AIP Journal of Applied Physics

Barrier voltage deformation of ZnO varistors by current pulse

E. R. Leite, J. A. Varela, and E. Longo

Citation: Journal of Applied Physics **72**, 147 (1992); doi: 10.1063/1.352175
View online: http://dx.doi.org/10.1063/1.352175
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/72/1?ver=pdfcov
Published by the AIP Publishing

Barrier voltage deformation of ZnO varistors by current pulse

E. R. Leite
3M do Brasil, Dep. Produtos Eletricos e Telcom, Campinas, S. P., Brasil

J. A. Varela
I. Q. UNESP, Araraquara, S. P., Brasil

E. Longo
Dep. Quimica, UFSCar, S. Carlos, S. P., Brasil

(Received 30 September 1991; accepted for publication 16 March 1992)

The phenomenon of electrical degradation in ZnO varistors was studied by application of high-intensity current pulses. A wave shape of 8×20 μs and rectangular waves of 1 and 2 ms were used. The degradation was estimated by reference electric-field variation and by Schottky voltage barrier deformation. The results showed that current pulses reduce both the height and the width of the barrier voltage. It was also observed that the donor density N_d did not change but the surface states density N_s decreased with degradation.

I. INTRODUCTION

ZnO varistors are known for having a nonohmic behavior, low leakage current, and high-energy-absorption capacity. These characteristics allow these materials to be used as surge arresters; however, they can be degraded during use. A typical ZnO varistor microstructure includes semiconducting ZnO grains, Bi_2O_3-rich intergranular phases, and $Zn_7Sb_2O_{12}$ spinel phases. The barrier voltage is formed among several types of grain boundary where the most effective are the ZnO-ZnO homojunctions and Bi_2O_3 thin layer between ZnO grains.[1]

A coherent model to describe the conduction mechanism was proposed by Eda[2] in which Schottky-type barrier voltages are separated by an isolating film of finite width. The conduction mechanism through Schottky barriers could be due to thermionic emission from the ZnO grain conduction band to the isolating film conduction band. According to this model the current density J and electric field E are related by

$$J=J_0 \exp[-(\phi-\beta E^{1/2})/kT], \quad (1)$$

where J_0 is a constant, ϕ the barrier voltage height (eV), β a constant related to the barrier voltage width W, k is the Boltzman constant, and T is the absolute temperature (K).

The barrier voltage of ZnO varistors can be electrically, chemically, and thermally degraded during use, leading to the reduction of ϕ and consequently to the increase of leakage current, which could be catastrophic for surge arresters. The degradation of these barriers has been extensively studied[3–5] but the effect of high-intensity current pulses on the degradation is not well known. Researches in degradation due to pulses[6–10] do not explain the whole phenomenon that is of fundamental importance for ZnO varistor technology.

This work aims to study the effects of several current pulses with different intensities and shapes on the degradation of ZnO varistors. Barrier voltage height ϕ and width W variation of ZnO varistor were analyzed by thermal activation.

II. EXPERIMENTAL PROCEDURE

ZnO varistor samples of 22 mm height and 45 mm diameter were obtained by conventional processing, and their compositions are given in Table I.

A current pulse generator (Haefely model E) of 50 kJ for a short width of 20 μs, and rising slope equal to 8 μs, i.e., an impulse of 8×20 μs, and a rectangular current pulse Haefely generator for a long-duration shot of 1 ms and amplitude of 75 A (1 ms/75 A) and 2 ms and amplitude of 150 A (2 ms/150 A), as shown schematically in Fig. 1, were used in this work. The degradation was estimated by measuring the reference electric field at 0.05 mA/cm^2 ($E_{0.05}$) as a function of the number of applied pulses and of the pulses energy. The $E_{0.05}$ was measured before and after each pulse cycle in dc bias under forward biasing voltage. A cycle was defined by five applied pulses and between each cycle enough time was allowed to cool down the sample to room temperature.

To verify the effect of current pulses on the barrier voltage, ϕ and W were determined before and after four cycles. To determine these parameters it was assumed that: (a) the barrier voltage is of Schottky type separated by an isolating film; (b) the conduction mechanism is by thermionic emission.

In the thermionic emission model, Eq. (1), the β constant is given by

$$\beta=[(1/nW)(2e^3/4\pi\epsilon_0\epsilon_r)]^{1/2}, \quad (2)$$

where n is the number of ZnO grains in series in a sample of width L (cm), W is the barrier voltage width (nm), e is the electron charge, and ϵ_0 and ϵ_r are the electric permittivities of the vacuum and material, respectively. Defining G as the average ZnO grain sizes,

TABLE I. Composition of ZnO varistors in mol %.

