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Effect of oxidizing and reducing atmospheres on the electrical properties of dense SnO_2-based varistors

Maria R.C. Santos [a], Paulo R. Bueno [a], Elson Longo [a], José A. Varela [b,*]

[a] LIEC- Departamento de Quimica, UFSCar, PO Box 676, 13565-905 São Carlos, SP, Brazil
[b] Instituto de Quimica, UNESP, PO Box 355, 14801-970, Araraquara, SP, Brazil

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Abstract

The SnO_2 based varistor systems recently presented in the literature appear to have a promising potential in commercial applications. Experimental evidence shows that there is a dependence of nonlinear constant values with thermal treatment under different atmospheres. Thermal treatments in oxygen and nitrogen rich atmospheres at 900°C prove this dependence, indicating that the nonlinear constant values are significantly lower when the material is submitted to a nitrogen atmosphere. Moreover, electrical properties can be restored when the varistor is subjected to thermal treatment at the same temperature in an oxygen atmosphere, indicating that the mechanism seems to be reversible. This paper discusses this behavior focusing in the grain boundary region. Ta_2O_5 mol% concentrations are also analyzed and the results indicate an optimum Ta_2O_5 concentration of 0.05 mol% for the electrical properties ($\alpha = 44$ and $E_B = 6150$ V cm^{-1}). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical properties; Grain boundaries; SnO_2; Ta_2O_5; Varistors

1. Introduction

Varistors are materials whose current-voltage characteristics are nonlinear. They are used both as protecting devices against voltage transients in electronic and industrial equipment and as surge arrestors.[1] Commercial varistors used in protection systems are based on SiC (silicon carbide) or on ZnO (zinc oxide). SiC based varistors have low nonlinearity coefficients ($\alpha = 5$) where α is the nonlinearity constant defined by the relation of ($I = KV^{\alpha}$), where I is current, V is voltage and K is a proportionality constant.[2]

The ZnO based varistors have very high nonlinearity coefficients ($\alpha = 50$) and their major phase consists of ZnO and of small amounts of Bi_2O_3, Sb_2O_3, CoO, MnO_2 and Cr_2O_3.[3,4] The reaction between the ZnO and the additives at high temperatures leads to the formation of several phases in the grain boundary of ZnO.[5,6] Thus, despite its chemical composition and its phases, the type of processing employed, as well as the sintering temperature, heating and cooling rates are fundamental to control and understand electrical properties of this ceramic.[7] In view of this fact, the literature contains extensive reports describing the influence of processing variables on the properties and mechanisms that govern these systems' properties.[8–14]

Other varistor systems based on $SrTiO_3$,[15] TiO_2[16–19] and, more recently, WO_3 varistors[20] have been described in the literature, but the nonlinearity of these systems is very low ($2 < \alpha < 12$) compared with that of the multicomponent ZnO varistors. Pianaro et al.[21] were the first to present an SnO_2 based system as the main candidate to substitute multicomponent ZnO varistors. In this varistor system, the addition of CoO to the SnO_2 leads to high densification,[21,22] which makes it possible to define the varistors' behavior. A high nonlinearity coefficient of ($\alpha = 41$) was obtained in the $SnO_2 \cdot CoO \cdot Nb_2O_5$ (1.0 mol% of CoO and 0.05 mol% of Nb_2O_5) system when 0.05 mol% of Cr_2O_3 was added. The major advantage of this system lies in its simple single-phase microstructure and its high electrical stability.[23] From a technological standpoint, these two characteristics are very important because they increase the service life of the material and facilitate the control of its processing. Scientifically, they are important because

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* Corresponding author.
E-mail address: varela@iq.unesp.br (J.A. Varela).

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they allow a direct study of the voltage barrier at the grain boundary and, therefore, a better understanding of varistor behavior and of the mechanisms that lead to this behavior.

Because we do not observe the segregation of the secondary phase in the SnO_2 varistor systems, we propose that the potential barrier is formed by the presence of trap states. These trap states could be related to oxygen species (O_2, O'_2, O' and O'') at the grain boundary interface due to defects such as Cr'_{Sn} and Co'_{Sn} that transfer electrons to oxygen.[24] In this work, we present results that demonstrate the importance of atmosphere for the nonlinear behavior of SnO_2 based varistor systems. These results are important to detail the model of voltage barrier formation and SnO_2 varistor behavior. The purpose of this study is also to determine the optimum Ta_2O_5 concentration for the electrical properties of SnO_2 varistor systems.

