mol%)

<table>
<thead>
<tr>
<th>Mol% Fe_2O_3</th>
<th>φ_B (eV)</th>
<th>β · 10^{-3} (V^1/2 cm^{-1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.49</td>
<td>7.10</td>
</tr>
<tr>
<td>0.05</td>
<td>0.97</td>
<td>4.46</td>
</tr>
<tr>
<td>0.10</td>
<td>0.99</td>
<td>3.63</td>
</tr>
</tbody>
</table>

Figure 3  Ln E versus ln J characteristic curves for the SnO_2 based varistor systems sintered at 1300 °C for 2h. (a) 0.9895 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5, (b) 0.9895 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.0005 Fe_2O_3, (c) 0.9885 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.001 Fe_2O_3.

Figure 4  Ln E versus ln J characteristic curves for the SnO_2 based varistor systems sintered at 1300 °C for 2h and measured at different temperatures: (a) 0.989 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.0005 Fe_2O_3, (b) 0.9885 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.001 Fe_2O_3.

Figure 5  Ln J versus E^{1/2} characteristic curves for the SnO_2 based varistor systems sintered at 1300 °C for 2h and measured at different temperatures: (a) 0.989 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.0005 Fe_2O_3, (b) 0.9885 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.001 Fe_2O_3.

Figure 6  Ln J versus 1/T characteristic curves for the SnO_2 based varistor systems sintered at 1300 °C for 2h and measured at different temperatures: (a) 0.989 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.0005 Fe_2O_3, (b) 0.9885 SnO_2 + 0.01 CoO + 0.0005 Nb_2O_5 + 0.001 Fe_2O_3.

The electronic charge, vacuum electric permittivity and material electric permittivity respectively.

The plot of ln E versus ln J for temperatures ranging from 16 to 175 °C is shown in Fig. 4. As observed in this plot the leakage current increase with increasing temperatures. The thermionic emission can be characterized by plotting ln J versus E^{1/2} and considering the ohmic region of the curves a linear plot is observed (Fig. 5). By extrapolating the curves to E = 0, values J_l(0) versus 1/T gives value of the potential barrier height (φ_B) (Fig. 6). Values for (φ_B) and β for the SnO_2 - CoO - Nb_2O_5 system and with 0.05 and 0.10 mol% of Fe_2O_3 are shown in Table IV. These values varies from 0.49 to 0.97 and 0.99 eV, while β decreases substantially which represents a increase in the potential barrier width (α ∝ β^2).

This behavior can be explained by the creation of point defects due to the solid solution of Fe_2O_3, in addition to the solid solution of Nb_2O_5 and CoO in the SnO_2 [4–8, 17, 18], according to the following equations:

Fe_2O_3 SnO_2 → 2Fe^{++}_Sn + V^{O•}_O + 3O_2,  \tag{6}
2Nb_2O_5 SnO_2 → 4Nb^{++}_Sn + V^{O•}_O + 10O_2,  \tag{7}
CoO SnO_2 → Co^{++}_Sn + V^{O•}_O + O_2.  \tag{8}

The increase in the potential barrier height and in the potential barrier width are associated to the increase of both, N_T and N_D due to the segregation of Fe_2O_3 next to the grain boundary as well as the creation of positive defect in the depletion layer (V^{O•}_O) and negative defects at the interface (Fe^{++}_Sn). After the adsorption of oxygen at interface there is a transfer of negative charges from

ε_e are the electronic charge.
Fe\textsubscript{Sn} and other negative species to the adsorbed oxygen which increase \( N\)\textsubscript{t}, then the increase of potential barrier can be associated to the increase of effective surface states (\( N_s \)) according to the following equation:

\[
\phi = \frac{\epsilon^2 N_s}{2\alpha N_d} \tag{9}
\]

