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Importance of oxygen atmosphere to recover the ZnO-based varistors properties

M. A. Ramírez · A. Z. Simões · P. R. Bueno · M. A. Márquez · M. O. Orlandi · J. A. Varela

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Abstract A methodology to recover the non-ohmic properties of ZnO based varistors after degradation with long and short duration pulses was proposed in this work. The basic idea consists in submitt the degraded ceramics at different temperatures and oxygen flows. Thermal treatment at 900 °C for 2 h with oxygen flow of 15 l/h allowed to obtain better non-linear coefficient (α = 52.5) compared to the standard sample. Rietveld refinement showed that with the thermal treatment, the oxygen species and the β-Bi_2O_3 phase, lost in the degradation process, are recovered in the grain boundary.

Introduction

ZnO varistor is a polycrystalline ceramic in which the electronic conduction mechanism is controlled by the presence of Schottky barriers existing in the grain-boundary region [1]. Depending on the intensity and frequency of the pulses and the different types of stresses such as normal operating voltage, transient, switching and lightning over voltages the varistor properties may be damaged. The degradation of non-ohmic properties is mainly accompanied by an increase in leakage current, a decrease of barrier height ϕ and the concentration of point defects near the grain boundaries which is prejudicial for the operation of surge arrester devices [2]. The degradation of these barriers has been extensively studied [3–4]. In the one hand, Eda [5] and Ramírez et al. [6] report two typical failures: cracking and puncture. On the other hand, Lengauer et al. [7] observed that the short duration pulses (fews μs) leads to a high current which favours a 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].

Santos et al. [9] showed that the atmosphere, due to the oxidizing mechanism at the grain boundary, strong affects the electrical properties. Bueno et al. [10] observed that 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. Otherwise thermal treatment in an O_2-rich atmosphere causes a significant increase in the N_d (positive space charge density in the depleted region) 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 a previous study Ramírez et al. [6] showed no phase

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M. A. Ramírez (✉) · M. A. Márquez
Faculty of Mines, National University of Colombia,
Medellín, Bloque M1-401, Colombia
e-mail: miganr@kenter.com

A. Z. Simões · P. R. Bueno · J. A. Varela · M. A. Ramírez
Department of Physics and Chemistry, UNESP,
Araraquara, S.P., Brazil

M. O. Orlandi
Department of Chemistry, UFSCar, São Carlos, S.P., Brazil

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 to 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 types of pulses (short and larger pulses).

Experimental procedure

After performing the degradation of commercial ZnO-based varistor (P1-standard) by applying long pulse (2000 µs rectangular wave form—P3) and short pulse (8/20 µs—P6) it was studied a methodology to recover (P6R) the non-ohmic electrical properties. It is reasonable to mention that all investigated samples are oxygen defficient due to the degradation process. Therefore, in order to recover the ZnO varistors properties, thermal treatments at different temperatures and oxygen flows were performed as follows: a selected piece of the pellet, free of cracks, puncture and defects was random choosen. The samples were heat treated at three different temperatures (800, 900 and 1280 °C) for 2 h using enriched oxygen flows atmospheres (5, 10 and 15 l/h) and static air with a heating and cooling rate of 5 °C/min. Phase analysis were evaluated by X-ray diffraction data (RIGAKU 20–2000) diffractometer under the following experimental condition: 50 kV, 150 mA, $20° \le 2\theta \le 120°$, $\Delta 2\theta = 0.02°$, $\lambda \mathrm{CuK}_\alpha$ monocromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 2 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-9807 [13]. The profile function used was the pseudo-Voigt. In order to quatify the amount of oxygen in different regions of the samples Wavelenght Dispersive X-ray Spectroscopy (WDX) was employed. The samples were polished with a diamond paste until a flat surface is reached. In_2O_3 standard sample was used as oxygen standard. The measurements were performed in a SEM (Zeiss, DSM 940 A) with voltage acceleration of 30 KV and emission current of 80 μA (the change in the current during the measurement was less than 1%). At least 10 measurements were collected in each region of interest and the data were treated in a statistical way. The mean grain sizes were determined by the intercept method [14]. For electrical properties, silver electrodes with area of 0.496 cm^2 were deposited on both surfaces of the sintered pellets. The electrical properties such as non-linear coefficient α, breakdown electric field E_b, barrier voltage per grain V_{gb} were calculated from E vs. J using current–voltage measurements using a high voltage unit (KEITHLEY Model 237), while impedance spectroscopy was 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. The barrier height ϕ_b was calculate from the results of impedance spectroscopy. The presence of the back-to-back Schottky-type barrier is inferred from the voltage dependence of capacitance. Capacitance calculations were made of the high frequency intercept associated with high frequency relaxation in the complex capacitance plane [15]. The applied voltage dependence of capacitance can be approximated using the Mukae approach [16] as