ZnO	Bi_2O_3	CoO	MnO_2	Sb_2O_3	Cr_2O_3
97.0	1.0	0.50	0.50	1.5	0.50

 0021-8979/92/130147-04$04.00

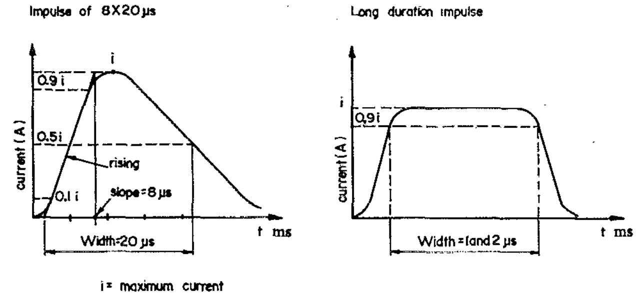

FIG. 1. Schematic representation of current pulses used in this work.

$$n = L/G, \tag{3}$$

G values were determined by scanning electron microscopy (SEM) using the line intercept method, obtaining 13 ± 4 μm. A dispersive energy unit (EDS) attached to the SEM was used to analyze the distribution of dopants in the ZnO varistors microstructure.

By plotting $\ln J$ vs $E^{1/2}$ in Eq. (1) a straight line is obtained where the slope is β/kT. Therefore the barrier voltage width W can be determined by Eq. (2). The plot of $\ln J$ vs $1/T$ of Eq. (1) is a straight line with a slope equal to $(\phi - \beta E^{1/2})/k$. By using β values, ϕ is determined. Both ϕ and W values were carried out in a range of temperature from 60 to 100 °C in a dc biasing test.

III. RESULTS AND DISCUSSIONS

A. Variation of reference electric field ($E_{0.05}$)

The variation of $E_{0.05}$ with the number of 500 A/cm^2 applied pulses of 8×20 μs is shown in Fig. 2. It is observed in this figure that there is a gradual reduction of $E_{0.05}$ indicating that the leakage current is increasing.[11] The discharge voltage at 500 A/cm^2 (E_{500}) for several applied pulses is shown in Table II. It is observed in this table that there is a little variation of E_{500} after four cycles of applied pulses (about 2%). By analyzing the results of Fig. 2 and Table II it is seen that the current pulses are modifying the

TABLE II. Variation of E_{500} with the shorts of 8×20 μs of 500 A/cm^2.

E_{500} before (V/cm)	E_{500} after one cycle (V/cm)	E_{500} after four cycles (V/cm)	ΔE_{500} max (%)
2830	2810	2773	2

barrier voltage localized at grain boundary leading to its degradation, but with negligible modification in the electric properties of ZnO grains.

Figure 3 shows the variation of $E_{0.05}$ with the pulse energy, which is estimated by

$$E = \int_0^t i^2\, dt, \tag{4}$$

where E is the pulse energy per resistence unit in A^2 s, i is the electric current, and t is the time (s). Rectangular current pulses of 1 ms/75 A and 2 ms/150 A and impulses of 8×20 μs were used.

Analyzing Fig. 3 a linear behavior of E_a/E_b with the ln of pulses energy can be seen (E_a is the $E_{0.05}$ after the applied cycles and E_b is the $E_{0.05}$ before the applied cycles). It is also observed in Fig. 3 that there is a limiting energy E_0 for degradation to start. Pulses with energy lower than that limit value do not cause degradation in the varistor. Thus, from Fig. 3, the empirical equation

$$E_a/E_b = 1 - p\ln(E/E_0) \tag{5}$$

can be proposed, where p is a constant that can be determined from the slope of the experimental curve of Fig. 3. The value of p obtained in this case (0.044) is related to degradation mechanisms and is a good parameter to verify the varistor degradation resistance.

B. Barrier voltage degradation

In order to verify the current pulse effect on the barrier voltage ϕ and W were determined in samples before and after four cycles of shorts of 8×20 μs of 250 and 500 A/cm^2. Table III presents data for ϕ and W before and

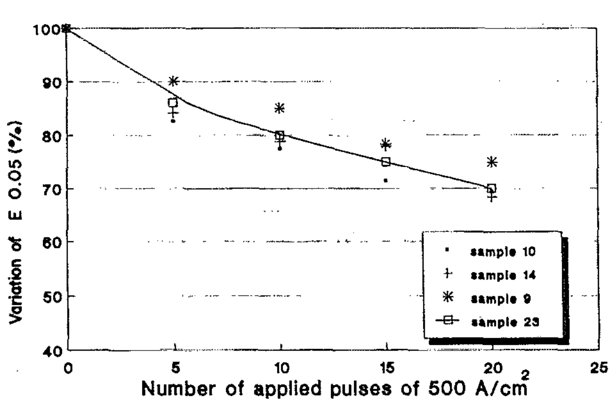

FIG. 2. Variation of $E_{0.05}$ with the number of 500 A/cm^2 applied pulses of 8×20 μs.

