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Grain-boundary segregation and precipitates in La_2O_3 and Pr_2O_3 doped $SnO_2 \cdot CoO$-based varistors

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Abstract

Structural heterogeneities in $SnO_2 \cdot CoO$-based varistors were analyzed by transmission electron microscopy. In $SnO_2 \cdot CoO$-based system doped with La_2O_3 and Pr_2O_3 two kinds of precipitate phases at grain boundary region were found. Using energy dispersive spectrometry they were found to be Co_2SnO_4 and $Pr_2Sn_2O_7$, presenting a defined crystalline structure. It was also identified that such precipitate phases are mainly located in triple-junctions of the microstructure. HRTEM analysis revealed the existence of other two types of junctions, one as being homo-junctions of SnO_2 grains and other due to twin grain boundaries inside the $SnO_2 \cdot CoO$ grain. The role of these types of junction in the overall nonlinear electrical features is also discussed.

Keywords: CoO; Grain boundaries; Microstructure-final; SnO_2; Varistors

1. Introduction

Metal-oxide varistors are a class of devices predominantly based on polycrystalline semiconductor ceramics, presenting highly nonlinear current-voltage characteristics due to the nature of their grain-boundary junctions. The ZnO-based varistors is the most exhaustively studied class of these ceramic materials and are commercially applicable in a wide range of electrical engineering and electronic devices.[1,2] The ZnO-based varistors with small addition of Bi_2O_3, Sb_2O_3, CoO, MnO, Al_2O_3 and other constituents such as Cr_2O_3 show highly nonlinear current-voltage characteristics with a sharp breakdown voltage above which large currents can be carried with only minor damage to the material.[1,2]

In spite of commercial application and exhaustive research on ZnO-based varistor systems, the mechanism of potential barrier formation and its relationship to the chemical of grain-boundary is not totally clarified. Even so, it was possible to develop other matrix ceramics either promising to commercial applications such as the class based on SnO_2.[3]

The main feature of SnO_2-based varistor system is its relatively simple microstructure when doped with CoO, presenting only one single phase under X-ray resolution, in which CoO forms a solid solution by substitution of Sn^{4+} ions by Co^{2+} or Co^{3+} ions, as reported and discussed in previous papers.[3–5] However, a precipitated phase (Co_2SnO_4) at the grain boundary is found when the EDS (energy dispersive spectroscopy) stage attached to the HRTEM (high-resolution transmission electron microscopy) and electron diffraction are used.[3,4] In contrast, ZnO-based varistor system, in the most common situation, has a complex microstructure containing several phases such as a bismuth-rich phase, a spinel (nominally $Zn_7Sb_2O_{12}$) and a pyrochlore (nominally $Zn_2Bi_3Sb_3O_{14}$) which are determined by the X-ray diffraction method.[1,2]

Despite these chemical differences, we have demonstrated that the nonohmic electrical response of SnO_2-based varistor is controlled by a potential barrier of Schottky-type nature, the same one frequently reported on for the traditional ZnO-based varistor system.[6] These findings are important inasmuch as they begin to provide evidence that the nature of nonlinear electrical properties in the $SnO_2 \cdot CoO$-based varistor system may be of the same nature of that observed in $ZnO \cdot Bi_2O_3$-based

