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Journal of the European Ceramic Society 24 (2004) 2591–2595

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Comparative characteristics of silver and copper electrodes on ZnO varistor ceramics

R.I. Lavrov, A.I. Ivon*, I.M. Chernenko

Department of Radiophysics, Dnepropetrovsk National University, UA 49050 Dnepropetrovsk, Ukraine

Received 27 March 2003; received in revised form 14 September 2003; accepted 20 September 2003

Abstract

The current–voltage characteristics of zinc oxide-based ceramics with silver electrodes created by silver baking and with copper electrodes obtained by electrodeposition of copper have been investigated in wide region of electric current. For ZnO varistors with copper electrodes the leakage current in 3–4 times is less than for varistors with silver electrodes. The reason of it is a thermal influence on ceramics at creation of silver electrodes. The transition layer between ceramics and the copper electrode, which has a negative influence on current–voltage characteristic at region of high electric current was not detected. The raster electronic microscopy indicates a good contact between ceramics and the copper electrode. The tearing strength for copper electrode is $(8.21\pm3.03)\times10^6$ newton·m^{-2} and is close to similar magnitude for a silver electrode.

Keywords: Electrical properties; Electrodes; Mechanical properties; Varistors; ZnO

1. Introduction

Zinc oxide-based ceramics with small additives of Bi_2O_3, Co_3O_4, MnO_2, Sb_2O_3 and other oxides is widely used at manufacturing of metal-oxide varistors (MOV).[1,2] The current–voltage characteristic (CVC) has the nonlinear exponent near 40–60 for MOV.[1] It allows to apply varistors for effective protection of electrotechnical equipments and electronic circuits from overvoltages.[2,3] At overvoltages the electrical current through the varistor can reach from several hundreds up to tens thousand amperes.[3] Therefore electrodes for varistor should satisfy the special requirements.

Firstly, electrodes should have a low electric resistance. Secondly, electrodes should not have a transition layer between ceramics and metal, which gives negative effect for current–voltage characteristic of varistor at high electric current. Thirdly, a good coupling between electrode and the surface of ceramics should take place.

At present time the silver and aluminum electrodes are used most widely at manufacturing of varistors. Silver electrodes are being created at temperature near 800 °C by means of the silver baking in an air atmosphere.[4] Aluminum electrodes are being created by means of the shooping .

The silver electrodes better satisfy the requirements, which were mentioned above. These electrodes have higher conductivity than aluminum electrodes and give a good coupling with the ceramic surface. The copper is also a good electrode material, because its conductivity is not much lower than the conductivity of silver. However, copper has advantage for varistors production as more cheap material. The compositions of copper-containing pastes for electrodes are known.[5] The annealing process for such pastes demands the neutral or reducing gas atmosphere. However, for varistor ceramics the thermal treatment in such atmosphere is not allowed, because it decreases nonlinearity of current–voltage characteristic.[6,7]

The copper electrodes can be created on dielectric surface by electrochemical methods.[8–10] However, known electrochemical methods usually use expensive salts of the noble metals. Besides as a rule, these methods give the transition layer between electrode and ceramics. This transition layer decreases the nonlinearity of CVC at high electric current. We have

* Corresponding author. Tel./fax: +7-380-0562-465523.
E-mail address: a_ivon@mail.ru (A.I. Ivon).

0955-2219/$ - see front matter
doi:10.1016/j.jeurceramsoc.2003.09.003

developed the electrochemical method for creation of the copper electrodes on ZnO varistor ceramics. This method not uses the noble-metals salts.

The purpose of this paper are comparative investigations of the electric parameters and characteristics for ZnO varistors with silver electrodes created by the silver baking and with copper electrodes created by electrochemical way.

2. Experimental

Investigations have been executed with ZnO ceramic disks for varistors. Disks had diameter of 20 mm and thickness of 1.00–1.34 mm for different samples. ZnO ceramics of the basic composition for varistors with additives of oxides Bi_2O_3, Sb_2O_3, Co_3O_4, Cr_2O_3, MnO_2[1] and also B_2O_3-doped ZnO varistor ceramics,[11] were used in this investigations.