Considering the SnO\textsubscript{2} varistor microstructure, a Schottky type electrical barrier can be ascribed to be most likely barrier at the SnO\textsubscript{2} grain boundary, since no intergranular insulating layer separating two SnO\textsubscript{2} grains as observed. The negative surface charge at the grain boundary interface is compensated by the positive charge in the depletion layer in the grain on both sides of the interface [9]. Based on previous studies, Gupta and Carlson developed a grain boundary defect model comprising the Schottky barrier [10]. In an attempt to explain the grain boundary barrier formation in SnO\textsubscript{2} varistor, an analogy to this model can be considered, as shown in Fig. 7. In our model, the intrinsic SnO\textsubscript{2} defects (\( V_{\text{Sn}}^{\prime}\prime\prime\prime\), \( V_{\text{Sn}}^{\prime}\prime\prime\), \( V_{\text{Sn}}^{\prime}\), \( V_{\text{Sn}}^0\)) and extrinsic defects created by the dopants CoO, Fe\textsubscript{2}O\textsubscript{3} and Nb\textsubscript{2}O\textsubscript{5} should be responsible for the grain boundary electrical barrier formation. These dopants form a solid solution with the SnO\textsubscript{2} high temperatures and create defects near the grain boundary according to Equations 3 to 5.

In Fig. 7, positively charged donors (\( V_{\text{Sn}}^0\), Nb\textsubscript{2}O\textsubscript{5}\)) extending from both sides of grain boundary are compensated by negative charged acceptors (\( V_{\text{Sn}}^{\prime}\prime\prime\prime\), \( V_{\text{Sn}}^{\prime}\prime\prime\), \( V_{\text{Sn}}^{\prime}\), \( V_{\text{Sn}}^0\), Co\textsubscript{2}O\textsubscript{3}\), Fe\textsubscript{3}O\textsubscript{4}\)) at the grain boundary interface. The oxygen can be adsorbed at the interface and react with negative defects according to the following equations [18–20]:

\[
\begin{align*}
O_2 &\rightarrow O^0_{2(ad)} \tag{10} \\
V_{\text{Sn}}^{\prime}\prime\prime &+ 4O_{2(ad)} \rightarrow 4O_{2(ad)} + V_{\text{Sn}}^{\prime}\prime\prime \tag{11} \\
V_{\text{Sn}}^{\prime}\prime &+ 2O_{2(ad)} \rightarrow V_{\text{Sn}}^{\prime} + 2O_{2(ad)} \tag{12} \\
V_{\text{Sn}}^{\prime} &+ 2O_{2(ad)} \rightarrow V_{\text{Sn}}^{\prime} + 4O_{2(ad)} \tag{13} \\
Co_{\text{Sn}}^{\prime\prime\prime\prime} &+ 2O_{2(ad)} \rightarrow 2O_{2(ad)} + Co_{\text{Sn}}^{\prime\prime\prime\prime} \tag{14} \\
Fe_{\text{Sn}}^{\prime\prime\prime\prime} &+ O_{2(ad)} \rightarrow O_{2(ad)} + Fe_{\text{Sn}}^{\prime\prime\prime\prime} \tag{15} \\
Fe_{\text{Sn}}^{\prime\prime} &+ O_{2(ad)} \rightarrow Fe_{\text{Sn}}^{\prime\prime} + 2O_{2(ad)} \tag{16}
\end{align*}
\]

The adsorbed oxygen at the grain boundary captures electrons from negatively charged defects at the grain boundary and stays at the interface. This effect was confirmed by impedance analysis [21].

4. Conclusions

Additions of 0.05 ± 0.10% of Fe\textsubscript{2}O\textsubscript{3} (in mol%) to the SnO\textsubscript{2} · CoO · Nb\textsubscript{2}O\textsubscript{5} system lead to decrease of both: mean grain size and leakage current as well as lead to increase of the non-linear coefficient and breakdown electric field. The potential barrier height are 0.97 and 0.99 eV similarly. The non-linear behavior of these ceramics can be explained by the formation of atomic defects in the depletion layer (\( V_{\text{Sn}}^{\prime}\prime\prime\prime\), Nb\textsubscript{2}O\textsubscript{5}\)) and at interface (\( V_{\text{Sn}}^{\prime}\prime\prime\prime\), \( V_{\text{Sn}}^{\prime}\prime\prime\), Co\textsubscript{2}O\textsubscript{3}, Co\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}). Moreover, the adsorbed oxygen at grain boundaries captures electrons from negatively charged defects at the grain boundary and is the major responsible for the negative charge density at the interface.

Acknowledgements

This work received financial support from Brazilian Research agencies FAPESP/CEPID and CNPq/PRONEX.

References


Received 20 September 2001 and accepted 30 January 2002

Figure 7. Atomic defect model proposed to explain the potential barrier formation at the grain boundaries of SnO\textsubscript{2} based varistor systems.