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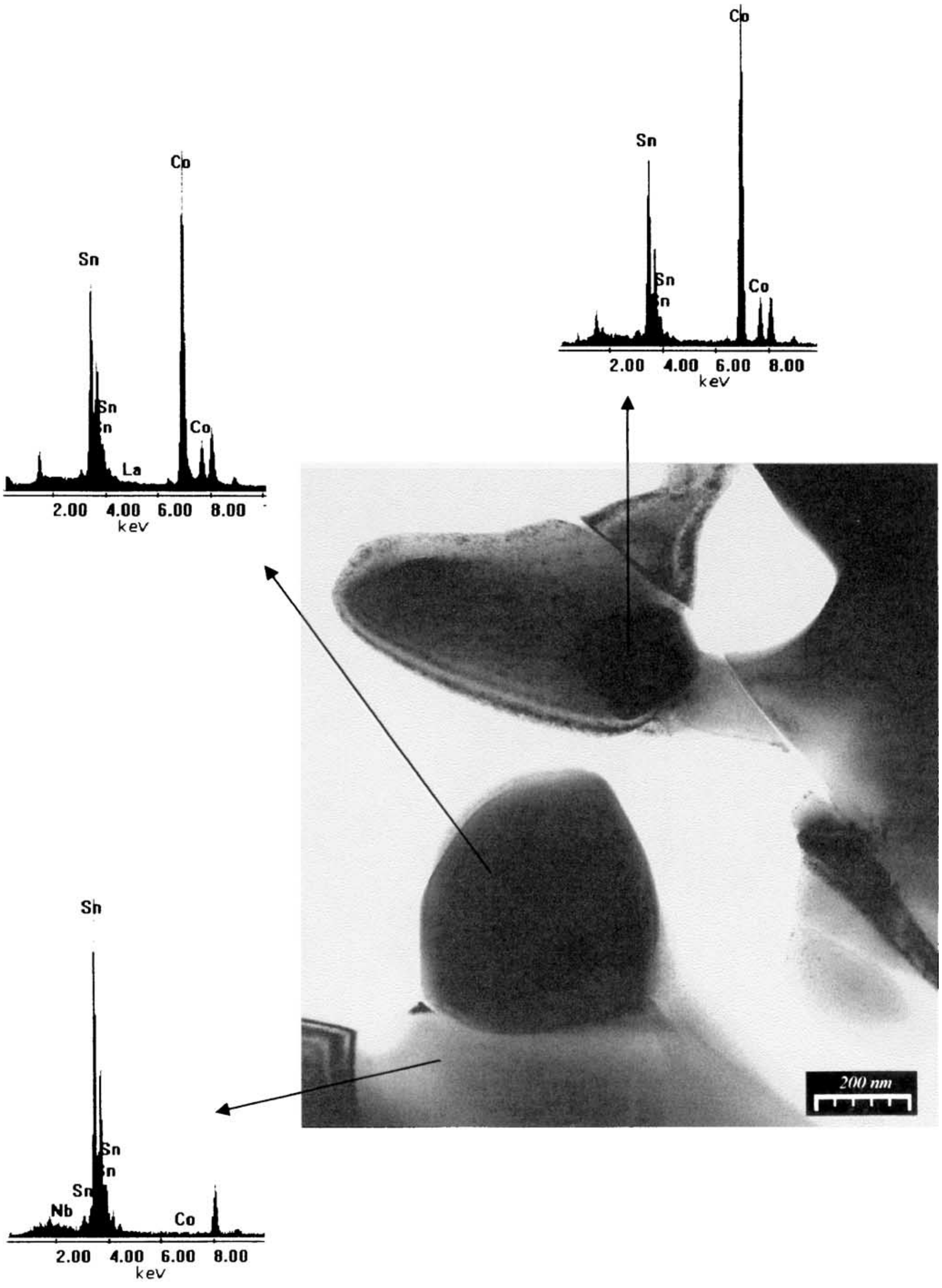
varistor system and is related to a Schottky-type barrier at the grain boundary.[6,7]

