RECOVERY OF THE NON-OHMIC PROPERTIES OF DEGRADED HIGH VOLTAGE COMMERCIAL ZnO-BASED VARISTOR.

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Abstract

The purpose of this work is to evaluate two different methodologies to re-establish non-ohmic properties of high voltage commercial ZnO based varistors after degradation with long duration (2000 ms) and short duration (8/20 μs) pulses. The main procedure is based on submit ZnO-based varistor devices at different thermal treatments in oxygen enriched atmosphere. The thermal treatment at 900°C for 2 hours with oxygen flow of 15 L/h showed h better non-ohmic electrical properties when compared to the standard samples.

Keywords: E. Varistors, C. Electrical properties, B. Electron microscopy.

I. INTRODUCTION

ZnO varistor is a polycrystalline ceramic consisting of a huge number of individual grain boundaries. The electronic conduction mechanism in this material is controlled by the presence of Schottky barriers existing in the grain-boundary region[1]. The varistor has been exposed to different types of stresses such as normal operating voltage, transient, switching and lightning over voltages. Depending on the intensity and frequency of the pulses the developed stress may damage the varistor. The degradation of non-ohmic properties is mainly accompanied by an increase in leakage current, a decrease of barrier heights ϕ and the chemical point defects near the grain boundaries which is prejudicial for the operation of surge arresters devices[2]. The degradation of these barriers has been extensively studied[3-4]. In the one hand, K. Eda[5] and M. A. Ramírez et al [6] report two typical failures: cracking and puncture. On the other hand, Lengauer et al [7] observed that the pulses of high current pulses and short duration (fews µs) lead to cracking failure. An absorbed layer of bismuth with a thickness of about 5 Å in a ZnO-based varistor is necessary to create potential barriers at the grain boundaries. The height of these potential barriers largely depends on the excess of oxygen present at the interface between grains in ZnO varistors[8].

M. R Santos *et al* [9] showed that the electrical properties are strong affected by the atmosphere, due to the oxidizing mechanism at the grain boundary. P. R. Bueno *et al* [10]observed that the thermal treatment in a N_2-rich atmosphere causes a decrease, mainly in the surface states (N_{IS}) of the double-Schottky barrier and in potential barrier height values, while thermal treatment in an O_2-rich atmosphere causes a significant increase in the (N_d) and, particularly, in the (N_{IS}) states in a thinner region of the grain boundary. Such approach suggests that the thermal treatment changes mainly the electronic states of the grain boundary region[11]. Therefore, the physical origin of the interfacial states is not an intrinsic effect caused by lattice mismatch at the boundary, but an extrinsic one resulting from metal atoms precipitated at the grain boundaries[12]. In previous study Ramírez *et al* [6] showed no phase changes for the failure samples and that the main cause of degradation is due to the oxygen deficiency in the grain boundary. Having in mind that few studies relate the recovering of commercial ZnO varistors, the main purpose of this work is to evaluate the possibility of recovering the non-ohmic electrical properties of commercial ZnO varistor after degradation with two different pulses (short and larger pulses).

II. EXPERIMENTAL PROCEDURE

After performing the degradation of commercial ZnO-based varistor by applying large pulse (2000 ms) and short pulse (8/20 μs) it was studied a methodology to recover the non-ohmic electrical properties. In order to recover the ZnO varistors properties, thermal treatments was performed upon two group of samples: (1) a selected piece of the pellet, free of cracks, puncture and defects having nonlinear coefficient $\alpha = 17.5$ (standard sample free of pulses has a nonlinear coefficient of 44.9); (2) re-sintered samples from the milled powders with $\alpha = 13.2$.

In methodology (1) the samples were calcinated at three different temperatures (800, 900 and 1280°C) for 2 h using enriched oxygen flow atmospheres (5, 10 and 15 L/h) and static air. In methodology (2) a complete re-processing of the ceramics is necessary, involving crushing and milling. For the recovered varistors using the method 2 is necessary to control the surface area and the milling time. It is observed that 2 hours of milling time allows to obtain appropriate particle size to perform the ceramic conformation process. In methodology (2) the samples were calcinated at four different temperatures (800, 900, 1280 and 1400°C) for 2 h using enriched oxygen flow atmospheres (10 and 15 L/h).