$$\left(\frac{1}{C}-\frac{1}{2C_0}\right)^2=\frac{2}{q\varepsilon_r\varepsilon_0 N_d}(\phi_b+V),$$

where q is the electron or elementary charge, ϵ_r is the relative permittivity, ϵ_0 is the permittivity of free space, N_d is the positive space charge density in the depleted region (free electron density) and ϕ_b is the barrier height of the system. C_0 and C are the capacitance per unit area of a grain boundary biased, respectively, with zero and V volts.

Results and discussion

Figure 1 shows the XRD for the samples thermal treated at (a) 800 °C, (b) 900 °C and (c) 1280 °C. At 800 °C and 900 °C the typical varistor phases were observed. The main observed phases were (wurtzita—ZnO), (β-δ Bi_2O_3) and ($Zn_2Sb_7O_{12}$ spinels) which are the phases of the no degraded varistor. However, it

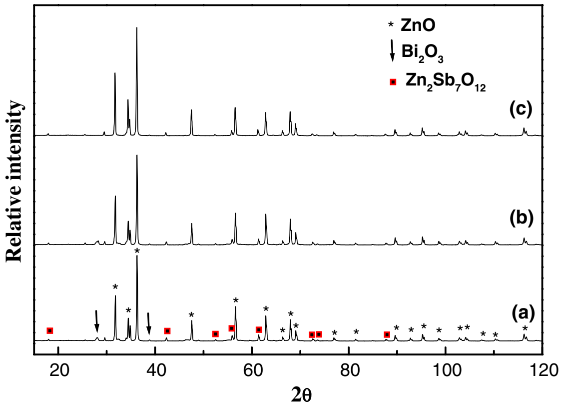

Fig. 1 XRD data obtained from the varistor recovered at different temperatures: (a) 800 °C, (b) 900 °C and (c) 1280 °C with oxygen flow of 10 l/h

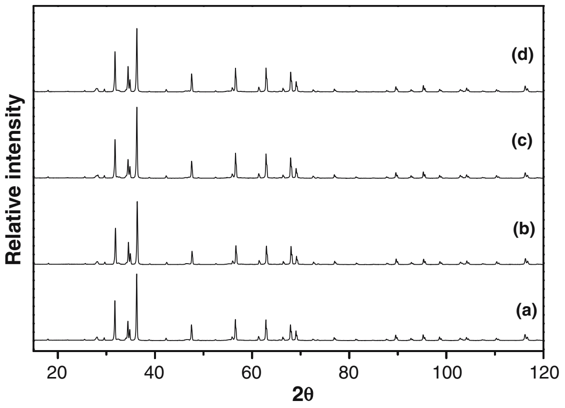

Fig. 2 XRD data obtained from the varistor recovered at 900 °C 2 h for different oxygen flows: (a) air, (b) 5 l/h, (c) 10 l/h and (d) 15 l/h