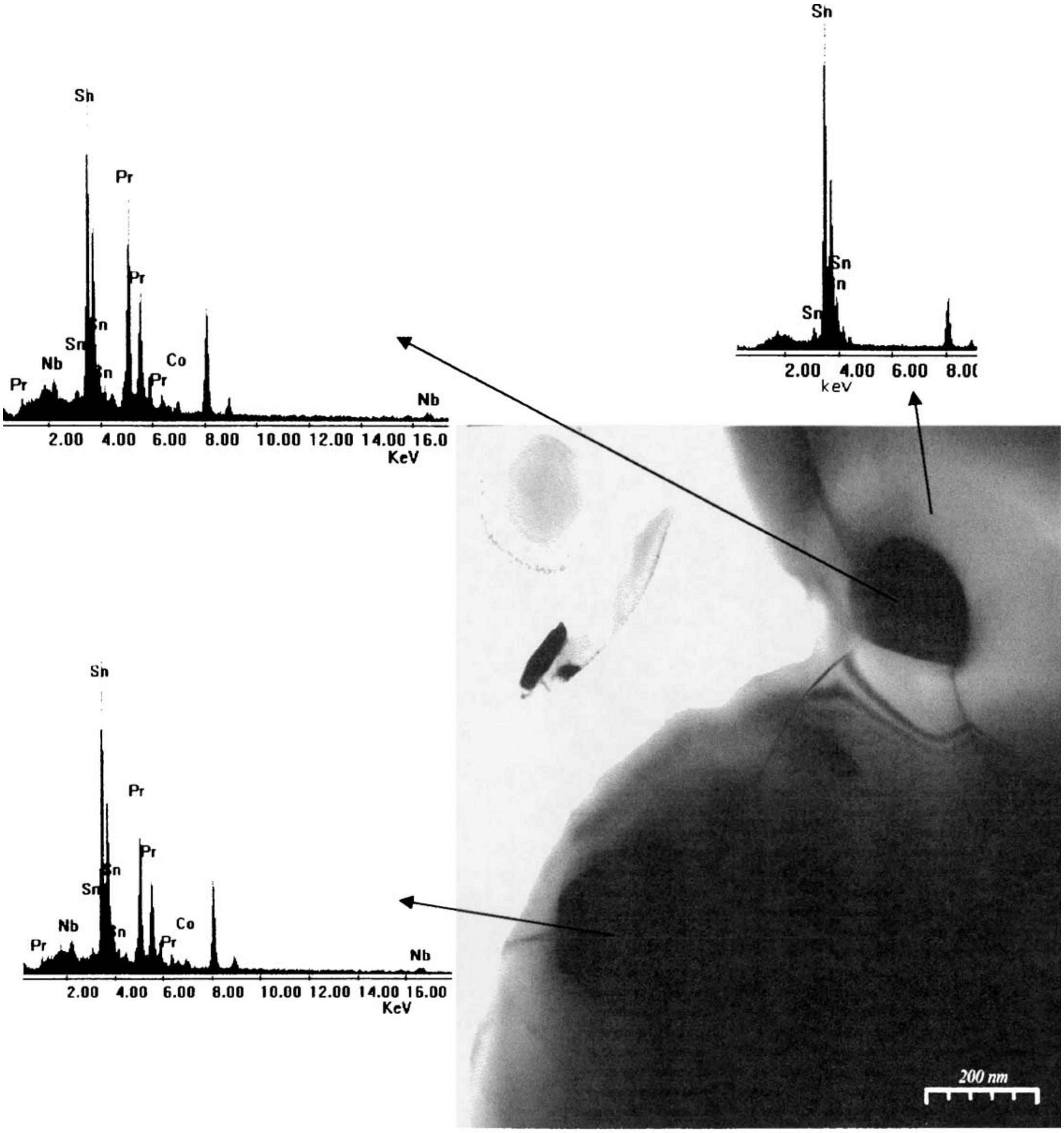
It is clearly established that diffusion and mass transport are more rapid along grain boundaries and that grain boundaries generally act as diffusion "short circuit". The diffusivity of grain boundaries is greater than that of the lattice. Such feature makes possible the enrichment of grain boundaries with oxygen species as was demonstrated mainly in SnO_2-based varistor system.[8] Such enrichment of grain boundaries controls the nonohmic properties and it is believed to be dependent of grain boundary segregation and/or phase precipitation.[7]

Therefore, the purpose of this study is to obtain information on microstructure heterogeneities using TEM analysis to try to understand how these heterogeneities presented in SnO_2-based varistor microstructure, mainly at grain boundary region, could improve or control nonohmic properties.



(a)

Fig. 1. Micrograph obtained by TEM obtained for the systems: (a) SCN–0.30%La_2O_3 and (b) SCN–0.30%Pr_2O_3 with their respective X-ray patterns.



(b)

Fig. 1 (*continued*).

2. Experimental procedure

The powders were prepared using ball milling in an alcoholic medium. The oxides used were SnO_2 (CESBRA), CoO (Riedel), Nb_2O_5 (CBMM), La_2O_3 (Aldrich) and Pr_2O_3 (Aldrich). The composition of the molar system was 98.665% SnO_2 + 1.00% CoO + 0.035% Nb_2O_5 + 0.30% X, with X being La_2O_3 or Pr_2O_3 (SCNLa or SCNPr). Our chemical analysis of SnO_2 indicated that the main impurities were Pb (<0.01%), Fe (<0.01%), Ge (<0.005%) and Cu (<0.005%) all expressed in moles.

The powders were pressed into pellets (11.0×1.3 mm) by uniaxial pressing, followed by isostatic pressing at 145 MPa. The pellets were sintered at 1250 °C for 2 h, then submitted to a cooling rate of 2 °C min^{-1} down to room temperature.