2. Experimental procedure

The powder was prepared using the ball milling process in an alcohol media. The oxides used were SnO_2 (Merck), CoO (Riedel), Ta_2O_5 (Aldrich) and Cr_2O_3 (Vetec). The composition of the molar systems was (98.95−X)% SnO_2 + 1.0% CoO + X% Ta_2O_5 + 0.05% Cr_2O_3 (SCTaCr), with X equal to 0.010, 0.035, 0.050 and 0.065%. 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 in mol%.

The powder was pressed into pellets (11.0×1.0 mm) by uniaxial pressing (20 MPa), followed by isostatic pressing at 210 MPa. The pellets were sintered at 1300°C for 1 h and slowly cooled to room temperature. Mean grain size was determined by analyzing the SEM micrographies (ZEISS DSM 940A) using the PGT software (ASTM-E112 norm). To take the electrical measurements, silver contacts were deposited on the samples' surfaces, after which the pellets were heat treated at 400°C for 1 h.

The tetragonal structure of SnO_2 (rutile structure) was confirmed as the single phase by X-ray diffraction (SIEMENS Model D-5000) on the mixed powder.

Current-tension measurements were taken using High Voltage Measure Unit (KEITHLEY Model 237). The nonlinear coefficient α was obtained by linear regression of points on a logarithmic scale of around 1 $mA.cm^{-2}$ and the breakdown electric field (E_B) was obtained at this current density.

The samples were subjected to treatments in O2 (under a flux of 10 1/min) and in N_2 (under flux of 10 1/mm) atmospheres at 900°C for 1 h. The electric behavior was checked throughout the above mentioned procedures and after each treatment.

3. Results

3.1. Effect of Ta_2O_5 concentration on the properties of SnO_2 varistor

Recently, Antunes et al.[25] showed that the Nb_2O_5 addition could be substituted in the same concentrations by Ta_2O_5 in the SnO_2 based varistor system without substantial alterations in its electric behavior. This indicates that the importance of this additive lies in its oxidation state (+5). As suggested by Pianaro et al.,[21] Nb_2O_5 contributes to an increase of the electronic conductivity at the SnO_2 lattice, due to the substitution of Sn^{+4} by Nb^{+5}, which creates an acceptor level according to the following reaction:

$$2Nb_2O_5 \xrightarrow{SnO_2} 4Nb^{\bullet}_{Sn} + V''''_{Sn} + 10O^{x}_{o} \quad (1)$$

Similarly, Ta_2O_5 contributes to an increase in the electronic conductivity in SnO_2, according to the reaction:

$$2Ta_2O_5 \xrightarrow{SnO_2} 4Ta^{\bullet}_{Sn} + V''''_{Sn} + 10O^{x}_{o} \quad (2)$$

To verify the influence of Ta_2O_5 on the varistor behavior of the SnO_2 based system, compositions containing Ta_2O_5 concentrations ranging from 0.010 to 0.065 mol% were considered. The samples with varying Ta_2O_5 compositions were heat treated at 900°C in different atmospheres. The nonlinear coefficient (α) and breakdown electric field (E_B) values are shown on Tables 1 and 2 , respectively. There is an optimum concentration around 0.050 mol% of Ta_2O_5 with a maximum value for nonlinear behavior and for the breakdown electric field ($\alpha = 44$ and $E_B = 6150$ V/cm). Fig. 1 shows the $J \times E$ plots for the SnO_2 based systems with different Ta_2O_5 concentrations. Fig. 2 shows the α and E_B values based on Ta_2O_5 mol% concentration for SCTaCr systems.

As shown in these two tables, the atmosphere strongly affects the nonlinear coefficient (α) and breakdown electric field (E_B) values. Oxidizing atmospheres lead to high values for both, α and E_B. One important point is that, after heat treatment in a reducing atmosphere (N_2), α and E_B values decrease substantially. However, both α and E_B can be restored after subsequent heat treatment in an oxidizing atmosphere.