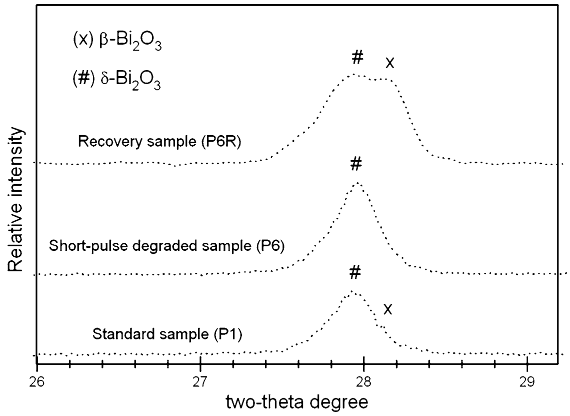

Fig. 3 Main peak of *β*-*δ* Bi_2O_3 phase for different samples: (a) Standart (P1), (b) Degraded (P6) and (c) Recovered (P6R)

is evident that at 1280 °C a strong peak related to the evaporation of *β*-*δ* Bi_2O_3 is not observed. This thin bismuth oxide layer is necessary to create the potential barrier improving the varistor properties. The role of Bi as the "grain boundary activator" is limited to supplying excess oxygen to the grain boundaries. Some authors also state that non-ohmic properties can be enhanced using "highly oxygenated" Bi_2O_3 as a starting material [12]. Figure 2 presents the X-ray data for the samples thermal treated at 900 °C for different oxygen flows. Besides the main phases in the standard sample, no additional phases were found when the varistors were thermal treated in oxygen atmosphere leading to adsorption in the grain boundary and the formation of the potential barriers. From the obtained X-ray data, it can be observed that all paterns are identical indicating no crystal phase changes with the increase of oxygen flow at a constant temperature. So et al. [17] 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 authors observed that sintering in oxygen atmosphere not only keep the non-linear characteristic but also improves the electrical stability, without formation of different phases as the typical encountered in ZnO varistors. Figure 3 illustrates the influence of the degradation process on the *β*-*δ* Bi_2O_3 phase ($2\theta = 28.1°$) present on varistor system. In the standard sample (P1) two phases are observed *β*-Bi_2O_3 and *δ*-Bi_2O_3. After degradation the *β*-Bi_2O_3 phase disappears and crystallizes the *δ*-Bi_2O_3 phase. In the recovered sample, there is the re-crystallization of the *β*-Bi_2O_3 phase while the *δ*-Bi_2O_3 phase remains constant. Consequently, one can mention that the recovery is important to re-establish the phases lost during the degradation process. In order to determine the influence of degradation and recovering process in the stress formed in the crystal it was necessary to perform Rietveld refinement. The following samples were studied: standard commercial sample (P1), degraded samples with short pulses (P6) and recovered sample (P6R) (Table 1). From Rietveld refinement two ZnO phases due compositional fluctuation are evident. One of these phases is more sensible to degradation according to the FWHM values. Gain of oxygen during the recovering process, the

Table 1 Rietveld refinement for samples P1 (standard), P3 and P6 (degraded) and P6R (recovered)

Sample	% Phase ZnO	Parameter *a* (Å)	Parameter *c* (Å)	Volume (Å^3)	FWHM (2*θ*)	*Atomic position of Zn^{+2} (Z)	**S$_{Occ}$ Zn^{+2}
P1	1 49.4	3.2545	5.2103	47.79	0.09382	0.3724	0.9521
	2 46.6	3.2508	5.2047	47.63	0.01526	0.3889	0.9144
P6	1 40.25	3.2556	5.2130	47.85	0.09638	0.3906	0.8706
	2 55.75	3.2508	5.2053	47.64	0.02186	0.3953	0.7885
P6R	96.0	3.2513	5.2051	47.65	0.04481	0.3703	1.0000

* Atomic position: Zn^{+2}: $x = 1/3$, $y = 2/3$, z = variable; O^{-2}: $x = 1/3$, $y = 2/3$, $z = 0$

