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CONDUCTIVITY OF GRAINS IN NONLINEAR OXIDE CERAMICS AND PROTECTIVE PROPERTIES OF VARISTORS

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The current-voltage characteristics of various compositions of nonlinear varistor ceramics based on ZnO (ZOC) and SnO_2 (TOC) are studied in a wide range of electric current. On the basis of obtained data were determined the parameters that allow finding the coefficients k_{prs} and k_{prl}, which define the protection levels against the switching surge and the lightning surge for surge suppressors on the basis of ZOC and TOC varistors. The lower the value of these coefficients are, the significantly higher the efficiency of surge protection is. A relationship between k_{prs}, k_{prl}, and the effective linear resistivity ρ_{lin} limiting the current of intergranular barriers in varistor ceramics are established. It is shown that the values of k_{prs} and k_{prl} increase with increasing ρ_{lin}, which value is determined by the bulk resistance of the ceramic grains. The studied TOC compositions have 2-3 times larger values of ρ_{lin} and more high values of k_{prs} and k_{prl} than ZOC. ZOC-based varistors with lower k_{prs} and k_{prl} values provide more effective surge protection than TOC-based varistors.

Keywords: varistor, ZnO-based ceramics, SnO_2-based ceramics, surge protection.

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1. Introduction

Ceramic materials based on ZnO and SnO_2 with the additives of other oxides have a highly non-linear current-voltage characteristic (CVC). This allows using them in the production of varistors intended for the protection of electronic and electrical equipment from overvoltage [1]. In particular, zinc oxide varistors are widely used in surge suppressors (SS) intended for protecting the power lines and electrical equipments from switching and lightning surges [2]. SS is connected in parallel to the protected object. Due to the high nonlinearity of the CVC of varistors, SS sharply reduces the resistance under the action of an overvoltage pulse. As a result, most of the overvoltage remains in the external electrical circuit and on the SS and the protected object, the voltage increases weakly.

An important parameter of varistors based on zinc oxide ceramics (ZOC) and tin oxide ceramics (TOC) is the protection coefficient k_{pr}. This parameter defines the level of surge protection. There are protection coefficients against the switching surge k_{prs} and the lightning surge k_{prl}, which are defined as

$$k_{prs} = \frac{E_{100}}{E_{0.001}}; \qquad k_{prl} = \frac{E_{1000}}{E_{0.001}}, \tag{1}$$

where E_{100}, E_{1000}, and $E_{0.001}$ are electric field strengths in ceramics at the current densities 100 A·cm^{-2}, 1000 A·cm^{-2}, and 0.001 A·cm^{-2}, respectively. The current density of 0.001 A·cm^{-2} corresponds to the operating condition of the varistor in the absence of overvoltage. In this case, a classification voltage U_C is applied to the varistor, which creates an electric field strength $E_{0.001}$ in the varistor material. In accordance with equation (1), the efficiency of surge protection is better as much as closer the values of k_{prs} and k_{prl} to unit.

As is known [3], the high nonlinearity of the CVC of varistor ceramics is associated with Schottky double energy barriers. Such barriers are formed in the surface region of the contacting grains of ZnO (SnO_2) during the ceramics synthesis. The cause for high nonlinearity of the CVC is a reversible electrical breakdown in the near-surface region of grains where the barriers are located. This breakdown is due to the mechanisms of Zener tunneling [4] and impact ionization [5]. The consequence of such mechanisms is a high nonlinearity of CVC with the nonlinear coefficient $\alpha \sim 50$ in the region of classification voltage U_C of varistor. It should be noted that at currents more than 1 A·cm^{-2}, the nonlinear coefficient α decreases with increasing current density. The cause of such behavior is the comparison in value of the linear resistance in grain volume and the nonlinear resistance in surface regions of the grains where double Schottky barriers are localized. In this case, the linear resistance of grains limits the nonlinear current through Schottky barriers. Therefore, the decrease of the nonlinearity coefficient α takes place. Decrease of α leads to increasing of electric field strengths E_{100} and E_{1000}. As a result, the protection coefficients k_{prs}, k_{prl} increase. This reduces the efficiency of surge protection.

The purpose of this work is to study the effect of bulk electrical conductivity of grains on the protective properties of varistors based on ceramics with a highly nonlinear current-voltage characteristic.

