Dependence of La$_2$O$_3$ content on the nonlinear electrical behaviour of ZnO, CoO and Ta$_2$O$_5$ doped SnO$_2$ varistors

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Received 17 February 2006; accepted 10 August 2006
Available online 30 August 2006

Abstract

The effects of La$_2$O$_3$ on the properties of (Zn, Co, Ta) doped SnO$_2$ varistors were investigated in this study. The samples with different La$_2$O$_3$ concentrations were sintered at 1400 °C for 2 h and their properties were characterized by XRD, SEM, $I$–$V$ and impedance spectroscopy. The grain size was found to decrease from 13 μm to 9 μm with increasing La$_2$O$_3$ content. The addition of rare earth element leads to increase the nonlinear coefficient and the breakdown voltage. The enhancement was expected to arise from the possible segregation of lanthanide ion due to its larger ionic radius to the grain boundaries, thereby modifying its electrical characteristics. Furthermore, the dopants such as La may help in the adsorption of O$'$ to O$''$ at the grain boundaries characteristics.

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Keywords: Varistors; Tin oxide; Lanthanides; Nonlinear electrical behaviour

1. Introduction

Metal-oxide varistors are a class of ceramic semiconductor devices with highly nonlinear current–voltage characteristics [1,2]. The ZnO-based varistor is the most exhaustively studied class of these ceramic materials and is commercially applicable in a wide range of electrical engineering devices and in electronics. The ZnO-based varistor consists predominantly of ZnO, with small additions of Bi$_2$O$_3$, Sb$_2$O$_3$, CoO, MnO, Al$_2$O$_3$ and other constituents such as Cr$_2$O$_3$. The material shows highly nonlinear current–voltage ($I$–$V$) characteristics, with a sharp breakdown voltage, above which large currents can be carried with only minor damage to the material. In the past few years, our research group has discovered a new class of polycrystalline ceramics composed predominantly of SnO$_2$ [3–13]. The main characteristic of this new varistor system is its simple microstructure, which has only one phase with X-ray precision, in which CoO forms a solid solution by the substitution of Sn$^{4+}$ ions for Co$^{2+}$ or Co$^{3+}$ ions, as reported and discussed in previous papers [3,15]. Dense SnO$_2$-based ceramics can be achieved by introducing dopants or by hot isostatic pressure processing [16]. The addition of CoO creates oxygen vacancies and Co$_{O''}$ or Co$_{s''}$ which can segregate at the grain boundaries [17]. Both defects can help in the formation of the Schottky barriers at grain boundaries. The function of ZnO is the creation of oxygen vacancies and Zn$_{O''}$ defects [18]. The latter are less segregated and contribute to the Schottky barrier formation. However, both additives lead to a highly resistive material. The addition of tantalum oxide creates Ta$_{s''}$ defect (donor) that increases the lattice conductivity of SnO$_2$-based ceramics [19]. Moreover, in small concentrations Ta$_2$O$_5$ does not segregate at the grain boundaries resulting in high grain conductivity. Excess of Ta$_2$O$_5$ causes segregation of defects at grain boundaries which decrease both bulk conductivity and grain size. P. R. Bueno et al. reported the preparation of SnO$_2$-based systems doped with La$_2$O$_3$ and Pr$_2$O$_3$. Their results indicate that La$_2$O$_3$ and Pr$_2$O$_3$ segregate at the grain boundaries, probably inducing electronic interface states that can trap charges at the SnO$_2$–SnO$_2$ interface and lead to significantly increased $α$ values [9,10].

The impedance spectroscopy (IS) technique has also been used to study polycrystalline tin oxide specimens. The IS technique allows for the separation of the three main contributions to the
electrical conductivity of a polycrystalline solid: bulk, internal surfaces like grain boundaries and electrodes [20]. This is accomplished by varying the frequency of the AC input signal over a wide range in order to cover the different responses that charges carriers have inside grains, at grain boundaries and at the specimen electrode interface. In our work, the La2O3 doped SnO2 ceramics were prepared using ZnO and CoO as densification mediators and Ta2O5 to increase the electric conductivity. The effect of lanthanum oxide on the structural, morphological and electrical properties of the SnO2·ZnO·CoO·Ta2O5 (SZCT) varistors was investigated. As a result, an optimum composition was obtained.