The silver baking at temperature 800 °C was used for the creation of silver electrodes. Electrochemical method was used for the creation of copper electrodes. This method has two stages: the creation of conducting layer on ceramic surface, which is intended for electrode and the electrodeposition of copper. The conducting layer with electrical resistance of a few hundreds ohm is being used as cathode at second stage of the process. We used the electrochemical reduction of oxides in surface region of ceramics for conducting layer creation. The diameter of electrodes was 17 mm and their thickness near 10 and 20 μm for different varistors.

Current–voltage characteristics have been measured on d.c. voltage in interval 10^{-12}–10^{-2} A. The measurement accuracy for voltage was ±0.5% and for electric current ±2%. The current wave of 8/20 μs was used for the measurement of CVC at high current (from 0.1 up to 1000 A). Peak magnitudes of electric current impulses and of voltage impulses were registered by the crest voltmeters with relative error of ±2%. The magnitude of electric current through a sample was measured as the voltage drop on precision resistor of 1 Ohm, which was connected consistently with a sample.

For measurement of the tearing strength for silver and copper electrodes the following technique was used. A tin-drop was soldered with an electrode surface area of 4–5 mm^2 and copper wire was soldered to this drop. A sample was fixed in the holder and force was applied to copper wire. We were measuring this force by the dynamometer. We were increasing the force and defining the cohesive force at a moment of separation of an electrode section. The tearing strength was calculated as the ratio of cohesive force to the area of detached electrode section. The values of the tearing strength were determined as the average magnitudes for 20–30 outcomes of measurement.

3. Results and discussion

Table 1 illustrates some parameters of ZnO varistors with silver and copper electrodes. Every parameter in this table is obtained as average magnitude for 20–30 varistors. Nonlinear exponent of CVC (α) for investigated samples are defined in the interval 10^{-4}–10^{-3} A as $\alpha = 1/\lg(U_{10}^{-3}/U_{10}^{-4})$. Where U_{10}^{-3} and U_{10}^{-4} are the voltage drops on varistor at electric currents of 0.001 and 0.0001 A, accordingly.

As from Table 1 follows, MOV with silver and copper electrodes have close magnitudes of nonlinear exponent α. The distinction of electric parameters is observed in a region of weak and high electric currents. In ohmic region of CVC (a weak electric current), the leakage current for varistors with copper electrodes in 3–4 times is less, than for varistors with silver electrodes. For MOV with copper electrodes the ratio U_{100}/U_{10}^{-3} is a little more, than for varistors with silver electrodes. Decrease of the leakage current for MOV at use of copper electrodes instead of silver electrodes is a positive factor, while increase of the ratio U_{100}/U_{10}^{-3} is a negative factor.

The current–voltage characteristics for MOV with copper electrodes and silver electrodes are shown in Fig. 1 (the curves 1 and 2). For exception of the specimen geometry in CVC, these characteristics are submitted in specific parameters: J—the density of electric current, E—the intensity of electric field. In such form the current–voltage characteristic reflect the properties of ZnO-based ceramics.

Table 1
Some parameters of ZnO varistors with the silver and copper electrodes

Electrode material	Leakage current at voltage 1 V, A	Voltage at 10^{-3} A U_{10}^{-3}, V	Nonlinear exponent (10^{-4}–10^{-3} A) α	Voltage at 100 A U_{100}, V	The ratio $\frac{U_{100}}{U_{10^{-3}}}$	Varistor thickness, mm	Note
Ag	$(2.83\pm0.38)\times10^{-11}$	220±4	63±7	329±4	1.490±0.014	1.22	ZnO ceramics of basic composition
Cu	$(8.16\pm0.42)\times10^{-12}$	247±5	58±4	385±4	1.562±0.015	1.34	
Cu	$(4.56\pm0.35)\times10^{-11}$	234±6	35±3	354±8	1.512±0.009	1.34	After annealing at 800 °C during 1 h
Cu	$(1.51\pm0.52)\times10^{-11}$	194±6	51±5	286±7	1.475±0.030	1.00	B_2O_3-doped ZnO ceramics