Table 3 shows the variation of Ta_2O_5 concentration on average grain size. There is no significant difference in the samples average grain size, and variations in the electrical properties with atmosphere are due only to the oxidizing effect that facilitates interpretation of these results.

Fig. 3 contains the SEM micrographs of the systems considered in this study. Although no secondary phases

Table 1
α Values for SCTaCr systems after thermal treatments at 900°C in different atmospheres

Atmosphere treatments	0.010 mol%	0.035 mol%	0.050 mol%	0.065 mol%
Without treatment	3	32	44	23
O_2 10 l/min flux	–	39	65	29
N_2 10 l/min flux	–	15	21	17
O_2 10 l/min flux (again)	–	36	54	24

Table 2
E_B values in V/cm for SCTaCr systems after thermal treatments at 900 °C in different atmospheres

Atmosphere treatments	0.010 mol%	0.035 mol%	0.050 mol%	0.065 mol%
Without treatment	2530	5820	6150	4800
O_2 10 l/min flux	–	6180	6200	5000
N_2 10 l/min flux	–	3220	5530	4200
O_2 10 l/min flux (again)	–	6000	6300	4900

were observed in the SEM micrographs, these phases might be precipitated at the grain boundaries, such as $CoSnO_3$ and $CoCr_2O_4$.[22] The relative densities of all samples exceeded 98% of the theoretical density and, according to the XRD analysis and other works in the literature,[21,25,26] no other phases besides SnO_2 rutile were observed.

3.2. The effect of atmosphere on the current-voltage characteristics

To verify the effect of oxidizing atmosphere on the current-voltage characteristics of SnO_2 based varistors, samples containing 0.050 mol% of Ta_2O_5 sintered in normal air ($\alpha = 44$) were further heat treated at 900°C in an oxygen rich atmosphere. The α value increased to 65. The same samples were then subjected to further heat treatment in nitrogen rich atmosphere and the α decreased to as low as 21. This was followed by another heat treatment at 900°C in oxygen, which partially restored the α value to 54. This cycling effect with the atmosphere is schematized in Fig. 4. This cycling effect is similar to that reported in ZnO based varistor system by Sonder et al.[27] Sonder et al. showed that restoration of the nonlinear current-voltage characteristics for totally reduced varistors requires much higher temperature (~600°C) than is required to degrade a totally oxidized one. It explains why the totally current-voltage characteristic restoration did not occur in our experiment.

There is ample evidence in the literature[35–40] to conclude that stability can be achieved in an otherwise unstable ZnO varistor when it is heated for several hours in an oxidizing atmosphere, preferably from 600 to 800°C. Based on the literature and on the results of this study, it is

