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Journal of the European Ceramic Society 25 (2005) 3011–3015
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Nonlinear properties and stability of SnO_2 varistors prepared by evaporation and decomposition of suspensions

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Available online 26 April 2005

Abstract

SnO_2 varistors doped with CoO, Cr_2O_3 and Nb_2O_5 were prepared by evaporation and decomposition of suspensions. The composition of the varistors was optimized to improve electrical properties, such as nonlinearity, leakage current and electrical stability. The best results were achieved with the following composition: 99.15% SnO_2 + 0.75% CoO + 0.05% Cr_2O_3 + 0.05% Nb_2O_5. Samples showed high density, reaching 99.5% of the theoretical density, as well as an homogeneous microstructure. The nonlinear coefficient was higher than 30 in the current range from 10^{-7} to 10^{-2} A/cm^2. The leakage current was 0.86 μA/cm^2. These samples showed high stability of electrical parameters when they were exposed to high current of 27 mA/cm^2 for different time periods up to 30 min.

Keywords: Varistor; Electrical properties

1. Introduction

Metal oxide varistors are ceramic devices used for voltage stabilization and transient surge suppression in electric power systems and electronic circuits.[1] The main feature of varistors is their high nonlinearity of the current–voltage characteristics. The most commonly used material is polycrystalline ZnO doped with various additives such as oxides of Mn, Co, Cr, Ni, Bi, Sb. Generally ZnO varistors contain three main phases: doped ZnO grains, spinel and an intergranular phase.[2–4] Recently, there has been increased interest in novel SnO_2 based varistors.[5,6] The main advantage of this new varistor system is its simple microstructure, which has only one crystalline phase. Commonly used dopants in preparation of SnO_2 varistors are CoO, MnO_2, Cr_2O_3, and Nb_2O_5. CoO and MnO_2 are usually used to improve densification of SnO_2 ceramics, and other dopants such as Cr_2O_3, Nb_2O_5 are usually used to improve electrical properties.[6–10] The most commonly used method for the production of ZnO, as well as SnO_2 varistors, is the conventional mixed-oxide method. The main advantage of this method is its simplicity, but it can yield an inhomogeneous distribution of dopants. For this reason some chemical methods such as Pechini method were applied to achieve homogeneous distribution of dopants and uniform grain size.[11,12] Unfortunately, the Pechini method is rather complicated and inconvenient for commercial applications. Also, this method can result in homogeneous distribution of dopants throughout the SnO_2 grains. Bearing in mind that the varistor effect is a grain boundary effect it is important to distribute dopants homogeneously on the grain boundaries. For this reason we applied simpler chemical method of evaporation and decomposition of solutions and suspensions,[13] which could provide a satisfactory distribution of dopants, and consequently good microstructure and electrical properties. The composition of SnO_2 varistors containing different amounts of CoO, Cr_2O_3 and Nb_2O_5 was optimized based on results of dc electrical measurements.

2. Experimental procedure

Samples of SnO_2 doped with CoO, Cr_2O_3 and Nb_2O_5 were prepared by the evaporation and decomposition of

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doi:10.1016/j.jeurceramsoc.2005.04.001

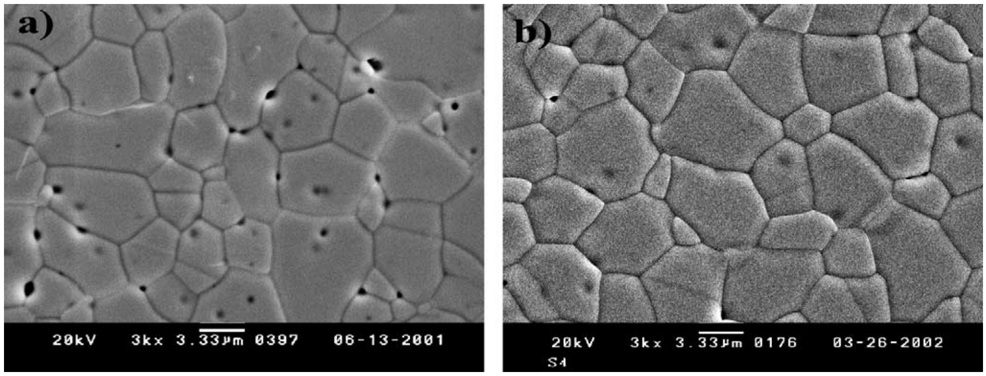

Fig. 1. SEM of doped SnO_2 of composition: (a) S1 and (b) S4.

solutions and suspensions. Starting materials were: SnO_2, $Co(CH_3COO)_2$, $Cr(NO_3)_3$, and Nb-citrate. Samples were prepared by the following procedure.