2. Experimental procedure

The powder was prepared using the mixed oxide method in alcoholic medium. All the oxides used were of analytical grade: SnO2 (Cesbras-Fine), ZnO (Synth), CoO (Riedel), Ta2O5 (Aldrich) and La2O3 (Vetec). The molar composition of the investigated systems was (98.95 −X)% SnO2 + 0.50% CoO + 0.50% ZnO + 0.05% Ta2O5 + X% La2O3, with X equal to 0.025, 0.050 and 0.075 mol%. The amounts of CoO and ZnO were always kept constant, because these additives were used to facilitate densification during sintering. The powder was pressed into pellets by uniaxial pressing followed by isostatic pressing at 210 MPa. The pellets were sintered at 1400 °C for 2 h in oxygen atmosphere and slowly cooled to room temperature (5 °C/min). The X-ray data were collected with a Rigaku-2000 diffractometer under the following experimental conditions: copper anode, 50 kV, 150 mA and CuKα radiation monochromatized by a graphite crystal. Mean grain size was determined by analysing the SEM micrographs (Topcom Sm-300). To perform the electrical measurements, silver contacts were deposited on the samples surfaces. Current–tension measurements were taken using High Voltage Measure Unit (Keithley Model 237). The breakdown electric field (Eb) was obtained at a current density of 1 mA cm−2. The impedance measurements were made with a frequency response analyser using frequency ranging from 100 Hz up to 4 MHz, with an amplitude voltage of 1 V. The pellets were put in a sample holder attached to a furnace. Measurements of real (Z') and the imaginary (Z") were made at temperatures ranging from 230 to 280 °C. The impedance data were analysed with the EQUIVCRT program [21].

Fig. 1. X-ray diffraction data of the varistor system doped with different aluminum concentrations: (a) without Al; (b) 0.025 mol%; (c) 0.050 mol%; (d) 0.075 mol%.

Fig. 2. SEM micrographs for the SZCT system doped with different aluminum concentrations: (a) without Al; (b) 0.025 mol% and (c) 0.075 mol%.
3. Results and discussion

Fig. 1 shows the X-ray diffraction analysis of a SnO$_2$-based varistor system with a molar concentration of 0.50% CoO + 0.50% ZnO + 0.05% Ta$_2$O$_5$ and several amounts of La$_2$O$_3$. No extra lines other than rutile tin oxide phase were observed, indicating the absence of any second phases. The tetragonal rutile structure was confirmed by X-ray diffraction. However, it is noted that the amount of lanthanum added is too small to be determined by XRD.

Fig. 2 shows the SEM micrographs of the systems considered in this study. As is clearly shown, the porosity is higher for the La$_2$O$_3$ doped systems. This increase in porosity is probably due to the segregation of La$_2$O$_3$ at the grain boundaries, which prevents mass transport through the grain boundaries, hindering the sintering process. La$_2$O$_3$ appears to exert an influence on the microstructure similar to that observed when Cr$_2$O$_3$ is added to the SnO$_2$–CoO–Nb$_2$O$_5$ system, as has been described previously [14], increasing the porosity of the system. Oxide dopants with $+$3 metal valence appear to be more effective in increasing the nonlinear properties, as discussed in Refs. [3,8,12]. The influence of processing in SnO$_2$-based systems containing La$_2$O$_3$ has also been discussed in a previous paper [12]. The high densification of tin dioxide ceramics was attributed to the zinc and cobalt effect in the SnO$_2$ lattice, which leads to the formation of oxygen vacancies. If one considers that diffusion of oxygen vacancies is the rate controlling step, the substitution of Sn$^{4+}$ by Zn$^{2+}$, Co$^{2+}$ or Co$^{3+}$ increases the sintering rate of SnO$_2$ ceramics.