The phase formation was evaluated by X-ray diffraction (RIGAKU 2000). For microstructural characterization, the samples were polished, chemical etched and analyzed in a scanning electron microscopy combined with EDS analysis (TOPCOM SM-300). The mean grain sizes were determined by the intercept method. For electrical properties, silver electrodes with area of 0.496 cm^2 were deposited on both surfaces of the sintered pellets. Current–voltage measurements were taken using a high voltage unit (KEITHLEY Model 237), while impedance spectroscopy were taken using a frequency response analyzer (HP 4194 A) at frequencies ranging from 100 Hz to 15 MHz, with an amplitude voltage of 1 V.

III. RESULTS AND DISCUSSION

Fig 1a shows the XRD data obtained by the varistors recovered from method 1 at 900°C for 2 hours in enriched oxygen flow (10 L/h). The main observed phases were (wurtzita - ZnO), (α-β Bi_2O_3) and ($Zn_2Sb_7O_{12}$ spinels) which are the phases of the varistor no degraded. The varistor recovered from the method 2 leads to the same phases (not shown in the article). S. J So *et al* [13] studied the degradation characteristics in accelerated DC test at 115°C when the ZnO varistors samples were sintered in different atmospheres: oxygen, air, nitrogen and argon. The obtained result indicates that sintering in oxygen atmosphere not only maintains the nonlinear characteristic but also improves the electrical stability, without formation of different phases as the typical encountered in ZnO varistors.

Fig 2 shows the SEM/EDS photography for the sample treated at 900°C for 2 hours in an enriched oxygen flow (10 L/h). It can be verified that the sample presents a dense and uniform microstructure. EDS analysis shows that ZnO forms solid solution with Co and Mn while $Zn_7Sb_{12}O_4$ spinels forms solid solution with Cr, Mn and Co dopants. From the obtained results it can be observed that the thermal treatment in enriched oxygen allows to recover the oxygen species lost during the degradation process.

Fig 3a shows the influence of oxygen flow on the electrical properties of the varistors thermal treated at 900°C for 2 hours by the method 1. The electrical properties such as nonlinear coefficient α, breakdown field E_r and barrier voltage V_b increase and the leakage current decreases when the samples were treated in enriched oxygen flow atmosphere (Table 1). These results confirm that the electrical properties are sensible to the oxygen species located on the grain boundary. The maximum nonlinear coefficient value $\alpha = 52.5$ was obtained for the thermal treatment at 900°C with oxygen flow of 15 L/h and is higher when compared to the standard sample. The thermal treatment in an enriched oxygen atmosphere is useful in the fabrication process allowing the prolongation of the varistor util life. Besides that, other consequence is to re-establish the electrical properties of the degraded varistors due to adsorption of oxygen species at the grain boundaries after thermal treatment in oxygen atmosphere.

Fig 3b shows the dependence of applied electric field as a function of current density at different temperatures. It was observed that an increase in the temperature leads to decrease the electrical properties due to the evaporation of bismuth oxide phase. Several authors verified the relation between the thermal treatment and the nonlinear coefficient. They observed that the nonlinear coefficient decreases close to 700°C due to phase transformation of β,δ Bi_2O_3 in γ Bi_2O_3, which is deleterious for electrical properties. This transformation starts at 600°C and after that at 800°C the inverse effect occurs (γ Bi_2O_3 in β,δ Bi_2O_3) until 1200°C. This result is only valid for varistors free of degradation. Previous report has suggested that the varistor characteristics are related to the particular crystalline form that the Bi_2O_3 takes on with oxygen at the grain boundary surface[8]. One of the fastest oxygen-ion conductors known, δ-Bi_2O_3, which is located at the grain boundary region, is essential to obtain a high degree of nonlinear behavior. The role of bismuth as the ‘‘grain boundary activator’’ is to avoid the excess of oxygen to the grain boundaries. The electrical properties of the varistors treated at the same temperature with different oxygen flows indicate that the oxygen is absorbed in the grain boundary and is responsible for the formation of the potential barriers. The samples treated with lower oxygen flow leads to a decrease in the electrical properties. Sonder *et al* [14] showed similar result in free degraded samples. They observed that the change in the electrical properties with the temperature and atmosphere utilized occurred (T<500°C) producing a short-circuiting surface layer that penetrated only a short distance into the varistors from the microcracks and interconnected pores. The breakdown voltage increased as function of treatment time and temperature upon reoxidation at (800°C).

The varistors recovered by the method 2 allow the re-establish of electrical properties at 900°C for 2 hours using enriched oxygen flow ranging from 10 to 15 L/h (Table 2). Comparing the re-establish for the varistor heat treated at 800°C (methods 1 and 2) it can be concluded that the lower grain size and the high porosity presented increase the breakdown voltage due to the increase in the number of effective barriers.

