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Electrostatic force microscopy as a tool to estimate the number of active potential barriers in dense non-Ohmic polycrystalline SnO₂ devices

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In the present work, electroactive grain boundaries of highly dense metal oxide SnO₂-based polycrystalline varistors were determined by electrostatic force microscopy (EFM). The EFM technique was applied to identify electroactive grain boundaries and thus estimate the amount of active grain boundary, which, in the metal oxide SnO₂-based varistor, was calculated at around 85%, i.e., much higher than that found in traditional metal oxide ZnO-based varistors. The mean potential barrier height value obtained from the EFM analysis was in complete agreement with the values calculated from the *C-V* measurements, together with a complex capacitance plane analysis that validates the methodology proposed here. © 2006 American Institute of Physics.

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Electrostatic potential barriers in the grain boundary region of metal oxide polycrystalline materials are known to be responsible for non-Ohmic electrical properties, which allow for the manufacture of devices known as metal oxide varistors (MOVs).¹⁻⁴ Non-Ohmic behavior is evidenced by the highly nonlinear current versus voltage (*I-V*) response, and this behavior is determined mainly by the aforementioned potential barriers¹⁻⁴ that exist in electroactive grain boundaries (GB). *I-V* plotting is used to calculate the empirical nonlinear coefficient (α), which is used as a parameter to measure the quality of MOV devices.^{3,4} Commonly, MOV devices are based on ZnO, SnO₂, TiO₂, SrTiO₃, and, more recently, on Ca_{1/4}Cu_{3/4}TiO₃.⁵

In MOV devices, the electrostatic potential barrier was found to be back-to-back Schottky type.^{3,6} The Schottky-type barrier is composed of negative charges trapped in the GB region, balanced by positive charges in the depletion layer in the zone adjacent to the grains.⁶ It is widely accepted that the oxygen species adsorbed at the interface between grains⁶ increase the negative charge trap and, therefore, the height of the potential barrier,^{6,7} promoting an increase in non-Ohmic behavior. The cause of GB oxidation is related to oxidized transition metals, e.g., Co, Mn, Cr, and Pr, segregated in grain boundary regions.^{6,7} The increase in non-Ohmic properties due to the higher degree of oxidation has already been proven to cause an increase in the mean barrier height values and in the amount of active (or effective) barriers.⁶⁻⁸ Therefore, the number of active barriers is an important parameter for the non-Ohmic properties, mainly because they are very

sensitive to structural and compositional variations.^{9,10}

A larger number of active barriers due to GB oxidation, for example, is the cause of decreases in leakage current.^{6,7} It is therefore important to describe how the back-to-back Schottky-type barrier height can be estimated based on the voltage dependence of the GB capacitance. Calculations of the GB capacitance are made from the high frequency intercept associated with high frequency relaxation in the complex capacitance plane.⁸ The use of the complex capacitance plane to calculate the grain boundary capacitance is very important because the methodology separates the related GB capacitance to the other relaxation processes existing in polycrystalline materials.⁸ The dependence of the applied voltage on the GB capacitance can be calculated using the equation:¹¹

$$\left(\frac{1}{C} - \frac{1}{2C_0}\right)^2 = \frac{2p^2}{qk\epsilon_0 N_d} \left(\phi_b + \frac{V}{p}\right), \quad (1)$$

where q is the electron or elementary charge, k is the dielectric constant (k to SnO₂ grain is ~ 14), ϵ_0 is the permittivity of free space, N_d is the positive space charge density in the depletion region (free electron density), and ϕ_b is the barrier height. C_0 and C are the GB capacitance per unit area of a GB biased, respectively, with zero and V volts. The average number of grains between electrodes is important to calculate the p parameter, which is the number of barriers between grains (obtained by calculating the thickness of the sample or the distance between electrodes divided by the mean grain size). Note that, in this approach, p is calculated based on the fact that all of the grains are considered electroactive, i.e., made of homogeneous active barriers, and, therefore, the ϕ_b calculated is an average value which depends on the p microstructural parameter. The previous approach has proven

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useful in calculating the barrier height value and in establishing a good relationship between potential barrier height and non-Ohmic properties.^{6,7} However, in most situations, the barrier height values may be poorly estimated if the materials contain few active barriers, mainly because the calculated p value would be higher than the real value. In other words, the p value is a source of error in the calculation of the potential barrier height and Eq. (1) must be used carefully.^{9,10} Therefore, a local observation of the GBs would improve the latter approach and also the understanding of the correlation between structure and properties.

Accordingly, the goal of this letter is to demonstrate the use of electrostatic force microscopy (EFM) as a tool to estimate the number of active barriers (also known as “good” barriers) in highly dense SnO₂-based polycrystalline varistor systems, particularly because EFM is capable of providing local information about the GB.

In EFM, when a voltage is applied between the tip and the sample, an interaction occurs between charges. For this reason, a variation in the accumulated charge energy can be observed along the whole sample and can be measured. A force (F) between the tip and the sample appears when a dc bias is applied, and is given by¹²

$$F = \frac{q_s q_t}{4\pi\epsilon_0 z^2} + \frac{1}{2} \frac{dC}{dz} (V_a - V_c)^2, \quad (2)$$