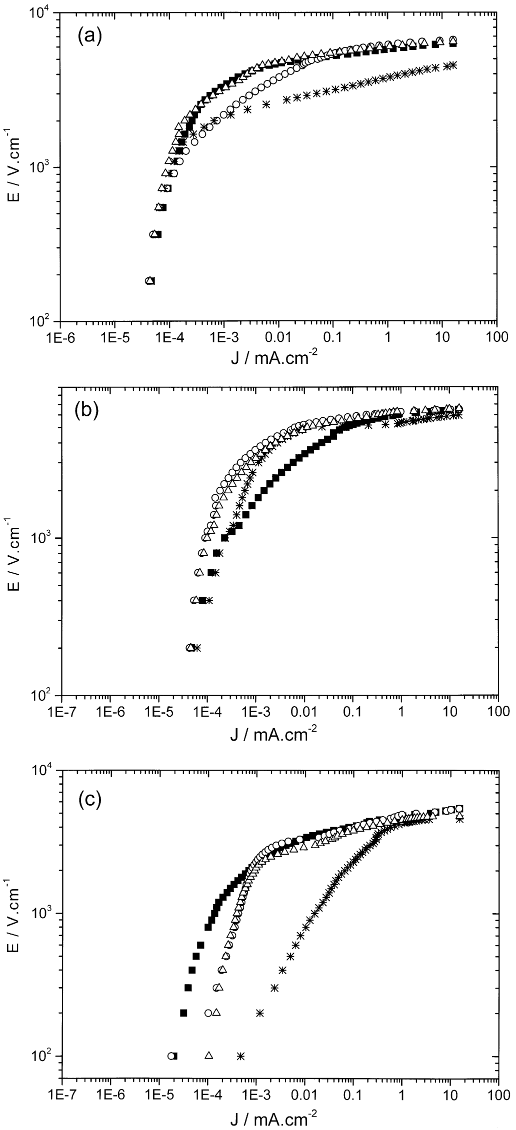


Fig. 1. J–E characteristic curves for the systems (a) 0.035 mol% SCTaCr system; (b) 0.050 mol% SCTaCr system; (c) 0.065 mol% SCTaCr system. (■) Without treatment; (○) O_2 10 l/min flux; (∗) N_2 10 l/min flux; (△) new O_2 10 l/min flux.

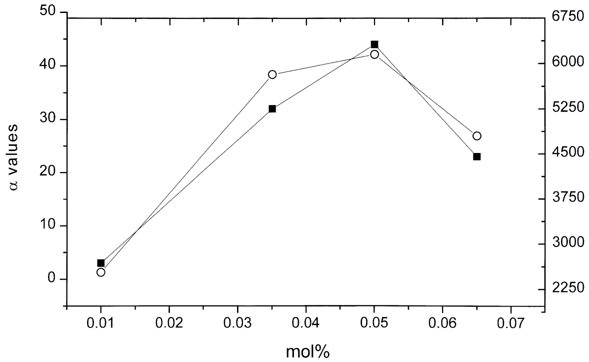


Fig 2. α (■) and E_B (○) values based on Ta_2O_5 mol% concentration for SCTaCr systems without atmosphere treatment.

proposed that oxygen from the atmosphere is adsorbed at the grain boundary and diffuses throughout these disordered layers, represented by quasi-chemical reactions. The occurrence of oxygen grain boundary diffusion in polycrystalline oxides such as ZnO[30,40] has already been established in the literature describing sintering studies and this assumption is, therefore, not unrealistic.

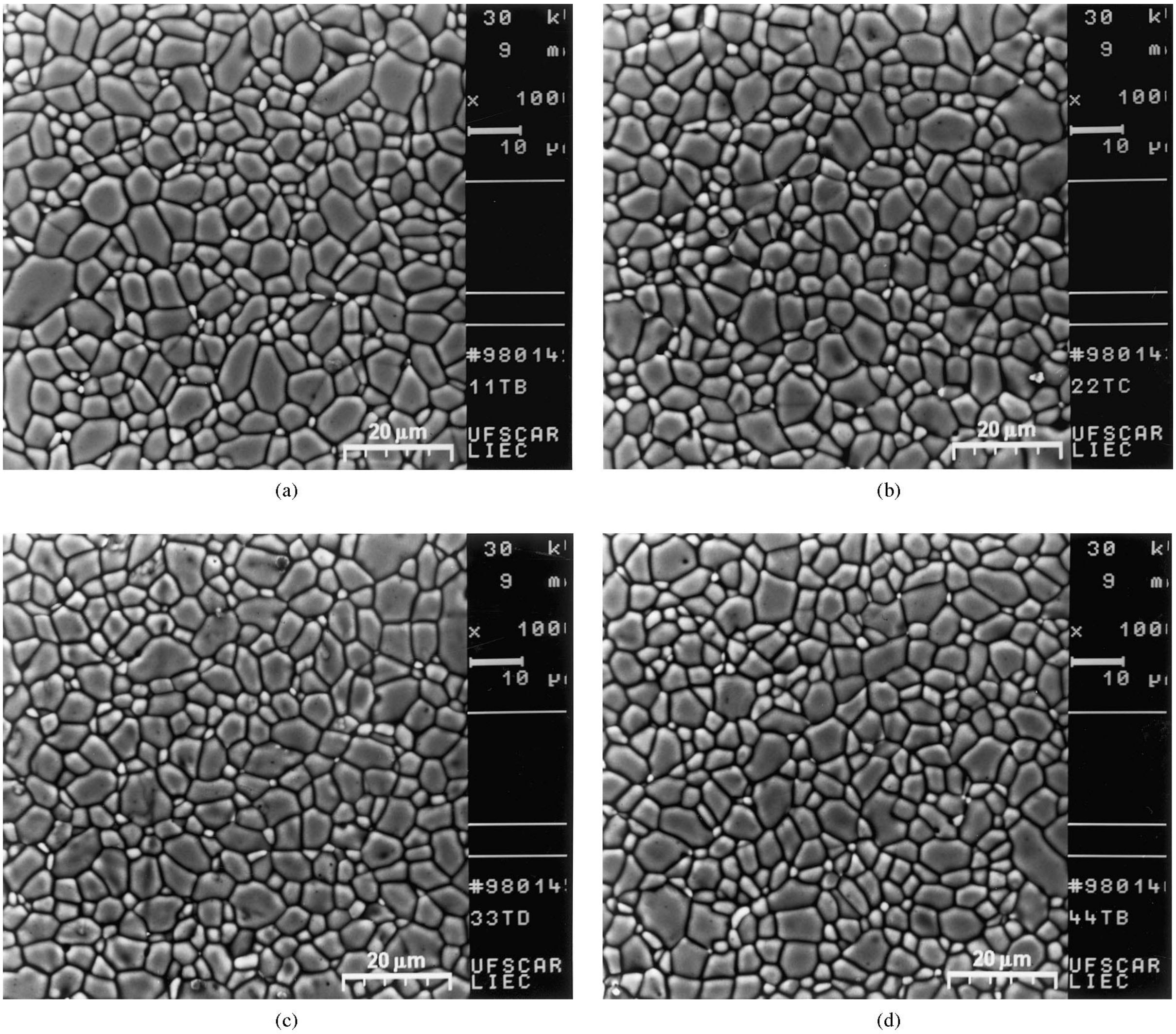
Table 3
Mean grain size and standard deviation of SCTaCr varistor systems