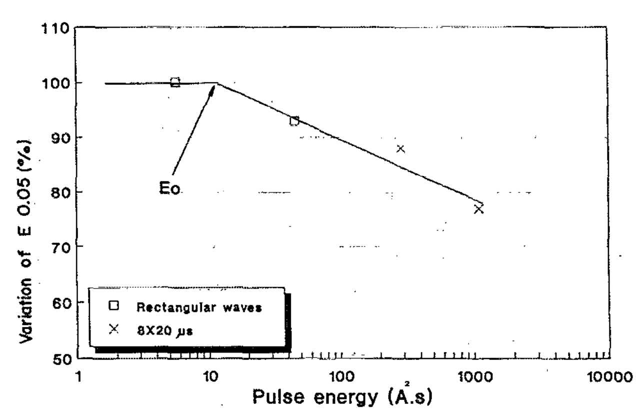

FIG. 3. Variation of $E_{0.05}$ with the pulse energy for applied pulses of 8×20 μs and rectangular pulses.

TABLE III. Values of ϕ and W before and after application of 20 current pulses.

	ϕ (eV)	W (nm)
Before applied pulses	0.40 ± 0.02	13 ± 1.5
After 20 pulses of 250 A/cm^2	0.40 ± 0.01	10.5 ± 0.9
After 20 pulses of 500 A/cm^2	0.34	7.9

after degradation. The value of ϕ measured is smaller than usually obtained[12] and it should be due to the low concentration of MnO_2 in the composition (listed in Table I). Pianaro[13] shows that the nonohmic characteristic of ZnO varistors increases with the increase of MnO_2 concentration in a six-component composition. This table shows that ϕ and W are deformed by current pulses, leading to degradation of the ZnO varistor. It is also observed in this table that W is more sensitive to degradation. From this fact it appears that the barrier voltage is deformed in two stages. In the first stage, the deformation is due to a decrease in the barrier width, and in the second stage it is due to lowering of the barrier height. These results are not in agreement with the degradation mechanism under dc bias, proposed by Hayashi *et al.*,[14] in which the first stage is due to lowering of the barrier height and the second stage is due to a decrease in the barrier width.

From the proposed model of Gupta and Carlson,[15] in which the barrier voltage of Schottky type is due to formation of an atomic defect at the ZnO grain boundary and that the negative charge states in the grain boundary are compensated by positive charges at depletion layer, a barrier model[16] is proposed in which

$$\phi=(e^2N_s^2)/(2\epsilon_0\epsilon_r N_d), \quad (6)$$

where N_s is the surface state density (negative charges) and N_d is the donor density (positive charges).

It is seen that the relative modification in N_s and N_d can explain the variation in ϕ. The reduction of ϕ can be promoted either by increasing N_d or decreasing N_s.

N_d is related to ϕ and W through the following equation:

$$N_d=\{2\epsilon_0\epsilon_r[\phi-(E_C-E_F)]\}/e^2W^2, \quad (7)$$

where E_C is the conduction-band minimum energy and E_F is the Fermi energy. It is observed in Eq. (7) that only $(E_C - E_F)$ is not known or measured in the varistor. This parameter was measured for a ZnO-CoO system[17] and its value is 0.30 eV. Figure 4 shows a typical microstructure of a ZnO varistor obtained by SEM. X-ray microanalysis obtained in this varistor shows that the main dopant in ZnO grains is cobalt; therefore, it seems to be appropriate to use this value for the ZnO varistor system. Thus, from these considerations, the N_d parameter was calculated for the varistor before and after application of shorts of 8×20 μs of 250 and 500 A/cm^2. Table IV presents data of the N_d parameter before and after pulse degradation. It is seen that N_d does not change significantly with the current pulse degradation.