The microstructure of sintered pellets was characterized by scanning electron microscopy (SEM) and by transmission electron microscopy (TEM). For thin-foil preparation, cylindrical specimens of 3 mm diameter were cut by an ultrasonic disc cutter. These cylinders were then ground gently with diamond paste to about 200 mm and then dimpled by mechanical polishing. These discs were then ion milling thinned to a thickness of less than 100 nm to allow electron beam transmission. The foils thus prepared, were examined with 120 kV TEM (Philips CM120) equipped with EDS facilities to determine elemental composition of the specimens. Lattice resolution was carried out using a Philips CM200, operating at a voltage of 200 kV. The addition of 0.30 mol% of La_2O_3 and Pr_2O_3 was chosen because it promotes an increase in the nonlinear electrical response of the device. The samples reached high values of α, nonlinear coefficient, of 19 and 46 respectively, when added to the $SnO_2 \cdot CoO \cdot Nb_2O_5$, system which presented $\alpha = 8$.

3. Results and discussion

Fig. 1 shows a darkfield TEM image of the SCN–0.30%La_2O_3 and SCN–0.30% Pr_2O_3 systems with their respective energy dispersive spectra. It can be observed by means of Fig. 1a that the precipitate phase founded at grain boundary region is rich in Sn and Co, whereas the grains are predominantly composed of SnO_2. Such results corroborate the results obtained in the literature.[4–6]