SCTaCr system (mol%)	Mean grain size (μm)	Standard deviation (μm)
0.010	4.5	2.1
0.035	4.6	2.1
0.050	4.8	2.2
0.065	4.8	2.2

Stucki et al. evidences that the height of potential barriers in ZnO varistors depends sensitively on the excess amount of oxygen (~1 monolayer) present at interfaces between grains.[28] This oxygen enrichment is influenced by thermal processing and by the electrical degradation.[28]

It was shown through complex plane analysis technique and Mott–Schottky approach that the barrier of ZnO and SnO_2 based varistor systems are of the same physical nature (Schottky-type barrier).[29] The results presented herein are in agreement and reinforce this observation.

The importance of the oxygen species for the formation of a voltage barrier in SnO_2 based varistor systems was discussed by Bueno et al.[24] The fact that the samples' varistor behavior is reversible when heat-treated in N_2 and O_2 indicates that there are very well defined adsorption sites. The results are also in agreement with



(a) (b)

(c) (d)

Fig. 3. SEM systems micrographs: (a) 0.010 mol% SCTaCr system; (b) 0.035 mol% SCTaCr system; (c) 0.050 mol% SCTaCr system; (d) 0.065 mol% SCTaCr system.

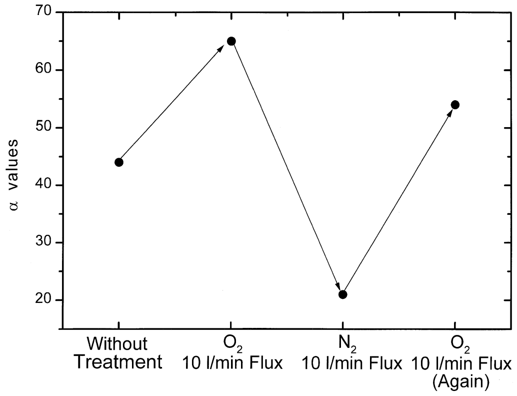


Fig. 4. Reversibility of α values based on atmosphere treatments of 0.05 mol% SCTaCr system.

Gupta's model[27] modified by Leite et al.[31,32] to describe the voltage barrier in the ZnO based varistor system.

