Journal of Alloys and Compounds 616 (2014) 372–377

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Grain resistivity in zinc oxide and tin dioxide varistor ceramics

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ARTICLE INFO

Article history:
Received 12 June 2014
Received in revised form 22 July 2014
Accepted 23 July 2014
Available online 1 August 2014

Keywords:
Oxide materials
Ceramics
Electrical transport
Grain boundaries
Varistors

ABSTRACT

In this paper the grain resistivity was measured for commercial ZnO-based and laboratory-made SnO_2-based varistor ceramics exhibiting highly nonlinear current–voltage characteristics at low current (1 mA cm^{-2}). The high-current study was performed in the current range 2–500 A cm^{-2} using recently developed technique based on a concept of the differential resistance and application of a single exponential voltage pulse. At 295 K commercial ZnO varistors exhibit some lower values of the grain resistivity 0.59–0.61 Ω cm in comparison with higher values 2.4–28 Ω cm for SnO_2 varistors. Respectively, the high-current nonlinearity coefficients for ZnO varistors are higher than for SnO_2 varistors. The capacitive currents did not affect the obtained results. The activation energy of electrical conduction at low fields (in the range of Ohm's law) for SnO_2 varistors (0.82–0.98 eV) is larger than for ZnO varistors (0.69–0.76 eV). The observed correlation between the high-current and the low-current properties of ZnO-based and SnO_2-based varistors is discussed.

1. Introduction

Zinc oxide based ceramics with small additives of some oxides exhibit highly nonlinear current–voltage ($I(U)$) characteristics and due to this property they are widely used as varistors [1–7]. These transient suppression devices are commercially available, however, various aspects in the area of oxide ceramic varistors still are the subject of investigations [8–11] including a search of new materials for varistors. Relatively high nonlinearity of $I(U)$ characteristics were observed in SnO_2-based ceramics [12,13]. Both types of metal oxide varistors (ZnO-based and SnO_2-based) comprised of highly conductive grains with significantly less conductive grain boundaries and exhibit rather similar electrical conduction mechanism controlled by the grain-boundary potential barriers.

Usually dc $I(U)$ characteristic of a varistor is approximated by the empirical expression $I = B_1U^{\alpha}$ or (using specific values)

$$J = BE^{\alpha}, \quad (1)$$

where J is the current density, E is the electric field, α is the nonlinearity coefficient and B is a constant. The α-value can be introduced as a ratio of the static resistivity $\rho_s = E/J$ to the differential resistivity $\rho_d = dE/dJ$. In the highly nonlinear region of the $I(U)$ characteristic α = const. Therefore, the equation

$$\alpha = (E/J)(dJ/dE) \quad (2)$$

can be integrated at α = const and mentioned expression (1) can be obtained. In practice, the nonlinearity coefficient is estimated as a slope of $J(E)$ characteristic presented in the double logarithmic scale $\log J \sim \log E$. At currents below $\sim 10^{-7}$ A cm^{-2} this slope is decreased, α is approached to 1 and Ohm's law takes place. At currents above $\sim$1 A cm^{-2} the upturn region at $J(E)$ characteristic is observed: the slope of $J(E)$ curve in $\log J \sim \log E$ scale (the nonlinearity coefficient) is approached to 1 due to a decreasing of the grain boundary resistance and non-zero value of the grain resistance [1–7]. In this current range decreasing resistance of the grain boundaries becomes comparable with fixed resistance of grains.

Recently SnO_2 varistors with improved high-current electrical parameters were developed [14–16]. The nonlinearity coefficient and the electric field at current density 1 mA cm^{-2} for these SnO_2 varistors [14–16] and ZnO varistors [5,7] are relatively close. High-current behaviour of metal oxide varistors is very important for the estimation of their quality, however, the high-current processes in metal oxide varistors are significantly less understood than electrical properties of these devices at low currents.

The decrease of the grain resistivity due to some additives leads to a displacement of the upturn region to higher currents [3–5]. For better protection performance the nonlinearity coefficient in the high-current range should be higher. In other words, the voltage

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http://dx.doi.org/10.1016/j.jallcom.2014.07.178
0925-8388/

clamping ratio (the ratio of two voltages dropped at a varistor at some high and low currents, for example, at 1 kA and 0.1 mA), $E_{1000}/E_{0.0001}$, should be as close to 1 as possible [5,9].