2. Samples and methods of investigation

Investigations were performed on the samples of ZOC varistors CH2-1 (manufacturer “Progress” plant) and SIOV-S20K250 (manufacturer Siemens Semiconductors). Further we will denote the samples of such ceramics as Z0 and Z1, respectively. Usually, the ZOC composition for zinc oxide varistors contains 95 – 97 mol.% ZnO and small additives of oxides Bi_2O_3, Sb_2O_3, Co_3O_4, MnO_2, and Cr_2O_3.

Studies of varistor ceramics based on SnO_2 were performed on the samples obtained in laboratory conditions. The composition and designation of samples for such ceramics are presented in the Table 1.

Table 1

Composition of the samples of varistor ceramics based on SnO_2

Designation	Composition, mol.%						
	SnO_2	CoO	Nb_2O_5	Cr_2O_3	Y_2O_3	$SrCO_3$	MgO
S1	97.4	2.5	0.05	0.05	0.05	–	–
S4	97.4	2.5	0.05	0.05	0.05	0.2	0.1

The samples for investigation had the shape of cylinder with a diameter of base from 12 mm to 20 mm for different samples and a height (thickness) from 0.7 mm to 2 mm. The bases of the cylindrical samples were used as the surface for electrodes. Electrodes were obtained by means of silver paste firing. All measurements were performed at an ambient temperature of 292 K.

The current-voltage characteristics on the direct current were measured in the range of 10^{-6} – 10^{-2} A cm^{-2}. The samples with electrodes whose diameter was smaller by 1 – 1.5 mm than the diameter of surfaces for electrodes were used. Currents and voltages were measured with a relative error of ±2% by V7-27 digital multipurpose tester. These data were used for constructing the current-voltage characteristics of ceramic samples in the coordinates $E \sim J$ and the coordinates $logE \sim logJ$. Here $E = U/L$ is the average value of electric field strength created by the voltage U in a sample of thickness L, $J = I/S$ is the average current density in a sample with electrode area S at the current I through the sample. CVC were used for the determination of the electric field strength $E_{0.001}$ and the nonlinearity coefficient $\alpha_{0.001}$. The value $\alpha_{0.001} = \Delta logJ/\Delta logE$ was found in the region of current density $J = 0.001$ A·cm^{-2}.

Investigations of the CVC at $J > 10$ A·cm^{-2} were performed on single voltage pulses with exponential form. In this case, we used the samples with small electrodes (area of 0.025 – 0.04 cm^2) to obtain large values of current density. Techniques for creating small electrodes and studying the CVC at high currents are described in [6]. Oscillograms of voltage and current during pulse tests were recorded using a double-beam storage oscilloscope C8-11.

For registering the current-voltage characteristics at high electric currents with a relative error not more than ±1.5%, raster images of oscillograms were used. Such images were obtained by means of photographing oscillograms from the oscilloscope screen by the digital camera OLYMPUS C-756. The values of current and voltage at various points of the CVC were determined on the basis of data obtained at scanning the coordinates of raster image by means of the program described in [7]. The CVC obtained in this way were used to determine the electric field strengths E_{100}, E_{1000} and nonlinearity coefficients α_{100}, α_{1000} at the current density of 100 $A \cdot cm^{-2}$ and 1000 $A \cdot cm^{-2}$, respectively.

The effective specific linear resistance ρ_{lin}, which limits the current of intergranular barriers of varistor ceramics in the region of current density J, was determined with an error of ±4% from raster images of oscillograms of current and voltage. The technique for measuring the ρ_{lin} was based on the differential resistance conception described in [8, 9]. When performing measurements of ρ_{lin}, we used the program presented in [10] for processing raster images of oscillograms. The dependences $\rho_{lin}(J)$ obtained in the region of high currents were used to determine the effective linear resistances ρ_{lin100} and $\rho_{lin1000}$ at the current density of 100 $A \cdot cm^{-2}$ and 1000 $A \cdot cm^{-2}$, respectively.

3. Experimental results and discussion

The parameters for different samples of varistor ceramics studied in this work are presented in Tab. 2. As can be seen, near the electric current density of 0.001 $A \cdot cm^{-2}$, all samples have a nonlinear coefficient of the current-voltage characteristic $\alpha_{0.001}$ not less than 30. In the region of high current, value of α decreases with current increasing. The cause for this is the limitation of current through intergranular barriers by the linear bulk resistance of grains in varistor ceramics. Current limitation occurs when all barriers in the current path between the sample electrodes operate in the regime of reversible electric breakdown caused by Zener tunneling and avalanche breakdown [4, 5].