The plots of current–voltage characteristic with high nonlinear exponent (the electric current density from 10^{-7} up to 10^{-2} A/cm^2) practically coincide for varistors with silver electrodes and with copper electrodes (Fig. 1). The distinctions take place only in the region of weak and high electric currents. The high-current plots of CVC are shown on Fig. 2 in more details. As from Fig. 2 follows, the current–voltage characteristic in a case of copper electrodes (curve 1) is displaced to region of smaller electric currents in comparison with CVC for varistor with silver electrodes (curve 2). The transition layer between ZnO ceramics and copper electrode may be the reason for the such behavior. Such transition layer can give the additional electrical resistance decreasing the magnitude of an electric current for given voltage. Increasing of the ratio U_{100}/U_{10}^{-3} will take place as outcome.

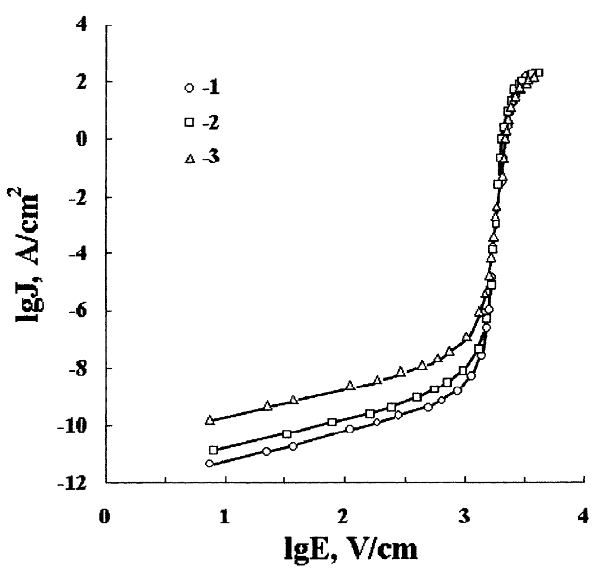

Fig. 1. Current–voltage characteristics of ZnO ceramics: 1—the copper electrodes, 2—the silver electrodes, 3—the copper electrodes are created after annealing of ceramics in an air atmosphere at 800 °C during 1 h.

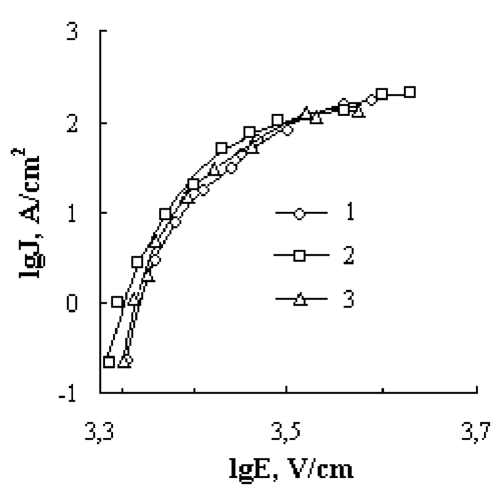

Fig. 2. The high-current plots of current–voltage characteristic for ZnO ceramics: 1—the copper electrodes, 2—the silver electrodes, 3—the copper electrodes are created after annealing of ceramics in an air atmosphere at 800 °C during 1 h.

Let's find relationship between the transition layer electric resistance and the ratio U_{100}/U_{10}^{-3}. For this purpose we shall designate the area of electrode as S, the specific electric resistance of transition layer as ρ_c, its thickness as d and use for approximation of CVC of ZnO-based ceramics the expression:[12]

$$J = J_0\left(\frac{E}{E_0}\right)^{\alpha}, \qquad (1)$$

where J_0—the electric current density at voltage U_{cer10}^{-3}, $E_0 = U_{cer10}^{-3}/L$ (L is a thickness of varistor disk, farther we assume $L >> d$), α— nonlinear exponent. U_{cer10}^{-3} is the voltage drop on ceramic disk of varistor at electric current 10^{-3} A, also U_{cer100} is the voltage drop at the current 100 A.