The estimation of the grain resistivity can be performed using the dielectric spectroscopy [2,17], the high-current pulses [2,18,19] and the infrared reflectance [20]. However, the accuracy of all these measurements is rather not very high. Recently a new pulse technique for the grain resistivity measurement in varistor ceramics was suggested [21]. Such technique allows obtaining more precise value of the grain resistivity with the relative error no more than ±4%. It applies the concept of the differential electrical resistance and can be used in the range of relatively not high current densities where heating of varistor is insignificant. Also, it would be useful to test this technique for varistor samples with high nonlinearity at low currents (at approximately 1 mA cm^{-2}) and different grain resistivity. With this aim a range of varistor samples prepared in different conditions was selected.

Thus, it would be interesting to measure the grain resistivity of different ZnO-based and SnO_2-based metal oxide varistors with high nonlinearity coefficient at low current (at 1 mA cm^{-2}) by mentioned pulse technique [21]. Additionally, this pulse technique [21] allows to measure the nonlinearity coefficient at high currents using the obtained differential resistivity (see Eq. (2)).

Therefore, in this work the grain resistivity in some ZnO-based commercial varistors and several SnO_2-based laboratory-made varistors are measured, the properties of these varistors in the range of current above ~10 A cm^{-2} are compared, and observed correlation between the high-current and low-current properties of ZnO-based and SnO_2-based varistors is discussed.

2. Materials and methods

Several metal oxide varistors were studied: the "sample Z-1" is ZnO-based commercial varistor (CH2-1, Russia); the "sample Z-2" is ZnO-based commercial varistor (SIOV-S20K250, Siemens Semiconductors) and the "samples S-0, S-1, S-2, S-3, S-4" are SnO_2-based laboratory-made varistors. The samples Z-1 and Z-2, additionally to ZnO (~97%), contain Bi_2O_3, Sb_2O_3, Co_3O_4, MnO_2 as additives. The composition of the sample S-0 is (mol.%): 97.4 SnO_2, 2.5 CoO, 0.05 Nb_2O_5, 0.05 Cr_2O_3. All other SnO_2-based samples S-1, S-2, S-3, S-4 (additionally to the sample S-0) contain 0.05 mol.% Y_2O_3. Additionally, the sample S-2 contains 0.1 mol.% $SrCO_3$, the sample S-3 contains 0.1 mol.% $SrCO_3$ and 0.1 mol.% MgO and the sample S-4 contains 0.2 mol.% $SrCO_3$ and 0.1 mol.% MgO. Respectively, the content of SnO_2 is slightly varied in these samples. Detailed compositions of the samples S-1, S-2, S-3, S-4 are presented in [15].

The microstructure of these materials was studied earlier [13–16,22]. According to these studies, ZnO-based samples contain ZnO grains doped with Co and Mn and a small amount of secondary phases with pyrochlore and spinel structures [22]. SnO_2-based samples contain SnO_2 grains with small quantities of $CoSnO_3$ phase [15,16].

The grain resistivity measurements in this paper were performed using pulse technique proposed recently [21]. Here only some key details of this technique are mentioned. The samples with Ag electrode area S = 0.02–0.035 cm^2 were used. The preparation details of samples with such a small area are described in [21]. The oscillograms of voltage and current were recorded using the dual-channel storage oscilloscope C8-11. Such oscillograms are actually the current–voltage characteristic in the parametric form with time as a parameter. These oscillograms were digitalized and processed with Adobe Photoshop CS and Microsoft Excel. The details of the oscillograms treatment are published elsewhere [23].

The static resistance $R_s = U/I$, the differential resistance $R_{dif} = dU/dI$ and the nonlinearity coefficient $\alpha = R_s/R_{dif}$ were calculated from the oscillograms at certain values of current I across a sample using the next formulas:

$$I = (I_1 + I_2)/2, \tag{3}$$

$$R_s = (U_1 + U_2)/(I_1 + I_2), \tag{4}$$

$$R_{dif} = (U_1 - U_2)/(I_1 - I_2), \tag{5}$$

$$\alpha = \frac{R_s}{R_{dif}}. \tag{6}$$

Fig. 1 shows how it was done. In Fig. 1 and in Eqs. (3)–(6) it is implied that I_1, I_2, U_1, U_2 are respective instantaneous values of current and voltage. The measurements in the present paper were conducted in the current density range 2–500 A cm^{-2}.