Appropriate amounts of $Co(CH_3COO)_2$, $Cr(NO_3)_3$, and Nb-citrate were dissolved in 25 ml of water to obtain solutions of different concentrations according to the desired composition of final powder mixture. Further, SnO_2 powder (5 g) was suspended in solution of $Co(CH_3COO)_2$, $Cr(NO_3)_3$ and Nb-citrate. The suspension was stirred and heated on the hot magnetic plate and dried at 140 °C for 5 h. Obtained powder mixtures were milled in agate mortar and calcined at 800 °C. After thermal treatment the obtained powders had the composition as given in Table 1.

The starting composition, S1, was chosen based on published data.[14] The set of samples, S2–S10, was prepared for optimization of composition. The composition of SnO_2 varistors was optimized on the basis of dc electrical measurements.

Powders were isostatically pressed at 250 MPa in pellets sized approximately 1 mm in height and 8 mm in diameter and sintered at 1300 °C for 1 h.

Sintered samples were characterized by X-ray (Siemens D-5000 powder diffractometer with graphite-monochromatized Cu Kα radiation) and SEM (Topcon SM-300). For dc electrical measurements a high-voltage source-measure unit (Keithley 237) was used. The non-linearity coefficient was calculated in the current interval 1–10 mA/cm^2. The breakdown field (E_C) was measured at 1 mA/cm^2, and the leakage current (j_L) was determined at an electrical field of 0.8 E_C. Measurements were performed using pulse current with logarithmic step, duration of pulses: 1 s, offtime: 3 s. Stability was investigated by monitoring change in voltage with constant current (0.1, 1 and 10 mA).

3. Results and discussion

X-ray diffraction analysis confirmed that single-phase ceramics were obtained. All samples contained only a SnO_2 phase and no secondary phases. Also, all samples showed high densities, higher than 98% of theoretical density, and homogeneous microstructures (Fig. 1). Almost fully dense ceramics, reaching 99.5% of theoretical density, were obtained for composition S4 (Fig. 1b). As can be seen (Fig. 1) samples S4 is almost without pores, and showed better microstructure in comparison to other compositions.

The electrical parameters of starting composition S1 were: $\alpha = 36$, $E_C = 253$V/mm and $j_L = 110\ \mu$A/cm^2. The current–voltage characteristic of this sample is shown in Fig. 2. Only the beginning of the non-linear part of the curve was obtained because of the high conductivity of the sample. The form of this curve is not good, transition from linear to non-linear part is not pronounced enough, resulting in a high leakage current.

According to the literature,[7,15,16] the role of CoO is to improve densification of SnO_2, but it also has influence on electrical properties. Nb_2O_5 and Cr_2O_3 have dominant influence on potential barrier height and consequently on current–voltage characteristic. Nb homogeneously incorporates into the SnO_2 lattice. On this way, the concentration of free electrons and conductivity increase, and consequently potential barrier decreases.[15,16] On the other hand, Cr segregate at grain boundaries and dramatically increases grain boundary resistivity, i.e. potential barrier is increased.[16,17] According to the role of additives explained

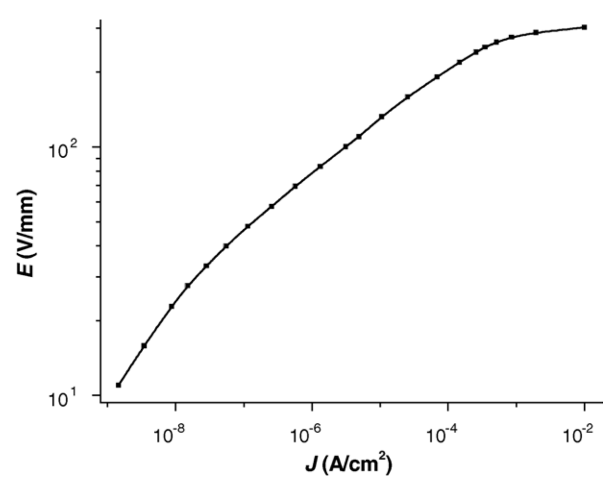

Fig. 2. Electric field vs. current density of the sample S1.