The surface state density N_s is given by

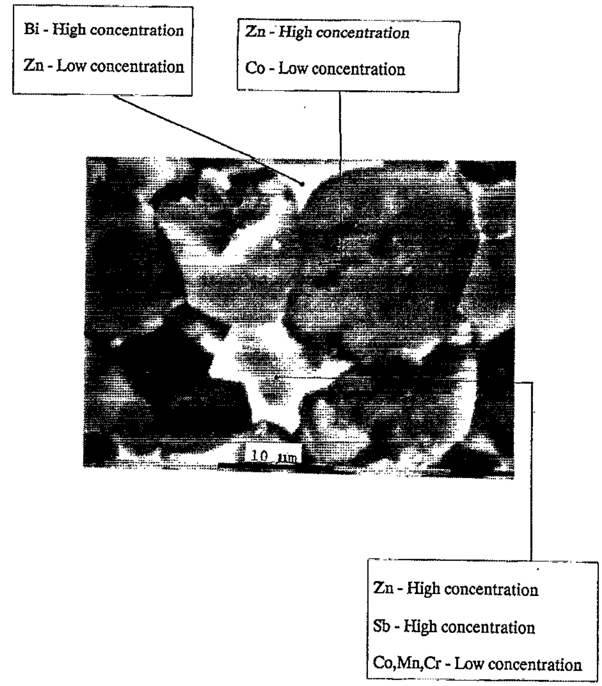

FIG. 4. Typical microstructure of ZnO varistor. The picture shows the points analyzed by x-ray microanalysis (3100×).

$$N_s=Q_s/e, \quad (8)$$

where Q_s is the total charge trapped at the interface and can be determined by

$$Q_s=2\int_0^W N_d\, e\, dx, \quad (9)$$

where x is the distance parameter that changes from 0 up to barrier voltage width W. By considering N_d independent of x,

$$Q_s=2N_d\, eW, \quad (10)$$

and then

$$N_s=2N_dW. \quad (11)$$

Equation (11) is the electric neutrality condition for the material. As N_d practically does not change, the reduction of the barrier width with degradation leads to a decrease in N_s. Thus the phenomena of degradation promoted by current pulses are due to the decrease of N_s, i.e., the decrease in negative charges located at the ZnO grain boundary, which can be either zinc vacancies or adsorbed oxygen. The decrease of N_s could be promoted by reactions between atomic defects with migration of positive charge

TABLE IV. Variation of N_d as function of applied pulses of 8×20 μs.

	$N_d \times 10^{-18}$ (cm^{-3})
Before applied pulses	0.65 (± 0.22)
After 20 pulses of 250 A/cm^2	0.76 (± 0.23)
After 20 pulses of 500 A/cm^2	0.60

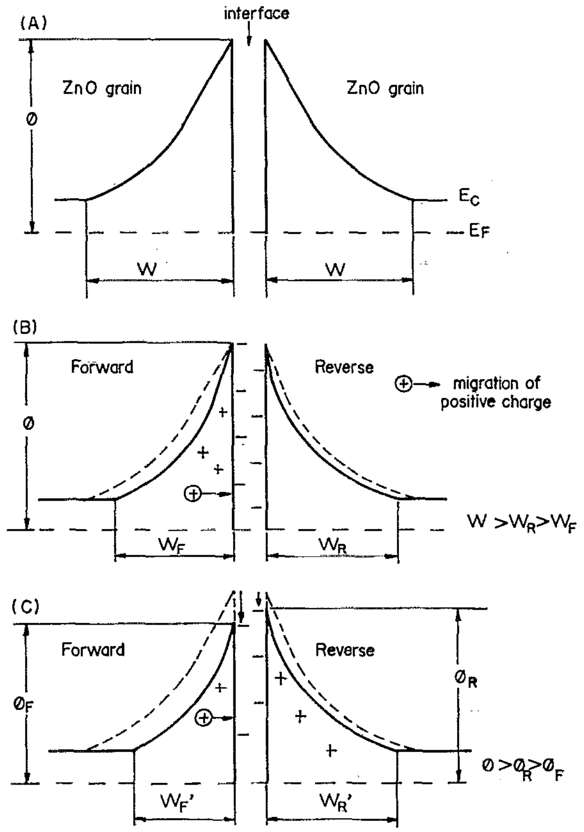

FIG. 5. This picture shows the bond diagram at the grain-boundary region. (a) Band diagram before pulse degradation. (b) After four cycles of 250 A/cm^2. In the first stage the migration of positive charge from depletion layer to grain boundary and the decrease in the barrier width can be seen. (c) After four cycles of 500 A/cm^2. In the second stage the chemical interaction between positive charge and negative charge at the grain boundary and lowering in the barrier height can be seen.