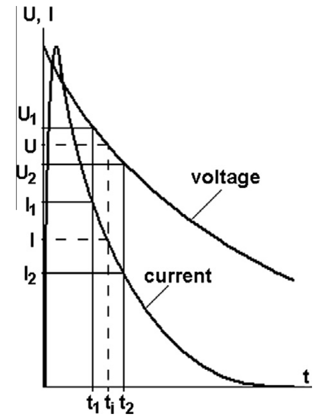

Fig. 1. Schematic images of current and voltage oscillograms explaining how they were used for calculation of the static resistance, the differential resistance and the nonlinearity coefficient at certain current.

The differential resistivity ρ_{dif} of the varistor sample was obtained in the form [21]:

$$\rho_{dif} \cong \rho_g + \frac{B^{-1/\alpha}}{\alpha J}, \tag{7}$$

where $J = I/S$ is the current density, B and α are constants in Eq. (1). The dependence $\rho_{dif} \sim 1/J$ can be plotted using the obtained experimental data. According to the technique [21], the extrapolation of this linear dependence to $1/J = 0$ gives the grain resistivity ρ_g.

Eq. (7) was obtained assuming that current across the barrier region is purely active. However, in a general case the total current across the barrier region at a moment t is a sum of the active and capacitive parts. The performed analysis shows that at a choice of the time constant of a single exponential voltage pulse more than τ = 300 µs, the active current is significantly greater than the capacitive one and Eq. (7) is correct. For different samples of ZnO and SnO_2 varistors it was found that if the capacitance of a forming capacitor is more than 300 µF, then the value of ρ_{dif} at $1/J = 0$ does not depend on the time constant τ of a single exponential voltage pulse. It means that the barrier capacitances in a varistor at such long pulses have enough time to become charged and due to that the capacitive current is significantly lower than the active current. Therefore, the measurements in the present paper were conducted using single exponential voltage pulses with the time constant τ = 450 µs.

The values of the grain resistivity were averaged using 6–9 independent measurements and the average values of the grain resistivity $\rho_{g\ average}$ and rms deviation σ were calculated according to the formulas:

$$\rho_{g\ average} = \frac{1}{N}\sum_{i=1}^{N}\rho_{gi}, \tag{8}$$

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\rho_{gi} - \rho_{g\ average}\right)^2}. \tag{9}$$

The relative errors were found as $\sigma/\rho_{g\ average}$.

The values of current and voltage at oscillograms were selected with 3 µs step. For calculation of the differential resistance the time interval $t_2 - t_1$ was three times greater than the step indicated above. The relative error at determination of voltage and current was not more than ±1.5%. The measurements were performed at 295 K.

The minimization of possible degradation is an important advantage of used technique [21]. It is well known that electrical properties of ZnO varistors are changed as a result of pulse stress [5]. In our experiments the electrical properties of metal oxide varistors were not changed as a result of the application of single exponential voltage pulses with above mentioned parameters.

To estimate the barrier height in the studied samples, the temperature dependences (300–370 K) of dc resistivity ρ at 3 V (where Ohm's law takes place) were recorded. Temperature (controlled by a copper resistance thermometer with the accuracy ±0.2 K) was changed with a rate 2 K/min. The activation energy of electrical conduction E_σ was found from ρ dependence according to the expression:

$$\rho = \rho_0 \exp(E_\sigma/kT), \tag{10}$$

where k is the Boltzmann's constant, T is the absolute temperature, ρ_0 is a constant.

The dc current and voltage were measured using source measure unit Keithley 237. The electric field and the nonlinearity coefficient were found at dc current density 10^{-3} A cm^{-2}. For estimation of the relative dielectric permittivity, the capacitance of the studied samples at 700 kHz was measured utilizing high-frequency LC measure unit E7-9.