Table 1
Compositions of varistor powder mixtures

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
SnO_2 (mol%)	98.9	99.4	98.92	99.15	99.17	99.12	99.13	99.13	99.11	99.25
CoO (mol%)	1	0.5	1	0.75	0.75	0.75	0.75	0.75	0.75	0.65
Cr_2O_3 (mol%)	0.05	0.05	0.05	0.05	0.05	0.1	0.05	0.07	0.07	0.05
Nb_2O_5 (mol%)	0.05	0.05	0.03	0.05	0.03	0.03	0.07	0.05	0.07	0.05

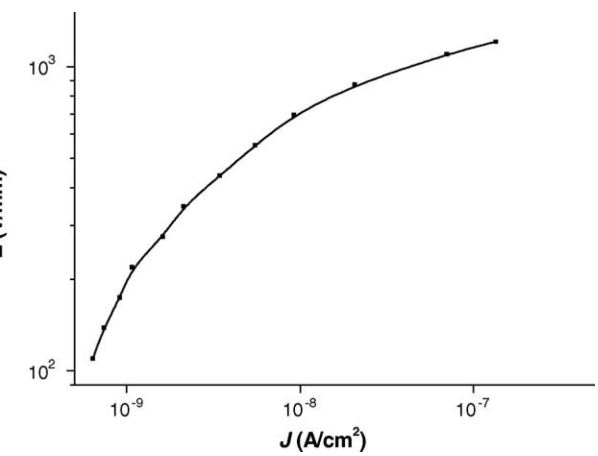

Fig. 3. Electric field vs. current density of the sample S6.

above, it is very important to control the ratio between concentrations of Cr and Nb, $c(\mathrm{Cr})/c(\mathrm{Nb})$. For example, S6 has the $c(\mathrm{Cr})/c(\mathrm{Nb}) = 3.33$ and shows high resistivity and high potential barrier. In the voltage range used in this study only the pre-breakdown region of the *E–J* curve was obtained (Fig. 3). Samples S3, S5 and S8 ($c(\mathrm{Cr})/c(\mathrm{Nb}) = 5/3$ or 7/5) were unstable and changes in electric field as a function of time were observed (Fig. 4). These changes are more pronounced for higher currents and can be explained by local heating of grain boundaries. At high currents the grain boundary region begins to heat, decreasing the resistivity of the grain boundaries. This results in decrease in electric field with time (Fig. 4). Because of instability, the results of electrical measurements are not reproducible and reliable. Unstable properties were also found in sample S2 which has the lowest concentration of Co.

E–J characteristics of the samples S4, S7, S9, and S10, which have $c(\mathrm{Cr})/c(\mathrm{Nb}) \leq 1$, are shown in Fig. 5. Samples S4, S9 and S10, which have $c(\mathrm{Cr})/c(\mathrm{Nb}) = 1$, reach the nonlinear part of the *E–J* curve for the almost the same values of electric field. This suggests the almost the same values of potential barrier height. In the case of $c(\mathrm{Cr})/c(\mathrm{Nb}) = 5/7$ (sample S7), lower values of α and shorter nonlinear part of the *E–J* curve were observed. The best characteristic was found in sample S4, and that is in accordance with the results of density measurements, while showed that sample S4 had the highest density. Sample S4 showed the following values of the electrical parameters: $\alpha = 35$, $E_C = 316$ V/mm and $j_L = 0.86\ \mu\mathrm{A/cm^2}$. It is emphasized that α was higher than 30 in the whole current interval from 10^{-7} to 10^{-2} A/cm^2. This sample has *E–J* characteristic that is stable with time (Fig. 6). For example, sample S4 showed the same *E–J* characteristics before and after the exposure to a current density of 27.4 mA/cm^2 for 30 min.