**S_{Occ} Zn^{+2} is the occupation factor for the Zn^{+2} specie. In the ideal structure the values of S_{Occ} for Zn^{+2} and O^{-2} is equal 1.0000. In degraded samples the reduced form Zn^0 substitutes parts of Zn^{+2} generating equal parts of oxygen vacancies microstrain in crystal lattice tends to disappear in proportion that oxygen vacancies are suppressed. However, the stoichiometric ZnO crystal is not stable under hard work regime, which leads to the non-stoichiometric ZnO_x phase. These results can be demonstrated by oxygen occupation factor (S_{Occ}) analysis, which shows a decrease for the P6 sample. There is a clear indication that the stress produced during the degradation process leads to generation of oxygen vacancies, which are recovered during the thermal tretament in oxygen atmosphere reaching at maximum value of 1.0000.

Figure 4a show the SEM photography for the standard sample. The standard sample presents a typical ZnO varistor microstructure. The matrix is composed of grains with size of about 10 μm surrounded by small spynel grains (1 μm) which can be located intra grains or at grain-boundary region. SEM-EDS for degraded with short pulse (Fig 4b, c) and the recovered sample at 900 °C for 2 h in an enriched oxygen flow 15 l/h

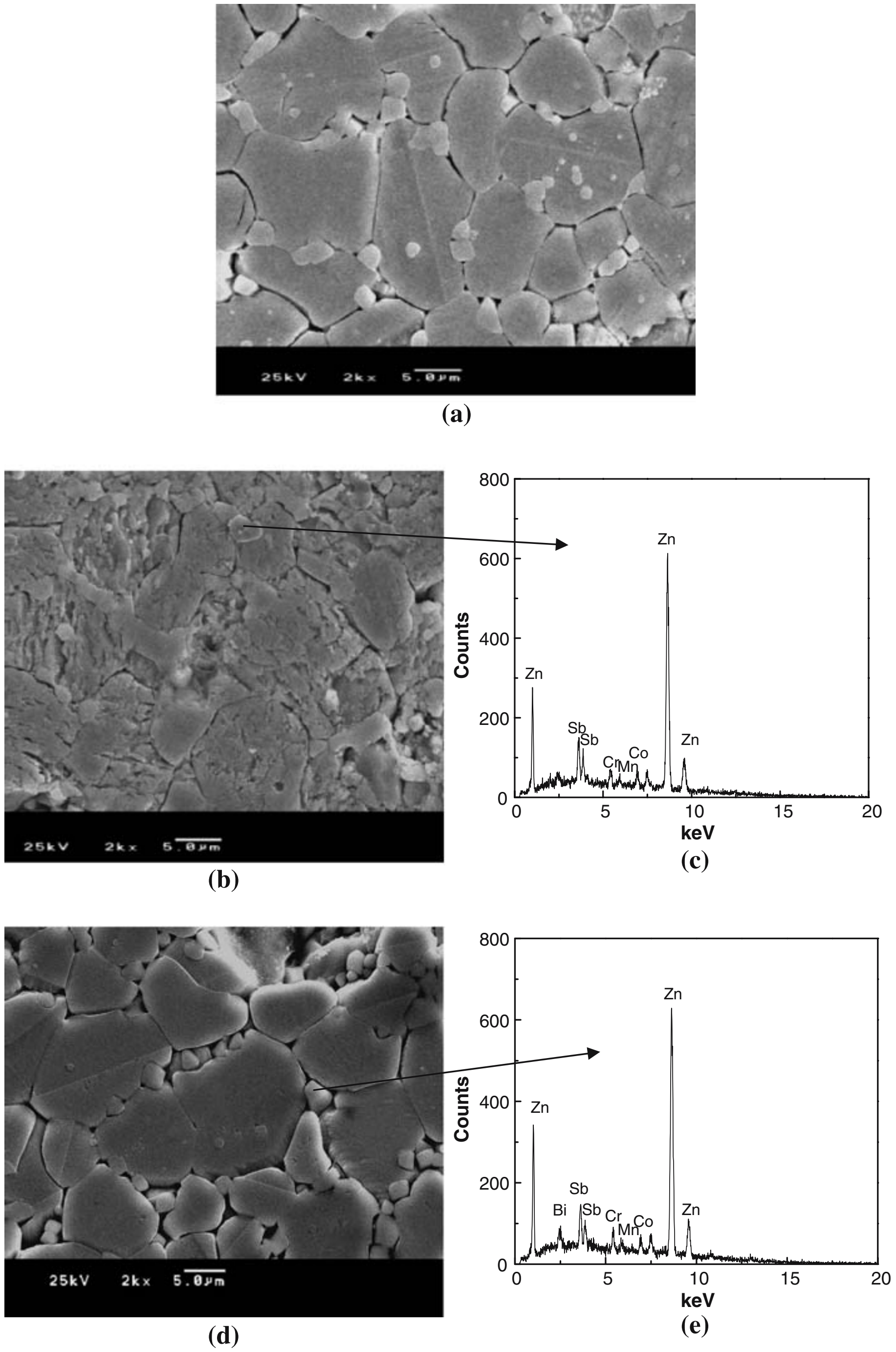

Fig. 4 (a) SEM for the standard sample. (b), (c) SEM/EDS for the degraded sample and (d), (e) SEM/EDS for the recovery sample at 900 °C with oxygen flow of 15 l/h

(Fig 4d, e). The stress caused by the degradation process affects the varistor microstructure inhibiting the visualization of some grain boundary area. The recovering process allows obtain a dense microstructure with morphology close to the standard sample. 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 EDS data a bismuth deficiency is clearly evident in the degraded samples probably due to the high tension pulses which increases the temperature close to the bismuth oxide volatilization (825 °C). When the sample was submitted to a thermal treatment at 800 °C in oxygen atmosphere, diffusional process was favoured because Bi_2O_3 forms a euthetic point with ZnO at 740 °C. In this way, Bi_2O_3 distributed along the sample contributes to the formation of effective barriers in the recovered sample. These results are in agreement with the XRD data. In order to evaluate the influence of