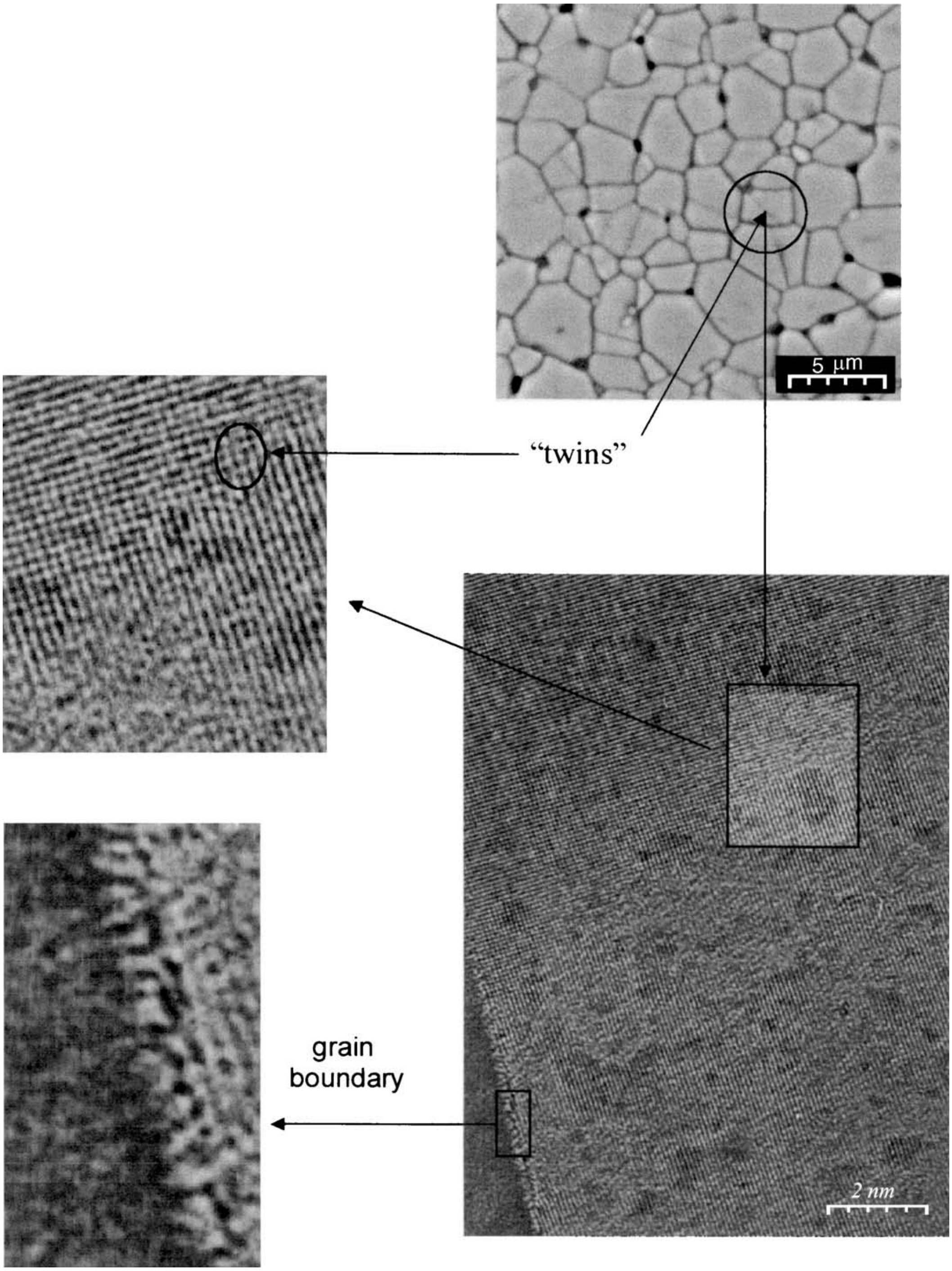


Fig. 2. High resolution micrograph obtained for the system SCN–0.30%La_2O_3 with its respective micrograph obtained by SEM.

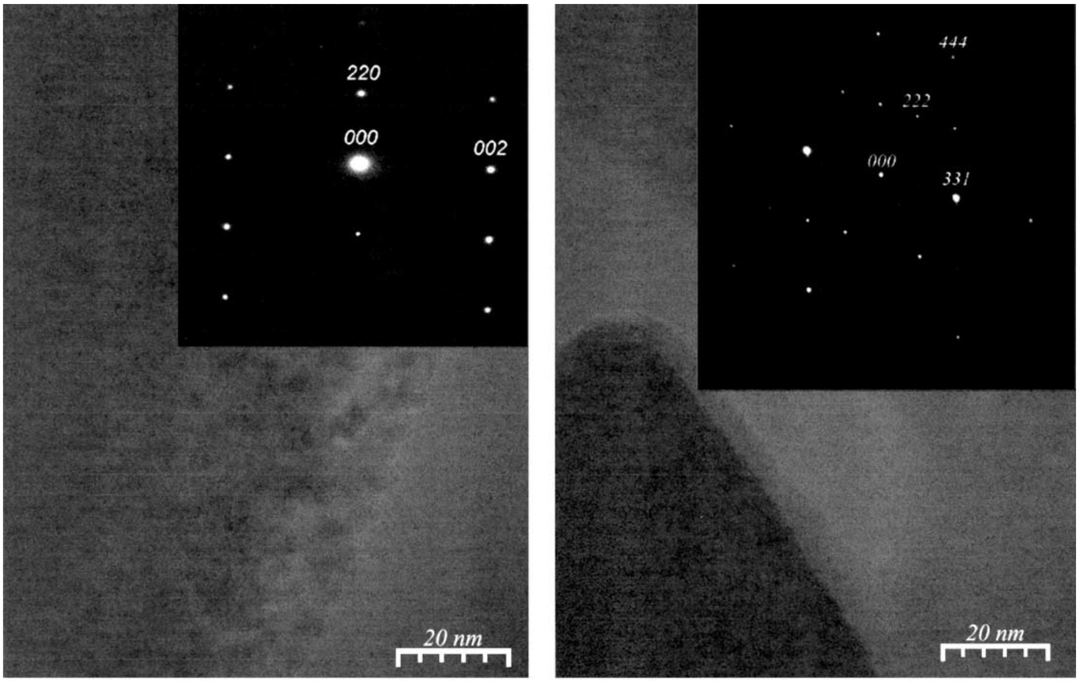
Another important observation could be taken from Fig. 1b, which shows that the precipitate is rich in Pr, the dopant element added in order to improve the non-ohmic features. The influence of trivalent oxides on the properties of varistors was already studied in detail by several authors.[9,10] These oxides, are not only incorporated into the chemical composition of the varistors to lower the electrical resistivity of grains, improving, in this way, the electrical nonlinearity in high current densities delaying the onset of voltage up, but also to increase the barrier voltage energy due to the segregation of metal at grain–grain junctions.

Turning our attention back to Fig. 1b, we found that the most possible precipitated phase present in the multigrain junctions of the latter sample, in agreement with JCPDS records, is $Pr_2Sn_2O_7$. It should be point out that the secondary phase founded is, for the most part, present in a multigrain junction of microstructure, particularly in the triple-grain junction.