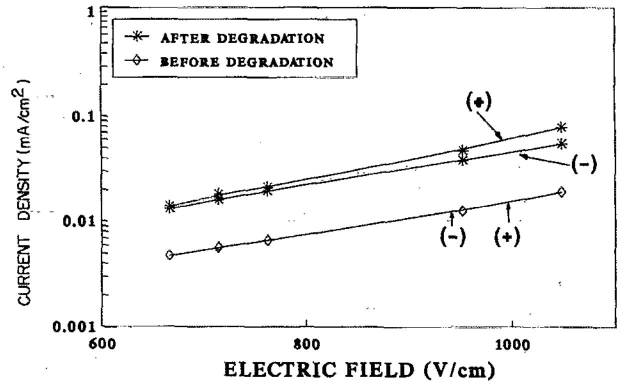

FIG. 6. *J-E* characteristics of ZnO varistors before and after four cycles of shorts of 8×20 μs of 500 A/cm^2. After the degradation asymmetrical characteristics are denoted, respectively, with forward bias (+) and with reverse bias (−).

from the depletion layer to the grain boundary, followed by a reaction with negative charge,[15] as shown schematically in Fig. 5. Figure 5(b) represents the first stage of the barrier voltage deformation, with a decrease in the barrier width. Figure 5(c) illustrates the second stage with a lowering of the barrier height and a continuous decrease in the barrier width. The first stage of barrier deformation can be related to the migration of positive charge in depletion layer and the second stage can be related to the reaction between positive charge and negative charge at the interface and a continuous migration of positive charge from the depletion layer to the grain boundary.

As shown in Fig. 6 the *J-E* characteristics of ZnO varistors were altered after four cycles of shorts of 8×20 μs of 500 A/cm^2. The change of the *J-E* characteristic measured by forward voltage to the biasing voltage was larger than that measured by the reverse voltage. This result explain the asymmetrical deformation of Schottky barriers proposed in Fig. 5 and is in agreement with the literature.[8–10]

IV. CONCLUSIONS

ZnO varistors are degraded by current pulses with higher energy than the limiting value. The state of degradation depends on the number of applied current pulses. The variation of the reference electric field $E_{0.05}$ due to the pulses energy is given by $E_a/E_b = 1 - p \ln E/E_0$, where E_0 is the limiting energy. Current pulses only degrade the barrier voltage but not the ZnO grains' electric properties. The experimental results suggest that the degradation is promoted by the decrease in N_s, i.e., by decreasing the negative charges trapped at the ZnO grain boundaries.

ACKNOWLEDGMENTS

The financial help given by 3M do Brasil, FAPESP, and CNPq is acknowledged. The authors also acknowledge 3M do Brasil for the technical help during the execution of this work and M. T. Jirschik, M. A. M. Carneiro, and P. S. P. Catão for helpful discussions.

[1] E. Olsson and G. L. Dunlop, J. Appl. Phys. **66**, 3666 (1989).
[2] K. Eda, J. Appl. Phys. **49**, 2964 (1978).
[3] K. Eda, A. Iya, and M. Matsuoka, J. Appl. Phys. **51**, 2678 (1980).
[4] K. Sato and Y. Teikada, J. Appl. Phys. **53**, 8819 (1982).
[5] T. K. Gupta and W. G. Carlson, J. Appl. Phys. **52**, 4104 (1981).
[6] C. G. Shirley and W. M. Paulson, J. Appl. Phys. **50**, 5782 (1979).
[7] K. Eda, J. Appl. Phys. **56**, 2948 (1984).
[8] M. Kobayashi, M. Mizuno, T. Aizawa, M. Hayashi, and K. Mitani, IEEE Trans. Power Appar. Syst. **PAS-97**, 1149 (1978).
[9] A. Bui, K. Abdullah, A. Loubierë, M. Tao, and Q. C. Nguyen, J. Phys. D **24**, 757 (1990).
[10] K. Eda, IEEE Electrical Insulation Mag. **5**, 29 (1989).
[11] T. K. Gupta and W. G. Carlson, J. Appl. Phys. **53**, 7401 (1982).
[12] L. M. Levinson and H. R. Philipp, Ceram. Bull. **65**, 639 (1986).
[13] S. A. Pianaro, M.S. thesis, UFSCar, São Carlos, Brazil, 1990.
[14] M. Hayashi, M. Haba, S. Hirano, M. Okamoto, and M. Watanabe, J. Appl. Phys. **53**, 5754 (1982).
[15] T. K. Gupta and W. G. Carlson, J. Mater. Sci. **20**, 3487 (1985).
[16] W. Heywang, J. Am. Ceram. Soc. **47**, 484 (1964).
[17] D. Binesti, Ph.D. thesis, University of Bordeaux I, Bordeaux, France, 1985.