recovering process it is necessary to control the amount of oxygen in the grain boundary where the varistor properties are predominant. From the obtained results, it can be observed that the thermal treatment in enriched oxygen allows recover the oxygen species lost during the degradation process (Table 2). The ZnO grains for the standard sample show higher amount of oxygen in the grain boundary supporting the model of Schottky barrier formation by adsorption of oxygen species at grain boundary. Otherwise, it was observed an oxygen deficiency at grain boundaries for the degraded samples. This observation is in agreement to what was proposed by Leite et al. [1] and Bueno et al. [10]. The main difference between the recovered and standard samples is the higher amount of oxygen absorbed in the grain boundary region for the recovered one.

Figure 5 shows the influence of oxygen flow on the electrical properties of the varistors thermal treated at 900 °C for 2 h. The *E* vs. *J* curve shows that the increase of oxygen flow leads to improvement in the electrical properties. A decrease in leakage current was noted for the samples thermal treated in enriched oxygen flow atmosphere indicating an increase in the barrier height (Table 3). These results confirm that the electrical properties are sensible to the oxygen species located on the grain boundary. The maximum non-linear 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 degraded sample ($\alpha = 13$). The thermal treatment in an enriched oxygen atmosphere is useful in the fabrication process allowing the prolongation of the varistor lifetime. Besides that, other consequence is the possibility to recover the electrical properties of the degraded varistors due to adsorption of oxygen species at the grain boundaries after thermal treatment in oxygen atmosphere.

Figure 6 shows the dependence of applied electric field as a function of current density at different temperatures. It was observed that an increase in temperature leads to decrease the electrical properties due to the evaporation of bismuth oxide. This phase acts as an effective barrier avoiding the electrons flow in the interface between grains. Several authors verified the relation between the thermal treatment and the non-linear coefficient. They observed that the non-linear 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.