Some authors have reported similar or lower values of α,[18,19] but others have noted extremely high α values.[20] Generally, the high values of α were measured over a very short interval or as a gradient function in one point (1 mA/cm^2), so it can't be treated as the really good result. It is very difficult to find literature data about values of leakage current for SnO_2 varistor, or if this value is given it is too

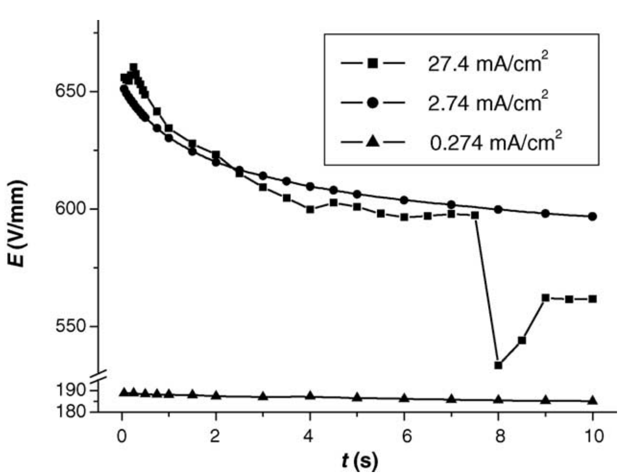

Fig. 4. Change of electric field as a function of time, for different values of current densities of the sample S8.

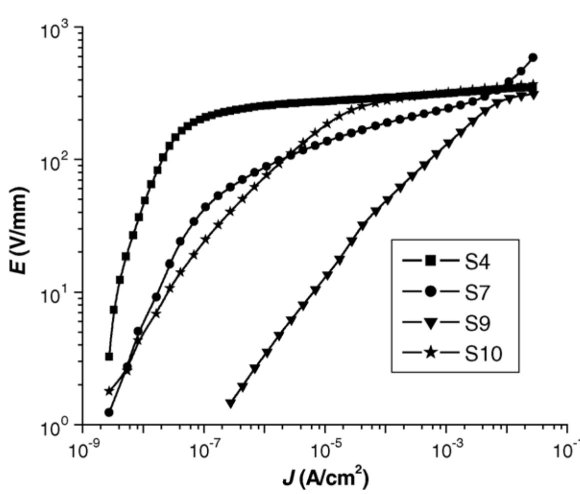

Fig. 5. Electric field vs. current density of the samples S4, S7, S9 and S10.

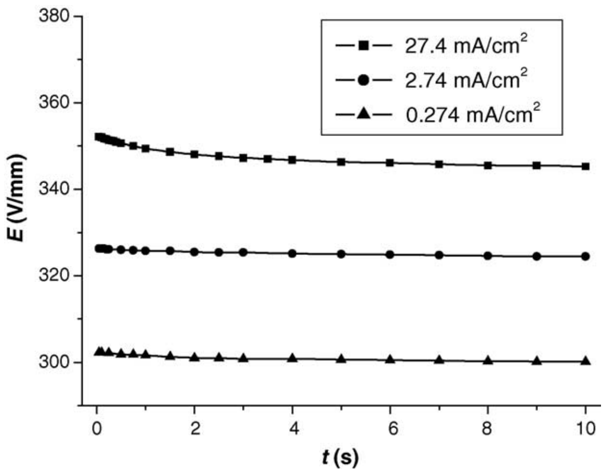

Fig. 6. Change of electric field as a function of time, for different values of current densities of the sample S4.

high (for example $j_L > 100\ \mu A/cm^2$) to be acceptible.[21] Our sample S4 showed a sufficiently low leakage current and a sufficiently high nonlinearity coefficient to satisfy the well-known criteria for good varistors ($j_L < 1\ \mu A/cm^2$, $\alpha > 30$).[4]

According to our previous investigation Nb showed homogeneous distribution through the SnO_2 grains. Co was incorporated in SnO_2 grains but also segregated to the grain boundary region. Cr is located mostly at grain boundaries.[16] This distribution could be most easily achieved using a chemical preparation method. Homogeneous distribution of dopants and uniform grain size can be obtained using Pechini method,[12] but unfortunately this complicated method is not convenient for commercial applications. The method of evaporation and decomposition of solutions and suspensions used in our work is a simplified chemical method that enables preparation of SnO_2 varistors with excellent electrical properties such as S4.

4. Conclusion

Evaporation and decomposition of solutions and suspensions was successfully applied to produce SnO_2 based varistors. The composition of the varistors was optimized based on results of electrical measurements. The best samples showed excellent electrical properties, nonlinearity coefficient higher than 30 in wide interval of currents (10^{-7} to 10^{-2} A/cm^2), low leakage currents of 0.86 $\mu A/cm^2$, and significant stability of the *E–I* characteristics.

Acknowledgements

This work was financially supported by FAPESP, Brazil, through the project number 99/06470-0, and by MNZŽS of Serbia through the projects numbers 1832 and 1603.

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