The grain–grain junction can also be observed by means of a high resolution micrograph for the SCN–0.30%La_2O_3 system, as showed in Fig. 2. The grain–grain boundary region is well revealed in such a kind of micrographic analysis. Another kind of junction was also founded, that well known as twin boundaries. Such a kind of junction is found inside SnO_2 grains.

From the comparison of Figs. 1 and 2 it is important to point out the difference between segregation and precipitation. As demonstrated, precipitate phases are presented and for us they are regions in which there is a higher amount of segregated transition metals, thus acquiring a particular crystalline feature that is richer in oxygen compared to the grain. Such distinct region is primarily adjacent to the SnO_2–SnO_2 junctions, or localized to at great extent on triple-grain junctions. As a result, we have noted that the oxygen enrichment of SnO_2–SnO_2 junctions is accompanied by the oxygen enrichment of the precipitated and, therefore, its oxidation can be easier monitored by the oxygen enrichment of the precipitate, such as foreseen by the mechanism of the model described elsewhere.[7] In fact, even the grain–grain junction has a breakdown distribution presenting a complicated pattern for by itself.[11] For that reason, we are considering that the SnO_2–SnO_2 type-junction with transition metal segregated in it is the main kind of junction controlling the overall nonohmic properties and, therefore, the electrically active barriers are, for the most part, present in such kind of junction.

On the other hand, one could imagine that the precipitate phase of transition metals at the grain boundary could contribute, as junctions that also display the active barriers. However, in reality, the direct influence of these secondary phases on the degree of nonlinearity is probably negligible, mainly when they are present in the triple-junctions. Even SnO_2–layer-SnO_2 junctions may not exert a direct influence on nonlinear electrical properties. However, if one believes that such kind of junction is important to the overall nonohmic behavior, then complications should be considered and the band structure of grain-boundary region should be different,



(a)

(b)

Fig. 3. Micrograph obtained for the system SCN–0.30%La_2O_3, and its respective X-ray pattern: (a) grain of SnO_2·CoO-based system and (b) precipitate of Co_2SnO_4.

more adequately described by Mukae et al.[12] In addition, it should be considered a more detailed discussion based on such band structure model in which the conductivity of the layer (precipitate) will be of summary importance. Indeed, the layer of precipitate phase is, for the most part, observed as being a region extended between grain-grain junction and precipitate in the triple-junction.

The grain–grain boundaries are also evidenced by HRTEM, indicating SnO_2–SnO_2 homo-junctions. Leite et al.[13] observed in SnO_2–MnO_2 systems using analytical electron microscopy of high resolution two phases: grains rich in SnO_2 and Mn_2SnO_4 precipitated at the grain boundary, besides two kinds of grain boundary: a thin Mn-rich and other thick Mn-poor.

Fig. 3 shows the select area electron diffraction in both SnO_2 grain and in the precipitates. The electron diffraction in the SnO_2 grain region revealed a well crystallized rutile type structure. Otherwise, the lattice parameters measured in the electron diffraction of the precipitates revealed a well crystallized Co_2SnO_4 cubic type phase. This was corroborated by the high concentration of Co and Sn observed in the EDS measurements in these precipitates.

Despite of microstructure heterogeneities observed in the present work, the most probable determinant factor for the existence of a Shottky-type barrier that controls the nonlinear electrical properties, continues to be the presence of an oxidation layer (oxidation of the segregated transition metals) at the grain-grain junction type.[6,7]

4. Conclusion

The TEM analyses of La and Pr doped SnO_2-based varistor were used to study the heterogeneities of $SnO_2{\cdot}CoO$-based varistor microstructure. Precipitation of secondary phases occurs at grain boundaries that were identified by EDS and electron diffraction as being Co_2SnO_4 and $Pr_2Sn_2O_7$, which are present mainly at triple-junctions of the $SnO_2{\cdot}CoO$ microstructure. HRTEM was applied to identify other kinds of junctions, one corresponding to homo-junctions of two $SnO_2{\cdot}CoO$ grains with segregated transition metals and other due to existing twins-grains.

Among all identified junction types, the one that most probably controls the overall nonohmic behavior is the grain-grain junction with segregated transition metal.

Acknowledgements

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