Table 2 Oxygen content (with WDS) in different varistor regions for samples P1 (standard), P3 and P6 (degraded) and P6R (recovered)

Sample	Region analyses	Oxygen content (counts/second) ± 2.0
P1	Bulk	50.4
	Boundary	139.7
P3	Bulk	136.5
	Boundary	112.8
	Twin	122.3
P6	Bulk	91.6
	Boundary	72.0
6R	Bulk	60.5
	Boundary	195.3

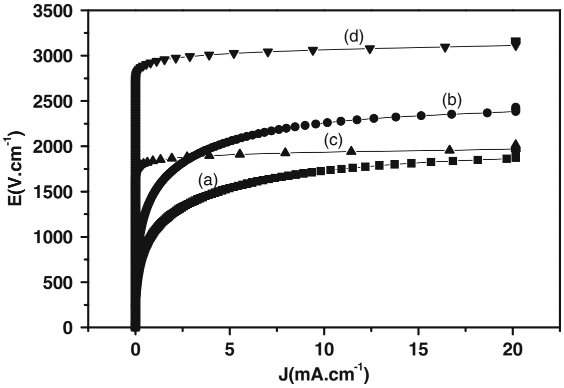

Fig. 5 Current density in dependence of applied eletric field for varistors thermal treated at 900 °C in different oxygen flows (a) air, (b) 5, (c) 10 and (d) 15 l/h

Table 3 Non-linear coefficient value (α), breakdown voltage (E_b), leakage current (I_l), means grain size (d), barrier voltage/grain (V_{gb}) for the degraded and recovered varistors

Thermal treatment	Oxygen flow (l/h)	Non-linear coefficient (α)	Breakdown field (E_b) (V/cm)	Leakage current (I_l) (μA)	Grain size (μm)	Barrier voltage (V_{gb})	Barrier height ϕ_b (eV)
Sample degraded		17.2	1893	6.542	10.1	1.91	
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	13.6	12.56	2.31	2.95
900	15	52.50	2939	22.7	10.30	3.03	3.49
1280	10	19.10	1080	1252	16.67	1.80	

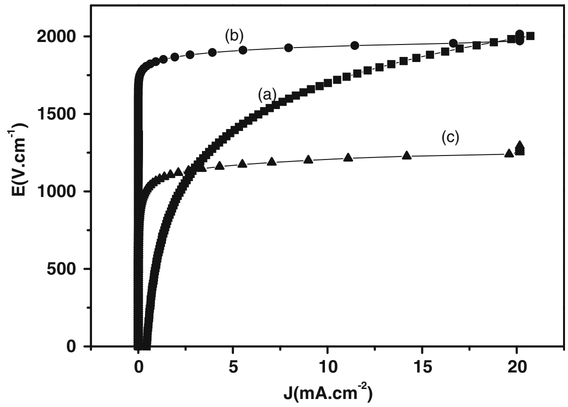

Fig. 6 Current density in dependence of applied eletric field for varistors thermal treated at different temperatures with oxygen flow of 15 l/h (a) 800 °C, (b) 900 °C and (c) 1280 °C

Previous report has suggested that the varistor characteristics are related to the particular crystalline form that the Bi_2O_3 possess 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 non-linear behavior. The electrical properties of the varistors treated at the same temperature with different oxygen flows indicate that the oxygen absorbed in the grain boundary 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. [18] showed similar result in free degraded samples. They observed that the change in the electrical properties with the temperature and atmosphere 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).

Conclusions

The present methodology showed efficiency to recover the electrical properties of ZnO varistor degraded with high-tension pulses. The recovered varistors presented better properties when compared to the standard sample after thermal treatment at 900 °C with oxygen flow of 15 l/h. The oxygen flow used during the recovering process supplies oxygen species, which absorbs in the grain boundary and control the potential barrier of the varistor. From the technological point of view, the thermal treatment at 900 °C allows the recovering of the electrical properties of ZnO varistors once the non-ohmic properties are reached at low temperatures when compared to the conventional process (1300 °C).

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