As shown in [11, 12], the disordering of varistor ceramics associated with a spread in grain sizes and heights of intergranular barrier leads to current localization in the percolation paths. When all barriers in percolation path are in the breakdown regime, this path has a low resistance and shunts paths containing at least one barrier not functioning in the breakdown regime. Just for such percolation paths, the current of intergranular barriers is limited by the linear bulk resistance of the grains. Such paths determine the CVC of varistor ceramics in the region of high electric currents. Localization of current in the percolation paths indicates that electric current is unevenly distributed over the cross section of ceramic sample.

Table 2

Parameters of varistor ceramics based on zinc oxide (Z0, Z1) and tin dioxide (S1, S2)

	$E_{0.001}$, $V \cdot cm^{-1}$	E_{100}, $V \cdot cm^{-1}$	E_{1000}, $V \cdot cm^{-1}$	$\alpha_{0.001}$	α_{100}	α_{1000}	ρ_{lin100}, $\Omega \cdot cm$	$\rho_{lin1000}$, $\Omega \cdot cm$	experiment		calculation	
									k_{prc}	k_{prs}	k_{prc}	k_{prs}
Z0	1512	2148	2582	42	10	4.3	2.35	0.6	1.42	1.71	1.47	1.79
Z1	1672	2355	2941	52	10.5	4.8	2.05	0.58	1.41	1.76	1.37	1.65
S1	2280	3770	4650	30	6.5	3.8	5.72	1.29	1.64	2.04	1,72	2,15
S4	2730	3985	5241	54	6.3	3.6	6.80	1.67	1.46	1.92	1.49	1.90

The distribution of the grain sizes in ceramics is the reason that different percolation paths between electrodes of a sample contain different number of grain boundaries with barriers. At increase of the voltage, at first the reversible breakdown takes place for percolation paths with smallest number of barriers. With the increase of voltage the number of percolation paths grows.

The effective linear resistivity ρ_{lin} measured in the region of current density J is determined by the number of percolation paths formed at this current density. From the data of Tab. 2 it follows, that the decrease of ρ_{lin} takes place with increasing of J. This is a consequence of the fact that with increasing voltage (current density) the increase of the number of parallel percolation paths. At the currents of about 1000 A·cm^{-2} or more, almost all possible current paths between the electrodes of a sample contain only intergranular barriers operating in the nonlinear regime. Therefore, ρ_{lin} is close to the specific bulk resistance of the grains in varistor ceramics ρ_g. In Tab. 2 the value of $\rho_{lin1000}$ is close to the value of ρ_g for different compositions of varistor ceramics.

The relationship between the parameters of varistor ceramics (Tab. 2) and the protection coefficients can be obtained. For the description of the current-voltage characteristic of intergranular barriers, we use the empirical dependence between the electric field strength E and the electric current density J [1]:

$$J = BE^{\alpha} \tag{2}$$

where B is a constant and α is the nonlinearity coefficient of CVC.

If we take into account the values of nonlinearity coefficient of CVC $\alpha_{0.001}$ and the electric field strength $E_{0.001}$ and also assume that $\alpha = \alpha_{0.001}$, then the expression (1) can be written in the form

$$J = 0.001\left(\frac{E}{E_{0.001}}\right)^{\alpha_{0.001}}. \tag{3}$$

It follows from (3), the average electric field strength E_b associated with a voltage drop on the grain boundaries in ceramics is determined as

$$E_b = E_{0.001}\left(\frac{J}{0.001}\right)^{\frac{1}{\alpha_{0.001}}}. \tag{4}$$

At the weak currents almost all voltage U applied to a sample drops in the grain surface regions with high resistance where barriers are localized. Therefore, the average electric field strength in ceramics is $E = E_b$. At high currents the part of the voltage U applied to the bulk resistance of grains becomes comparable to the voltage drop in the surface region of grains. This contribution E_g to the electric field strength E can be represented as $E_g = J\rho_{lin}$. Since $E = E_b + E_g$ for the CVC of varistor ceramics in the region of high electric currents, the following empirical expression can be obtained:

$$E = J\rho_{lin} + E_{0.001}\left(\frac{J}{0.001}\right)^{\frac{1}{\alpha_{0.001}}} \tag{5}$$

