Microstructural and Nonohmic Properties of ZnO, Pr$_6$O$_{11}$ Co Polycrystalline System

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The microstructure and electrical properties of varistors composed of (95-x) ZnO + x Pr$_6$O$_{11}$ + 5 CoO (ZPC), (x = 0.1, 0.5 and 1.0) and sintered at 1300 and 1350 °C, were investigated. According to X-ray diffraction, several phases (ZnO, Pr$_6$O$_{11}$ and Pr$_3$CoO$_5$) are present when x = 1.0. Using Scanning Electron Microscopy, all of these compositions contain precipitates. These phases are important regarding the development of the microstructure and the electrical properties. The samples with x = 0.1 introduce the best nonohmic behavior (α ≈ 9.0), however when x = 0.5 the electrical properties are highly degraded due to the small quantity of effective barriers. The density of superficial states $N_s$ and donor concentration $Nd$ decreases with Pr$_6$O$_{11}$ addition. The decrease in the donor concentration is attributed to the annihilation of the donor defects according to the transformation of praseodymium oxides from Pr$_6$O$_{11}$ to Pr$_3$O$_5$.

Keywords: electrical properties, varistors, grain boundary, microstructure

1. Introduction

ZnO varistor ceramics are resistor devices manufactured by sintering ZnO powder containing various minor additives. It has been recognized that at least two different classes of additives must be added to the ceramic varistors in order to obtain good nonohmic characteristics. The first class of such additives are varistor-forming oxides (VFO), such as Bi$_2$O$_3$, La$_2$O$_3$, BaO, V$_2$O$_5$, and glass frits. The second class of additives are 3d transition-metal oxides, which improve significantly the nonohmic characteristics. Zinc oxide ceramics, containing Pr$_6$O$_{11}$ and CoO, which exhibit current nonohmic characteristics, were first reported by Mukae et al. In fact, the history of Pr$_6$O$_{11}$-based ZnO varistors is similar to the Bi$_2$O$_3$-based ZnO varistors, but they have not been adequately studied. However, the Pr$_6$O$_{11}$-based ZnO varistors don’t have volatilization of components and they own a simpler microstructure when compared with Bi$_2$O$_3$-based varistors, which is an important fact for the stability and degradation phenomena. Most of commercial ZnO varistors are ZnO-Bi$_2$O$_3$-based varistor ceramics, possessing as major additive Bi$_2$O$_3$. Although they exhibit excellent varistor performance, they possess few drawbacks due to the high volatility and reactivity of Bi$_2$O$_3$, at a sintering temperature above 1000 °C. Another flaw of Bi$_2$O$_3$-based varistors is that they need many additives to obtain high nonlinearity and stable electrical properties. ZnO varistors generally contain three phases, such as ZnO grains, Bi$_2$O$_3$-rich intergranular layer and spinel particles. To overcome the problems in Bi$_2$O$_3$-based varistors, ZnO varistors using praseodymium oxides as VFO have been reported. On the other hand, Pr$_6$O$_{11}$-based ZnO varistors are reported to have only two-phases detected by X-ray diffraction, namely, ZnO grains and intergranular layers enriched with praseodymium. The absence of a spinel phase increases the active grain boundary area through which the electrical current flows. Therefore, the effective cross-section area of the elements is increased. Several studies describe the dependence of varistor properties on processing conditions of Pr-doped ZnO varistors, especially in the field of grain boundary formation. It is very important to understand the structure, composition and properties of the boundaries since they have a strong influence on electrical properties. Our purpose is to investigate the microstructure, the current density-electric field ($J$ vs. $E$) characteristics, and the capacitance-voltage ($C$-$V$) characteristics of ZPC varistor systems.

2. Experimental Procedure

The varistor systems (95-x) mol% ZnO + x mol% Pr$_6$O$_{11}$ + 5 mol% CoO (x = 0.1, 0.5 and 1.0) were prepared from the mixture of oxide precursors method, all of them being analytical grade oxides: ZnO (Aldrich-99.99%), Pr$_6$O$_{11}$ (Aldrich-99.9%) and CoO (Riedel-99.9%). The starting materials were attrition-milled in water for 3 hours. Then the dry slurry was calcined at 750 °C in air for 2 hours. The calcined powders were pulverized using agate mortar and pestle and after 2 wt. (%) polyvinyl alcohol (PVA) binder addition, granulated by sieving 200-mesh screen to produce the starting powder. The powder was uniaxially pressed into discs of 12 mm diameter and 1 mm thickness at a pressure of 80 MPa. The pellets were sintered at 1300 and 1350 °C for 2 hours with a heating rate of 5 °C/min followed by furnace cooling. The samples were characterized by X-ray diffraction (XRD, Rigaku, 20-2000), 40 kV and 150 mA from 2θ = 20° to 80°, $\Delta 2\theta = 0.02^\circ$, with Curved wavelength monochromatized by a graphite crystal. To obtain the Scanning Electron Microscopy (SEM) microographies (ZEISS® DSM 940 A) the sintered samples were polished and thermally etched by heating at 100 °C below the...
sintering temperature during 30 minutes. The average grain size \(d\) was determined by the linear intercept method, given by \(d = 1.56 L/MN\), where \(L\) is the random line length on the micrograph, \(M\) the magnification of the micrograph, and \(N\) is the number of the grain boundaries intercepted by lines\(^{15}\). Gold contacts were deposited on the samples surfaces by sputtering in order to measure the nonohmic properties. Current-voltage measurements were taken by using a High Voltage Measure Unit (Keithley Model 237). The breakdown electric field \(Eb\) was obtained at a current density from 1 mA.cm\(^{-2}\) and the leakage current \(I_l\) was measured at 0.80 Eb. In addition, the nonlinear coefficient \(\alpha\) was determined from linear regression of \(\log J\) vs. \(\log E\) in the 1-10 mA.cm\(^{-2}\) region. The impedance measurements were made with a frequency response analyzer (HP 4294 A LF) using frequency ranging from 40 Hz up to 110 MHz. The capacitance-voltage \((C-V)\) characteristics of ZPC varistors were measured as a function of frequency with the variable applied bias voltage (0-38 V). The donor concentration \(Nd\) of ZnO grains and the barrier height \(\phi_h\) at the grain boundary were determined from the slope and intercept of straight line, respectively, using the Equation 1:

\[
\left(\frac{1}{C} - \frac{2p^2}{qke_0N_d}\right)^2 = 2p^2/qke_0N_d \left(\frac{V}{p} + \phi_h\right)
\]

proposed by Mukae et al.\(^{16}\). In this equation \(C\) is the capacitance per unit area of grain boundary, \(C_0\) is the capacitance when \(V = 0\), \(V\) is the voltage applied per grain, \(q\) is the electronic charge, \(e_0\) is the permittivity of free space, \(k\) is the dielectric permittivity of ZnO (≈8.5) and \(p\) is the number of barriers between grains (obtained by calculating the distance between electrodes divided by average grain size). The density of the interface states \(N_{IS}\) at the grain boundary was determined using the Equation 2:

\[
N_{IS} = \left(\frac{2ke_0N_d\phi_B}{q}\right)^{1/2}
\]

Once the donor concentration and barrier height are known, the depletion layer width \(\omega\) of either side at the grain boundaries was determined by the Equation 3:

\[
N_d\omega = N_{IS}
\]

\[ (3) \]

### 3. Result and Discussion

Figure 1a shows XRD pattern for the samples of the ZPC system sintered at 1300 °C. The samples with \(x = 0.1\) and 0.5 contain only a wurtzite ZnO phase (card PDF 36-1451), while when \(x = 1.0\), the sample contains a praseodymium sesquioxide phase, Pr\(_2\)O\(_3\) (card PDF 47-1111), and exhibits a low intensity peak of Pr-rich \(\text{Pr}_2\text{CoO}_4\) (card PDF 34-1282). XRD pattern for the samples sintered at 1350 °C are shown on Figure 1b. The difference concerning the sample sintered at 1300 °C is that for \(x = 1.0\) the Pr\(_2\)CoO\(_4\) phase is not observed. At high (1350 °C) sintering temperature, a densification occurs through the movement of grain boundaries \(\text{Pr}_x\text{CoO}_3\) strongly influences the grain size, which gets its maximum average value of 30 μm for \(x = 0.5\) (see Table 1). Figures 2d, 2e and 2f show micrographs of the samples sintered at 1350 °C. The presence of a larger amount of precipitates in the grain boundary is an obvious indication for the liquid phase of all compositions, at the temperature interval between 1300 and 1350 °C. Micrographs show that the average grain size reaches a maximum when \(x = 0.5\). The increase of the average grain size by addition of a small amount of dopant \((x = 0.5)\) may be caused by some lattice defects, similar to that related to the La doped BaTiO\(_3\), which is reported elsewhere. Further addition of Pr\(_2\)O\(_3\) above 0.5 mol% causes the suppression of grain growth (except for the sample with \(x = 1.0\) mol% and sintered at high temperature). Such suppression has been also reported for 2 mol% rare-earth (Sm, Eu, Y and Er) doped ZnO. The reason for this suppression has been attributed to the pinning effect during the movement of grain boundaries\(^{16-19}\). In the light of variations of intergranular material, the liquid phase formation temperature is expected to occur between 1300 and 1350 °C depending on the system’s composition. The crystals generation for the sample with \(x = 1\) and sintered at 1350 °C suggests that the liquid phase has the lowest temperature formation in this case. EDS analysis (not shown) determined that the precipitated phase is Pr-rich.

Figure 3a and 3b show the nonohmic behavior \((E \text{ vs. } J)\) of ZPC varistors sintered at 1300 and 1350 °C, respectively. More detailed concerning the \(E \text{ vs. } J\) characteristic parameters, including the breakdown electric field \((Eb)\), leakage current \((I_l)\), nonlinear coefficient \((\alpha)\), are summarized in Table 1. The amount of 0.5 mol% Pr\(_2\)O\(_3\) is
not appropriate for varistor properties. This can be associated with the presence of a small number of effective barriers in the grain boundaries, besides the grain growth, generating few barriers among electrodes. The nonohmic properties have a significant increase for $x = 1.0$, as the highest value of the breakdown electric field since this dopant level inhibits grain growth, as shown by SEM.