The applied electric field as a function of current density for the different systems is given in Fig. 3. The nonlinear coefficient $\alpha$ was obtained by $\alpha = \log(I_2/I_1)/(V_2/V_1)$ where $V_1$ and $I_1$ as well as $V_2$ and $I_2$ are the corresponding values of voltage and current for two points that can be chosen arbitrarily [22]. The $\alpha$ values were obtained from the curves $E \times J$ for current densities between 1 and 10 mA cm$^{-2}$. The highest nonlinear coefficient ($\alpha = 20$) was obtained when molar concentrations of 0.025 mol% La$_2$O$_3$ were added to SnO$_2$, presenting an electric breakdown field of 4400 V/cm. The addition of La$_2$O$_3$ in concentrations varying from 0.025 to 0.075 mol% leads to a substantial modification in the electrical behaviour of the SnO$_2$–ZnO–CoO–Ta$_2$O$_5$ ceramics. The electric behaviour of the system without La$_2$O$_3$, although nonlinear, is highly resistive. The samples containing 0.025 mol% La$_2$O$_3$ are more resistive in the grain boundary (electrical breakdown close to 4400 V/cm) and possess a nonlinear coefficient equal to 20, as mentioned before. Comparing the results presented in Table 1 and Fig. 3, it can be stated that the addition of La$_2$O$_3$ decreases the grain size increasing the nonlinear coefficient and the breakdown electric field. Similar results were found by P. R. Bueno et al. [10] where they described the DC electrical behaviour of the SCN and SCNCr systems as a function of different Cr$_2$O$_3$ molar concentrations. SCN presents a varistor behaviour with $\alpha$ equal to 58 and a breakdown electric field ($E_b$) of 1870 V/cm. When 0.05% Cr$_2$O$_3$ was added to the system, the $\alpha$ value increased to 41 and the breakdown field to 3990 V/cm [22].

Fig. 4(a)–(c) shows the Nyquist diagrams of SZCTLa with 0.05% La$_2$O$_3$ at three different temperatures. The semicircles observed in Fig. 4(b) were obtained by convolution of two time constants in the system. So, the electrical response can be fitted by an equivalent electrical circuit composed by two series circuits of a resistance and capacitor in parallel. Two hypotheses may be considered to explain these two time constants: The first hypothesis suggests that one time constant is related to the grain boundary barrier and the second is associated with the grain barrier. The weakness of this model is that the grain resistivity thus calculated is at least four orders of magnitude higher than the literature values for grain resistivity of SnO$_2$ [23]. The second hypothesis supposes the existence of different defects and/or adsorbed species at the grain boundary region, not necessarily at the same grain boundary. The two time constants are due to these kinds of defects. The second hypothesis is more probable, since the possibility of existence of different adsorbed species and defects on SnO$_2$ was described in the literature [24]. It is possible that at temperatures higher than 200 °C the following species predominate at the grain boundary structure:

$$\text{La}_2\text{O}_3 \rightarrow 2\text{La}_{\text{Sn}}^+ + \text{O}^{2-} + 3\text{O}^{2-}$$  \hfill (1)

$$\text{La}_{\text{Sn}}^- + \text{O}_2^- \rightarrow \text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})}^2$$  \hfill (2)

$$\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})} \rightarrow \text{La}_{\text{Sn}}^0 \text{O}_{2(\text{ads})}^2$$  \hfill (3)

$$\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})} + \text{La}_{\text{Sn}}^- \text{O}_{2(\text{ads})} \rightarrow (\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})})^2$$  \hfill (4)

$$2(\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})}) \rightarrow (\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})})^2$$  \hfill (5)

$$\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})} + \text{La}_{\text{Sn}}^- \text{O}_{2(\text{ads})} \rightarrow (\text{La}_{\text{Sn}}^+ \text{O}_{2(\text{ads})})^2$$  \hfill (6)

Table 1

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<th>Lanthanum</th>
<th>α</th>
<th>$E_b$ (V/cm)</th>
<th>$I_b$ (mA)</th>
<th>$V_b$ (V)</th>
<th>$\phi_b$ (eV)</th>
<th>$\beta$ (eV V$^{-1/2}$ cm$^{1/2}$)</th>
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</table>

Fig. 3. Applied electric field as a function of current density for the SZCT system doped with different aluminum concentrations: (a) without Al; (b) 0.025 mol%; (c) 0.050 mol%; (d) 0.075 mol%.
From these results one may say that the species that are truly responsible for the barrier formation are \( O' \) to \( O'' \). The \( \text{LaSn} \) generates the sites to promote the adsorption of electrophilic species. These defects, \( O' \) to \( O'' \), are not equally present at the same grain boundary. One of them is probably predominant at a grain. This behaviour leads to a random distribution of both defects, and to different charge transport paths in the sample.