where q_s is the surface charge, q_t is the charge induced at the tip, z is the distance separating the tip from the sample, V_a is the applied voltage, V_c is the contact voltage between the tip and the sample, and dC/dz is the derivative of the sample-tip capacitance. In the present study, the electrostatic forces were measured as a function of tip bias in a highly dense polycrystalline MOV based on SnO₂ with the following composition: 98.90%-SnO₂, 1.00%-CoO, 0.05%-Nb₂O₅, 0.05%-Cr₂O₃ (SCNCR), all in molar percentage. Details of powder processing and sintering of this composition are given in Ref. 13. It is important to mention that the system is highly dense (>98.5%) to prevent the porosity from influencing the estimation of the p parameter. For the electrical measurements, silver contacts were deposited on the samples' parallel surfaces. I - V measurements were taken using a high voltage measurement unit (Keithley, model 237). The active potential barrier height value (ϕ_b) was estimated according to Eq. (1), based on a methodology described in detail in Ref. 8 using an impedance analyzer (HP, model 4194A) in the frequency range of 100 Hz to 15 MHz and a voltage amplitude of 0.5 V. For this system, in order to avoid the influence of deep traps, a frequency of 100 kHz was adopted. Lastly, for the electrical force measurements, the samples' surfaces were polished for about 24 h with 0.05 μ m gamma alumina (Buehler, No. 3) suspended in distilled water, using a vibratory polisher (Buehler, model Vibromet 2). The electrical force measurements were taken in an indoor atmosphere using an atomic force microscope (AFM) (Digital Instruments, Nanoscope IIIa) in the tapping mode. Bias voltage from -4 to +4 V was applied to the tip by AFM and the substrate was grounded. The tip was scanned at a constant tip-sample separation of 25 nm.

Figure 1(a) shows a typical AFM (height mode) image of the varistor morphology, and Figs. 1(b)–1(i) show the EFM images (frequency mode) as a function of applied bias voltage. The EFM images indicate that increasing the bias tip

FIG. 1. (a) AFM image ($1 \times 1 \mu\text{m}^2$) of the SnO₂-based varistor surface. (b) Electrostatic force microscopy (EFM) scans with tip bias increasing from -3 to 4 V. The tip sample separation was 50 nm in all the AFM images

voltage (with positive or negative signal) caused an increase in the negative charges stored in the GB region. The charge accumulation observed in the GB region in Fig. 1 indicates the presence of active potential barriers or active grain junctions. Furthermore, it is important to stress the existence of inactive junctions, as indicated by the black arrows in Fig. 1(b).

Based on the EFM images, the percentage of effective barriers ($\%n_e$) was calculated using the following relationship: $\%n_e = 100(n_e/n_T)$, where n_e is the number of junctions with accumulated charge (active barriers) and n_T is the total number of grain junctions or GB. The total number of grain-to-grain junctions obtained was 62 (takes over two different samples). A total number of 53 of these junctions were considered active junctions. This means that about 85% of the grain-to-grain junctions in the SCNCR system were active potential barriers. At this point, it is important to point out that this value is higher than that reported for ZnO-based varistors, which is generally considered to range from 15% to 33%.^{14,15} As Fig. 1 shows, the charge density varied as a function of bias voltage applied between the tip and the surface of the SCNCR sample. At higher negative or positive voltages, the charge density was higher and its value decreased as the bias voltage decreased, reaching a minimum value in the range of 1–2 V, which is consistent with Schottky barriers. The electric response for voltages around these values is related to the existence of a minimum force at the tip, corresponding to the contact potential between the tip and the surface of the sample, according to Eq. (2).

For each pixel of the frequency mode image obtained from EFM it is possible to associate a capacitive potential energy¹⁶

$$E = hfZ_m, \quad (3)$$

where h is the Planck constant, f is the resonant frequency at the tip, whose variation is used to generate the EFM image, and Z_m is an image scale factor. So, calculating the capacitive

FIG. 2. Energy vs tip bias plot illustrating the minimum charge condition.

potential energy of GB regions for several images at different biases, it was possible to obtain the pattern of capacitive potential energy as a function of the applied voltage. This pattern was used to obtain the minimum voltage value corresponding to the mean value of potential barrier height for the active junctions, which was found to be 1.4 V (Fig. 2).

Now, it is important to compare this value to the one that can be obtained through the conventional use of Eq. (1) combined with a complex capacitance analysis.^{6–8} Table I presents the comparative values and other typical non-Ohmic parameters of the MOV system studied here. Therefore, α and electric breakdown field (E_b) were found to be about 75 and 6900 V cm⁻¹, respectively. The ϕ_{EFM} and ϕ_{conv} are the mean values of potential barrier height obtained by fitting the EFM data and by the conventional methodology of combining of Eq. (1) with the complex capacitance analysis, respectively. It is important to emphasize that, for the calculation of ϕ_{conv} , the p parameter was corrected to consider 85% of active potential barriers, i.e., $p=0.85L/d$ (L is the sample thickness and d the mean grain size). The values obtained by

TABLE I. Results of nonlinear coefficient (α), breakdown electric field (E_b), mean barrier height value obtained from the EFM data analysis (ϕ_{EFM}), mean barrier height value obtained by combining Eq. (1) and the complex capacitance plane analysis (ϕ_{conv}), mean grain size (d), and relative density (ρ) obtained for the SCNCr system.

System	α	E_b (V cm ⁻¹)	ϕ_{EFM} (V)	ϕ_{conv} (V)	d (μm)
SCNCr	75	6900	1.4	1.3	2.4

the different methodologies were found to be in good agreement.

The value of 85% of active potential barriers must be the origin of the better correlation obtained between barrier height values and non-Ohmic properties in metal oxide SnO₂-based (85%) compared with metal oxide ZnO-based varistors (15%–35%). The larger number of active potential barriers in metal oxide-based SnO₂ is possibly related to the difficulty in obtaining low voltage varistors of such systems.

To conclude, it was demonstrated that the EFM technique can be used as a tool to estimate the amount of electroactive grain boundaries in MOV systems based on highly dense SnO₂. The validation of the EFM for this purpose was possible due to the total agreement between the mean potential barrier height calculated from the EFM analysis and the height obtained from C - V measurements allied with the complex capacitance plane.

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