The mechanism of O_2 adsorption species in the SnO_2 based varistor has already been described and is linked with the Cr'_{Sn} defect and the Co'_{Sn}.[24] This mechanism is very important in understanding barrier formations in SnO_2 varistor systems. SnO_2 based varistor systems containing no Cr_2O_3, present low α value ($\alpha = 8$). However, optimizing the cooling rate during processing can increase this value. Lowering the cooling rate can cause the α values to increase up to 24, as shown by Leite et al.[33] The increase in the α values for slow cooling rates can be ascribed to the oxidizing effect of CoO during heating up to 600°C followed by the reducing effect at temperatures above 1000°C.[34] Eq. (3)–(5) represent CoO oxidation and reduction.

$$2CoO + \frac{1}{2}O_2 \xrightarrow{600^{\circ}C} Co_2O_3 \tag{3}$$

$$Co_2O_3 + CoO \xrightarrow{800^{\circ}C} Co_3O_4 \tag{4}$$

$$Co_3O_4 + CoO \xrightarrow{1000^{\circ}C} 3CoO + \frac{1}{2}O_2 \tag{5}$$

Therefore, the cobalt oxide, when in the + 3 reduction state, can affect the adsorption of oxygen species in SnO_2 grain boundaries in a similar way as chromium oxide. Otherwise, when in the + 2 state, the cobalt oxide can affect the adsorption of oxygen species in SnO_2 grain boundaries as represented by Eqs. (6)–(9).

$$Co''_{Sn} + O_2 \xrightarrow{SnO_2} Co''_{Sn}\cdot O_{2(ads)} \tag{6}$$

$$Co''_{Sn}\cdot O_{2(ads)} \xrightarrow{SnO_2} Co'_{Sn}\cdot O'_{2(ads)} \tag{7}$$

$$Co'_{Sn}\cdot O'_{2(ads)} \xrightarrow{SnO_2} Co^{x}_{sn}\cdot (O')_{2(ads)} \tag{8}$$

$$2Co^{x}_{Sn}\cdot (O')_{2(ads)} + Co''_{Sn} \xrightarrow{SnO_2} 2Co^{x}_{Sn}\cdot (O'')_{2(structral)} + Co^{x}_{Sn} \tag{9}$$

Based on a theoretical study, Santos et al.[41] proposed a model in which $Zn_i^{\bullet}$ species near the grain boundary decrease the negative surface state due to redistribution of the charge and favor oxygen adsorption. The adsorption of O', O_2', and O_2 at the ZnO surface stabilizes the ZnO system, increasing the varistor properties. In their work, Santos et al.[41] proposed that desorption of these species leads to ZnO varistor degradation. Leite et al.[31,32] explain that the low degradation rate of ZnO based varistor in an oxygen rich atmosphere is due to the adsorption of O'' and O' species at the grain boundaries.

Thus, the adsorption phenomenon of the oxygen species in a disordered layer at the grain boundary seems to be largely responsible for the properties of varistor systems, since it is the dominant and extremely important mechanism for the performance of these ceramic devices. Fig. 5 depicts how O_2 species could interact with the grain boundary surface and modify the potential barrier in varistors.

Although the mechanisms that lead to the formation of electrical barriers in ZnO and SnO_2 based varistors appear to be similar, there are some basic differences between the two systems. SnO_2 varistors, differently from ZnO based varistors, need small dopant concentrations for good α values. Ta_2O_5 (+ 5 valence metals) amounts above 0.050 mol% do not promote an increase in α values when treated in O_2 rich atmosphere. This may be explained by associating the $Ta^{\bullet}_{Sn}$ defect with Cr'_{Sn}. According to Eq. (2), the addition of Ta_2O_5 causes the formation of $Ta^{\bullet}_{Sn}$. This is equivalent to an electronic defect and can be represented by:

$$Ta^{\bullet}_{Sn} \xrightarrow{SnO_2} Ta^{x}_{Sn} + h^{\bullet} \tag{10}$$

An excess of $[h^{\bullet}]$ resulting from a higher concentration of Ta_2O_5 could cause a decrease in E_B value by the reaction illustrated in Eq. (10), since the smallest E_B values were obtained for 0.065 mol% SCTaCr systems in all the atmospheres used (see Table 2). The excess of electron holes could decrease the effect of the negative charged defects at the interface, responsible for electric barrier formation.