The electric resistance of a transition layer is in-sequence with the electric resistance of ceramic varistor disk. Therefore

$$U_{10}^{-3} = U_{cer10}^{-3} + 10^{-3}\rho_c\frac{d}{S} \qquad (2)$$

$$U_{100} = U_{cer100} + 100\rho_c\frac{d}{S}. \qquad (3)$$

ZnO-based ceramics has a high resistivity at low electric currents. Therefore, the second member of the sum can be omitted in expression (2). Then from (2) and (3) we shall get the following expression for the ratio U_{100}/U_{10}^{-3}:

$$\frac{U_{100}}{U_{10^{-3}}} = \frac{U_{cer100}}{U_{cer10^{-3}}} + \frac{100\rho_c d}{U_{cer10^{-3}}\cdot S}. \qquad (4)$$

If to take into account that $U_{cer10}^{-3} = E_0 L$ and to define from (1) the ratio $U_{cer100}/U_{cer10}^{-3} = (10)^{5/\alpha}$, then we can get the such expression for U_{100}/U_{10}^{-3}:

$$\frac{U_{100}}{U_{10^{-3}}} = (10)^{5/\alpha} + \frac{100\rho_c d}{E_0 S}\cdot\frac{1}{L}. \qquad (5)$$

As from this expression follows, if the transition layer with $\rho_c \neq 0$ between ceramics and electrode has place, then the ratio U_{100}/U_{10}^{-3} should depend from the varistor disk thickness L. This ratio is increasing at the decreasing of the varistor thickness.

For investigation of the dependence of ratio U_{100}/U_{10}^{-3} from L, we polished ZnO ceramic disks to necessary thickness and then created the copper electrodes. The data of such investigation in coordinates $U_{100}/U_{10^{-3}} \sim 1/L$ are shown in Fig. 3. Apparently, the ratio $U_{100}/U_{10^{-3}}$ practically does not depend on thickness. It allows to conclude, that the transition layer with appreciable electric resistance is not formed between copper electrode and a surface of ZnO-based ceramics at creating the electrodes by means of the method, which we used.

The observed distinctions of parameters for MOV with copper and silver electrodes are probably caused by thermal history of ZnO-based ceramics. As known, the heat treatment has a significant effect on electric properties of this material.[13] For creation of silver electrodes the heating up to temperature near 800°C is necessary,[4] while at the creation of copper electrodes, the ceramics is not subjected by thermal influence because electrochemical process is being executed at the temperatures not more 50°C.

For testing the effect of thermal history on electrical properties of MOV with copper electrodes, the ceramic disks were annealed previously on air at temperature 800 °C during 1 h and then the copper electrodes was created. In Table 1 and Figs. 1 and 2 (curve 3) the data of investigation for electric parameters and current–voltage characteristics of such samples are represented. As from these data follows, the heat treatment increases the leakage current of varistors and decreases the ratio $U_{100}/U_{10^{-3}}$. It gives reason to believe that the distinctions of parameters and CVC for varistors with silver and copper electrodes is caused by thermal influence at the creation of silver electrodes. The positive quality of electrochemical method for creation of copper electrodes is absence of thermal influence. It allows to decrease the leakage current for MOV (Table 1). As regards the ratio $U_{100}/U_{10^{-3}}$, which is describing the protective properties of varistors, probably this ratio does not depend on electrode material and is defined by nonlinear properties of ZnO-based ceramics. It indirectly is confirmed by the data for B_2O_3-doped ZnO ceramics (the Table 1). As from the Table 1 follows, these varistor disks with copper electrodes have smaller magnitude of the ratio $U_{100}/U_{10^{-3}}$ than varistors disks with silver electrodes. The probable reason of the above mentioned distinction in the ratio $U_{100}/U_{10^{-3}}$ for varistors with the basic composition of ZnO ceramics is the different varistor disks parties used at creation of copper electrodes and silver electrodes.

Fig. 4 represents the data of raster electron microscopy for the boundary region between a copper electrode and ceramics. The well-defined border between ceramics and copper is observed. The transition layer is not observed visually and good contact between ceramics and copper takes place.