From (1) and (5) for protection coefficients k_{prs} and k_{prl} one can obtain:

$$k_{prs} = \frac{100\rho_{lin100}}{E_{0.001}} + 10^{\frac{5}{\alpha_{0.001}}}, \tag{6}$$

$$k_{prl} = \frac{1000\rho_{lin1000}}{E_{0.001}} + 10^{\frac{6}{\alpha_{0.001}}}, \quad (7)$$

In the Table 2 the values of coefficients k_{prs} and k_{prl} calculated by (1) using the experimental E_{100} and E_{1000} and the values of these coefficients calculated by (6), (7) using ρ_{lin100}, $\rho_{lin1000}$, $E_{0.001}$, $\alpha_{0.001}$ are shown. As can be seen, there is a correspondence between the experimental and calculated values of k_{prs} and k_{prl}.

As follows from the relations (6) and (7), values of k_{prs} and k_{prl} increase with increasing values of ρ_{lin100} and $\rho_{lin1000}$. This means that at the same values of parameters $\alpha_{0.001}$ and $E_{0.001}$ the efficiency of surge protection for varistors based on ceramics with large values of ρ_{lin} is worse than for varistors with lower values of ρ_{lin}. Since the value of ρ_{lin} is determined by the bulk resistivity ρ_g of grains, the efficiency of surge protection can be improved by the value decrease of ρ_g. This can be realized by finding oxide additives to ceramic composition that reduce ρ_g without decreasing the nonlinearity of CVC.

According to (6), (7), the protection coefficients k_{prs}, k_{prl} have minimum values when $\rho_{lin} = 0$. These values are determined by expressions:

$$k_{prs(\min)} = 10^{\frac{5}{\alpha_{0,001}}}; \quad k_{prl(\min)} = 10^{\frac{6}{\alpha_{0,001}}}. \quad (8)$$

At $\alpha_{0,001} = 50$ $k_{prs} = 1.26$, $k_{prl} = 1.32$. It is possible to reduce k_{prs}, k_{prl} and improve the surge protection by increasing the nonlinearity coefficient $\alpha_{0.001}$.

The effective linear resistivity ρ_{lin}, which limits the current of barriers in varistor ceramics, increase the minimum values of the protection coefficients $k_{prs(min)}$, $k_{prl(min)}$, on the quantity $100\rho_{lin}/E_{0.001}$ and $1000\rho_{lin}/E_{0.001}$, respectively. The magnitude of this additive decreases with an increase of $E_{0.001}$. Therefore, for varistors based on the ceramics with relatively small values of $E_{0.001}$, one should expect larger values of k_{prs} and k_{prl}. Such varistors provide less effective protection against overvoltage than varistors with larger values of $E_{0.001}$.

Based on the data presented in Tab. 2, we can conclude that varistor ceramics based on SnO_2, though it has a high nonlinearity coefficient $\alpha_{0.001}$, its values of ρ_{lin} are approximately 2-3 times larger. The results of this are the higher values of protection coefficients k_{prs}, k_{prl}. Therefore, at present, TOC based varistors are less effective for surge protection than ZOC based varistors. To improve the protective properties of TOC varistors, it is necessary to search the ceramic compositions with lower effective linear resistivities ρ_{lin}, which limits the current of intergranular barriers.

Conclusions

The current-voltage characteristics of the nonlinear varistor ceramics based on ZnO (ZOC) and SnO_2 (TOC) of different compositions were studied in a wide range of electric current. On the basis of obtained data the coefficients $k_{prs} = E_{100}/E_{0.001}$ and $k_{prl}= E_{1000}/E_{0.001}$ were determined; they characterize the level of protection against switching surge and lightning surge ($E_{0.001}$, E_{100}, and E_{1000} are electric field strengths at the current density of 0.001 $A\cdot cm^{-2}$, 100 $A\cdot cm^{-2}$ and 1000 $A\cdot cm^{-2}$, respectively). The lower the values of these coefficients are, the more effective the surge protection is. A relationship between k_{prs}, k_{prl} and the effective linear resistivity ρ_{lin} limiting the current of intergranular barriers in varistor ceramics was established. It was shown that the values of k_{prs} and k_{prl} increase with increasing value of ρ_{lin}, the magnitude of which is determined by the bulk resistance of grains in ceramics. The tin oxide ceramics have values of ρ_{lin} 2-3 times greater than for the zinc oxide ceramics and, as a result, larger values of k_{prs} and k_{prl}. Therefore, ZOC based varistors with lower coefficients of k_{prs} and k_{prl} provide more effective surge protection than TOC based varistors.

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