IV. CONCLUSIONS

The methodology proposed showed efficiency to re-establish the electrical properties of ZnO varistor degraded with pulses of high tension. The varistors free of macroscopic failure present better properties when compared with the standard sample after thermal treatment at 900°C with oxygen flow of 15 L/h. For this process the oxygen species adsorbed in the grain boundary controls the potential barrier. The ceramics with nonlinear characteristics that exhibits degradation can have the electrical properties re-established. Meanwhile, the re-establish of varistors which present failures (cracking and puncture) is not completely recovered. From the technological point of view the thermal treatment at 900°C allows to re-establish the electrical properties of ZnO varistors once the non-ohmic properties are reached at low temperatures when compared to the conventional process (1300°C).

ACKNOWLEGMENTS

Mastery in Engineering of Materials and Process, DIME, Faculty of Mines and Academic Direction of the National University of Colombia-Sede Medellín by the financial support of this research and the facilities offered by CMDMC-LIEC at the Chemistry Institute-UNESP and Department of Chemistry-UFSCar.

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FIGURE AND TABLES CAPTIONS

Fig 1. X ray data obtained from the varistor recovered with oxygen flow of 10 L/h at 900°C (method 1).

Fig 2. SEM/EDS obtained from the varistor recovered with oxygen flow of 10 L/h at 900°C (method 1).

Fig 3a. E vs J for the varistors thermal treated at 900°C in different oxygen flows (method 1).

Fig 3b. E vs J for samples thermal treated at different temperatures with oxygen flow of 10 L/h.

Table 1. Nonlinear coefficient value (α), breakdown voltage (E_r), leakage current (i_f), mean grain size (d), barrier voltage per grain (v_b) for the varistor degraded and recovered by the method 1.

Table 2. Nonlinear coefficient value (α), breakdown voltage (E_r), leakage current (i_f), mean grain size (d), barrier voltage per grain (v_b) for the varistor degraded and recovered by the method 2.

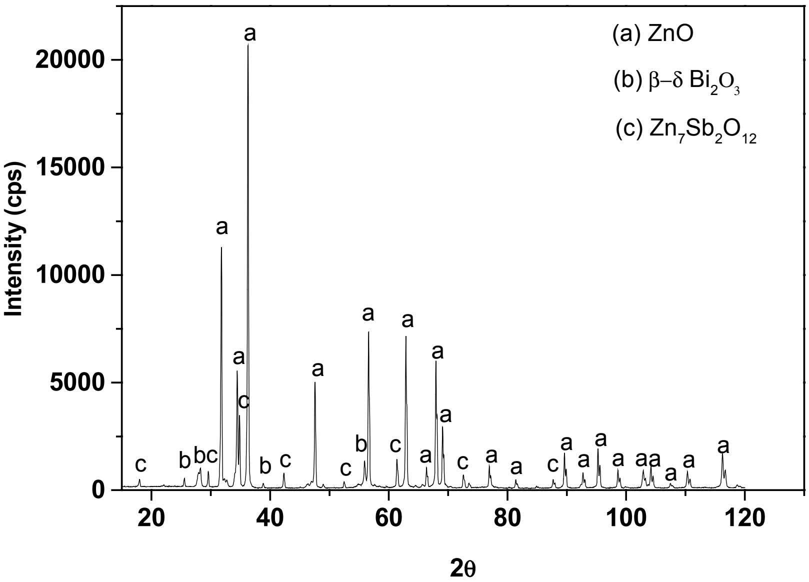

Fig 1. M. A Ramírez, A. Z Simões , M. A Márquez, P. R Bueno, M. O Orlandi, E. Longo, J. A Varela.