It can be observed from Table I, that the nonohmic behavior of $0.1 \text{ mol} \%$ Pr$_{6}$O$_{11}$ doped system sintered at 1300 °C is superior when compared with the sample with the same composition sintered at 1350 °C. This indicates, that the liquid phase is important for homogenizing dopants, but the electric properties of this phase is as well an important aspect. For instance, praseodymium has several oxidation states in the ZnO-based varistors, which can change dramatically the electrical behavior. The valence change is very sensitive to the applied process, as well as the Pr$_6$O$_{11}$ amount. This aspect should be carefully evaluated. In ZnO:Bi$_2$O$_3$-based varistor systems, changes also occur in both phases, the amorphous and crystalline phase of Bi$_2$O$_3$ during the processing or its useful life.

The samples of micrographs showed in Figures a), b), c) have been sintered at 1300 °C and d), e), f) at 1350 °C.

Table 1. The current-voltage ($I-V$) and capacitance-voltage ($C-V$) characteristic parameters of ZPC varistors with different content of Pr$_6$O$_{11}$ additive sintered at 1300 and 1350 °C. The nonlinear coefficient ($\alpha$) has been calculated for range values between 1-10 mA/cm$^2$ and leakage current ($I_L$) calculated at 20% of the breakdown electrical field.

<table>
<thead>
<tr>
<th>Samples*</th>
<th>$E_b$ (V/cm) ± 100</th>
<th>$I_L$ (µA) ± 1</th>
<th>$\alpha$ ± 10</th>
<th>$d$ (µm) ± 1</th>
<th>$N_b$ ($m^{-3}$) ± 0.02</th>
<th>$N_{IS}$ ($m^{-2}$) ± 0.01</th>
<th>$\phi_B$ (eV) ± 0.01</th>
<th>$\omega$ (nm) ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 (1300)</td>
<td>1050</td>
<td>174</td>
<td>9.0</td>
<td>22</td>
<td>1.17</td>
<td>2.08</td>
<td>0.454</td>
<td>10.3</td>
</tr>
<tr>
<td>0.1 (1350)</td>
<td>308</td>
<td>217</td>
<td>6.5</td>
<td>26</td>
<td>1.01</td>
<td>2.30</td>
<td>0.483</td>
<td>9.86</td>
</tr>
<tr>
<td>0.5 (1300)</td>
<td>201</td>
<td>210</td>
<td>3.8</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.5 (1350)</td>
<td>40</td>
<td>613</td>
<td>1.7</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0 (1300)</td>
<td>1584</td>
<td>235</td>
<td>8.2</td>
<td>11</td>
<td>0.68</td>
<td>1.34</td>
<td>0.286</td>
<td>10.0</td>
</tr>
<tr>
<td>1.0 (1350)</td>
<td>425</td>
<td>287</td>
<td>5.5</td>
<td>35</td>
<td>0.57</td>
<td>2.04</td>
<td>0.674</td>
<td>8.5</td>
</tr>
</tbody>
</table>

*The first number indicates Pr$_6$O$_{11}$ amount, the second number that this between parentheses indicates the sintered temperature.
between the (1/C – 1/2C)^2 vs. dc voltage (except the samples with x = 0.5 and sintered at 1350 °C) indicating that the barriers formed at the grain boundaries of highly dense ZnO are of Schottky nature.

The corresponding Mott-Schottky plot is shown in Figures 6a and 6b. The observed frequency, depending on capacitance in conjunction with the information on grain size, reflects the averaged Mott-Schottky response. The \( \phi_B, N_d, N_{IS} \) and \( \omega \) values calculated from this averaged Mott-Schottky response is displayed in Table 1. It is observed in this table that increasing the temperature from 1300 to 1350 °C, \( N_d \) decrease due to oxidation of Zn donor defects. \( N_d \) decrease is accompanied by an increase of interfacial states density \( N_{IS} \) and height barrier \( \phi_B \), as well as decrease of depletion layer \( \omega \). The values of barrier height \( \phi_B \) are calculated based on the fact that all the grains are considered electroactive. The obtained values are small, indicating that not all the barriers are active. In ZnO-Bi\(_2\)O\(_3\)
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1350 °C which does not follow a Mott-Schottky behavior), this aspect is related to a lower number of electrically active barriers. According to DRX, doping with 1.0 mol% Pr$_6$O$_{11}$ generates secondary phases of Pr$_2$O$_3$ and the properties have been recovered, showing similar electric parameters like the samples doped with 0.1 mol% Pr$_6$O$_{11}$. SEM analyses showed that all compositions contain precipitates Pr-rich, which should be carefully studied, specifically regarding the oxidation state and their influence on the nonohmic properties. ZPC systems own a simpler microstructure than ZnO, Bi$_2$O$_3$ traditional varistors and a potential application for low-tension varistors. However new dopants should be used in order to increase the potential barrier and decrease the leakage current.

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References