Thus, a reduction in the interface state density of the system could be expected through an excess of electron holes. This is the same analytical treatment given by Ikeda et al.[42] in the TiO_2 rutile structure, which possesses the same structure as the SnO_2 semiconductor used in this study. Ikeda et al. concluded that the segregation of solutes of positive and negative effective charge, i.e. donors (Nb_2O_5) and acceptors (Al_2O_3),

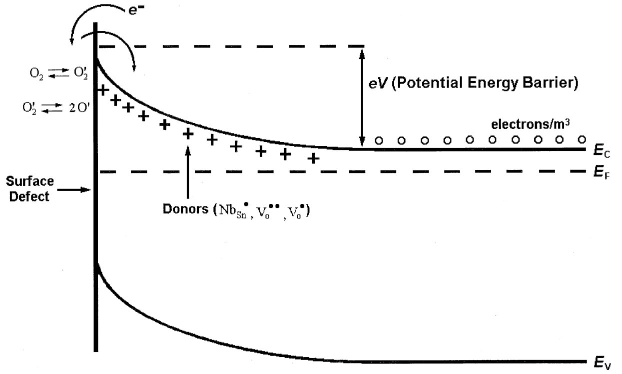


Fig. 5. Schematic representation describing some possible surface and bulk phenomena and its effect in voltage barrier in SnO_2 based varistor systems.

depends on the overall doping level, temperature, and oxygen pressure. When there is an excess of donor Nb_2O_5, it is compensated in the lattice by titanium vacancies and, in this kind of composition, a segregation of $\mathrm{Nb^{\bullet}_{Ti}}$, is seemed. Cr_2O_3 and Nb_2O_5 dopants cause a similar effect on the TiO_2 lattice, compared to SnO_2, and this system has also a varistor behavior, as already reported in the literature.[19] Considering that the addition of Nb_2O_5 in SnO_2 has similar effect to that of Ta_2O_5 in SnO_2, the present hypothesis appears plausible.

Therefore, the role of $\mathrm{Co''_{Sn}}, \mathrm{Cr'_{Sn}}, \mathrm{Sn''_{Sn}}, \mathrm{V''''_{Sn}}$ and V''_{Sn} (due to the reduction of Sn^{+4} to Sn^{+2} in the interstitial sites) would be related to the increase the O_2'', O' and O'' adsorption at the grain boundary interface, causing a decrease in the conductivity by the donation of electrons to the O_2 absorbed at the grain boundary surface. The role of $\mathrm{Co''_{Sn}}, \mathrm{Cr'_{Sn}}, \mathrm{Sn''_{Sn}}, \mathrm{V''''_{Sn}}$ and $\mathrm{V''_{Sn}}$ species would be to generate sites to promote the adsorption of electrophilic species (forming a depletion layer). The experimental data presented in this paper reinforce this hypothesis, since both α and E_B are quite dependent on the oxidizing atmosphere. Experiments are under way to elucidate these statements.

In summary, the level of negative defect sites created at the grain boundary interface is of fundamental importance for good nonlinearity properties in SnO_2 varistor systems.

4. Conclusions

The experimental results indicate that the α and E_B of the SCTaCr varistor system depend on the Ta_2O_5 concentration. Concentrations up to 0.05 mol% increase those properties due to tin vacancy formation. Higher concentrations, however, decrease these properties owing to decreased trap states at the grain boundary.

The partial oxygen pressure in the sintering atmosphere of the SnO_2 based varistor is a decisive factor in the varistor properties. The degradation of the voltage barrier of SnO_2 based varistor, when heat treated in nitrogen, and the subsequent restoration of this voltage barrier by heat treating in an oxygen atmosphere suggests that the chemical origin of the interface states may be due to the chemisorbed oxygen on the grain surfaces. The results suggest that the maximum concentration of oxygen species at grain boundary interface depends on the level of adsorption sites that are created by negative defects such as $\mathrm{Co''_{Sn}}, \mathrm{Cr'_{Sn}}, \mathrm{Sn''_{Sn}}, \mathrm{V''''_{Sn}}$ and $\mathrm{V''_{Sn}}$.

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