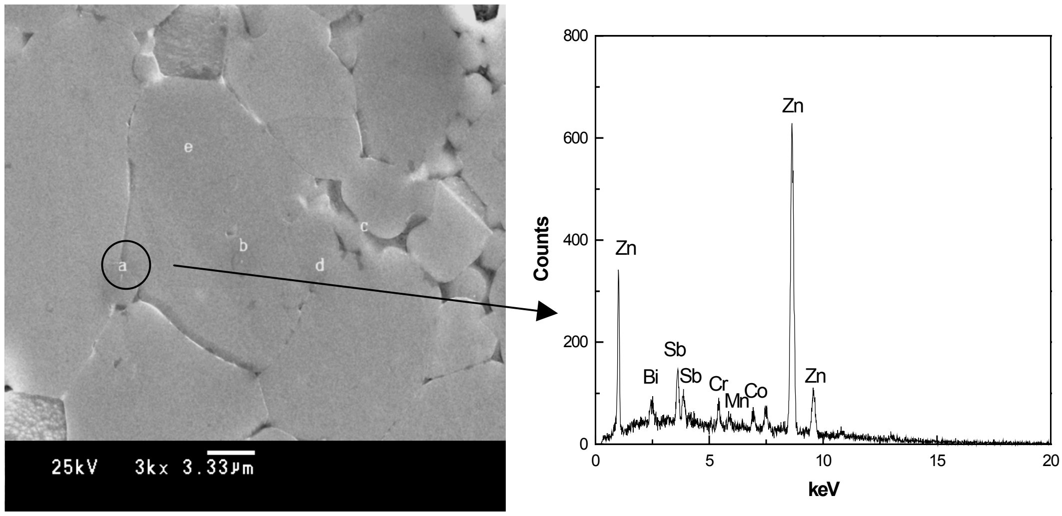

Fig 2. M. A Ramírez, A. Z Simões , M. A Márquez, P. R Bueno, M. O Orlandi, E. Longo, J. A Varela.

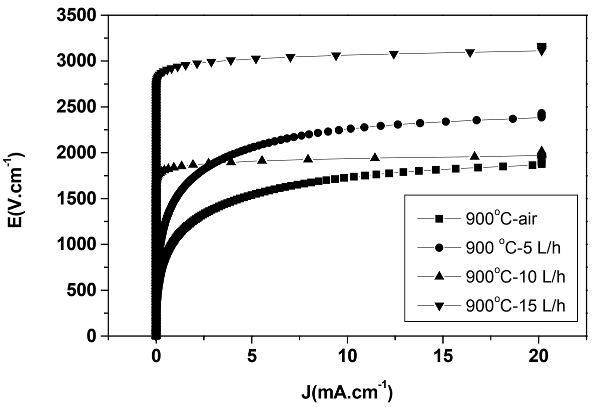

Fig 3a. M. A Ramírez, A. Z Simões , M. A Márquez, P. R Bueno, M. O Orlandi, E. Longo, J. A Varela.

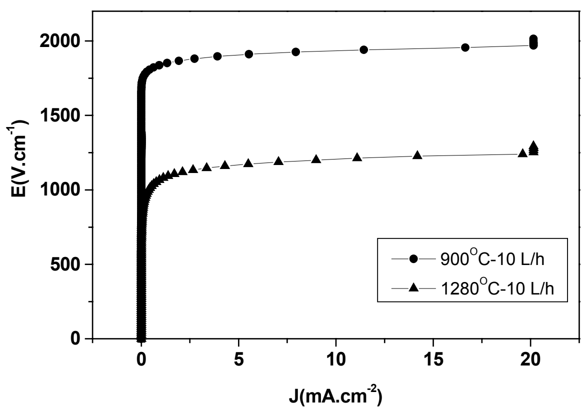

Fig 3b. M. A Ramírez, A. Z Simões , M. A Márquez, P. R Bueno, M. O Orlandi, E. Longo, J. A Varela.

Table 1. M. A Ramírez, A. Z Simões , M. A Márquez, P. R Bueno, M. O Orlandi, E. Longo, J. A Varela.

Degraded Samples	**Nonlinear coefficient (α)**	**Breakdown field (Er) (V/cm)**	**Leakage current (if) (mA)**	**Grain size (μm)**	**Barrier voltage (V)**	**Height barrier ϕ_b (V)**
	17.2	1893	6.542	10.1	1.91	
800-10	2.71	1020	200	10.66	1.02	
800-15	34.30	2368	21.55	11.00	2.60	
900-air	4.70	1063	150.7	10.20	1.08	2.79
900-5	5.60	1492	131.6	10.50	1.57	2.85
900-10	39.80	1840	0.0136	12.56	2.31	2.95
900-15	52.50	2939	0.0227	10.30	3.03	3.49
1280-10	19.10	1080	12.523	16.67	1.80	

Table 2. M. A Ramírez, A. Z Simões , M. A Márquez, P. R Bueno, M. O Orlandi, E. Longo, J. A Varela.

Degraded Samples	**Nonlinear Coefficient (α)**	**Breakdown field Er (V/cm)**	**Leakage current if (mA)**	**Grain size (μm)**	**Barrier voltage (V)**	**Height barrier ϕ_b (V)**
	13.2	2088	28.16	9.71	2.03	
800-10	4	2508	220.75	1.8	0.45	
900-10	25.8	6064	35.65	6.48	3.92	2.22
1280-10	18.5	1477	39.88	11.24	1.66	1.97
1400-10	3.5	152	215.41	25.63	0.39	