The influence of \( \text{La}_2\text{O}_3 \) concentration on the average grain size is shown in Table 1. The mean grain size was obtained by the intercept method. There are significant differences in average grain size with the increase in \( \text{La}_2\text{O}_3 \) concentration. The increase of \( \text{La}_2\text{O}_3 \) content results probably in a segregation at the grain boundaries which might decrease the grain boundary mobility leading to a decrease in the grain size. The grains are regularly distributed with an average grain size from 9.0 to 13.3 \( \mu \text{m} \) (Table 1). The mean values of \( \alpha \), \( E_b \) number of effective voltage barriers (\( V_b \)), and \( \phi_b \) (barrier height) are also displayed in Table 1. The effective voltage barriers were determined using the expression: \( V_b = E_b \cdot n \), where \( n \) is the number of grains in a line of length \( L \) and \( G \) is the mean grain size. The \( V_b \) can be estimated as \( V_b = E_b \cdot G / L \). Higher breakdown electric field \( E_b \) due to the reduced grain size and higher barrier voltage per grain \( V_b \) were obtained for \( \text{La}_2\text{O}_3 \), \( \text{ZnO} \), \( \text{CoO} \) and \( \text{Ta}_2\text{O}_5 \) doped \( \text{SnO}_2 \) varistors. There was a decrease in the number of effective barriers of the system doped with 0.075 mol% in \( \text{La}_2\text{O}_3 \). Besides that, \( \text{La}_2\text{O}_3 \) causes a significant increase in the barrier height. The increase in the potential barrier height and decrease in the barrier width are associated to the increase of both negative states at the interface between the \( \text{SnO}_2 \) grain (\( N_s \)) and donor concentration (\( N_d \)) due to the segregation of \( \text{La}_2\text{O}_3 \) next to the grain boundary as well as the creation of positive defects in the depletion layer (\( V_0 \cdot \cdot \cdot \)) and negative defects interface (\( \text{LaSn} \)). This suggests that the electronic states of the grain boundary region change with the addition of \( \text{La}_2\text{O}_3 \).

Building up a high and narrow potential barrier at the grain boundary is the last condition required for obtaining a varistor with a high nonlinear coefficient. The obtained data show that doping the SZCT system with \( \text{La}_2\text{O}_3 \) at a level of 0.05 mol% builds up an optimized barrier at the grain boundary. Bueno et al. [10] observed that the activation energies for the \( O' \) species on the \( \text{SnO}_2 \) surface are 0.39, 0.77 and 1.0 eV at temperatures higher than 200 °C (low frequency). At low temperatures (high frequency), \( V_0 \cdot \cdot \cdot \) species were found. The corresponding energy in the present article is 0.96 indicating that the \( O' \) to \( O'' \) species predominate at the grain boundary and are responsible for the nonlinear electrical properties (Fig. 5).

### 4. Conclusions

The electrical properties of the SZCT varistor system depend on the \( \text{La}_2\text{O}_3 \) concentration. A nonlinear coefficient of 20 for the \( \text{SnO}_2 \) varistor doped with 0.025 mol% \( \text{La}_2\text{O}_3 \) was obtained. The increase of the breakdown electrical field with increasing \( \text{La}_2\text{O}_3 \) doping is mainly attributed to the decrease of the grain size. The impedance results show the existence of two time constants in the varistor system investigated. The results suggest different kinds of defects in the grain boundary region. The activation energy...
obtained from this varistor indicates that the O’ to O″ species predominate at the grain boundary and are responsible for the nonlinear electrical properties.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq, and CAPES.

References