The tearing strengths for silver and copper electrodes are represented in the Table 2. As from this table follows, the tearing strength for copper electrode created by the electrochemical method is close to similar magnitude for silver electrode created by the silver baking. We observed the dependence of the tearing strength for copper electrodes from presence of the black layer on ceramic surface. The black layer in the surface region of ceramic disk is forming at the baking and has some distinctions of composition in comparison to bulk of ceramic disk. The investigations have shown,[14] that this layer has thickness about 3 – 5 μm, is enriched by spinel ($Zn_7Sb_2O_{12}$) in comparison to bulk of ceramics and contains insignificant amount of free Bi_2O_3. The black layer has also the heightened content of oxygen in comparison to bulk of ceramics and ZnO grain orientation predominantly in direction [001].

Table 2 represents also the tearing strength of copper electrode for ZnO ceramic disk with black surface layer and without it. We have removed the black layer from ceramic disk surface intended for electrode by means of the etching in 20% HNO_3. As shown in the Table 2, the tearing strength of copper electrode for ceramics with black surface layer is five times less than for ceramics

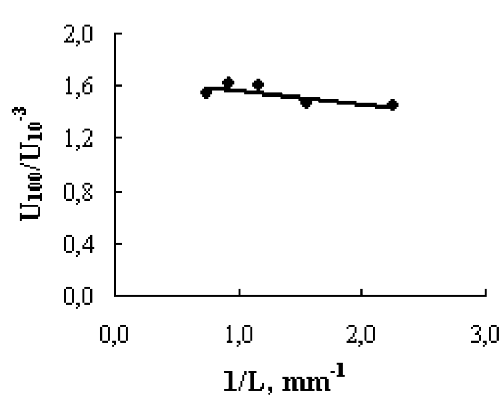

Fig. 3. Dependence of the ratio $U_{100}/U_{10^{-3}}$ from thickness of the varistor disk L in coordinates $U_{100}/U_{10^{-3}} \sim 1/L$.

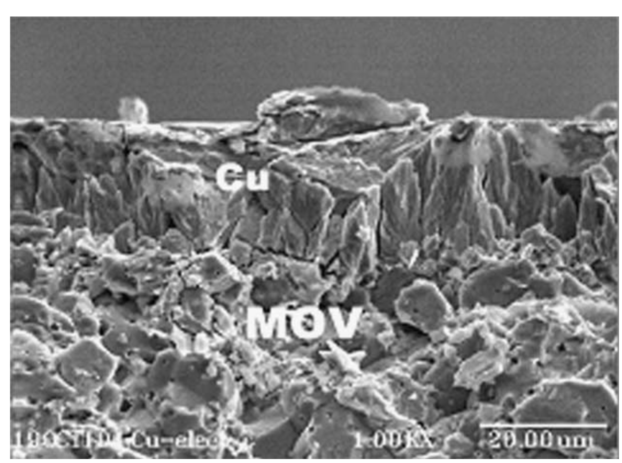

Fig. 4. Microstructure for the border region of copper electrode and MOV material in zinc oxide varistor.

Table 2
The tearing strength for the silver and copper electrodes on ZnO-based ceramics

Electrode material	Electrode thickness, μm	The tearing strength, newton·m^{-2}	Note	The type of varistor ceramics
Ag	10	$(7.15\pm2.17)\times10^6$		
Cu	10	$(8.21\pm3.03)\times10^6$	Black surface layer is removed by etching in 20% HNO_3	ZnO ceramics of basic composition
Cu	10	$(1.64\pm0.43)\times10^6$	Electrodes are created on a black surface layer	
Cu	20	$(8.26\pm2.62)\times10^6$	Surface was etched in 20% HNO_3	B_2O_3-doped ZnO ceramics

without this layer. This result may be explained by the distinction of mechanical properties for the material of black layer and for bulk material of ceramic disk. Such distinction may be expected because the distinction of composition for surface region and for bulk region of ZnO-based ceramics[14] has place. The smaller magnitude of the tearing strength for copper electrode on varistor disks with the black layer is probably conditioned by the smaller magnitude of breaking strength for material of black layer and also may be caused by worse adhesion of copper on the black layer than for the bulk material of ceramics. Let's notice, that the black layer does not influence magnitude of the tearing strength for silver electrode created by the silver baking. It may be caused by the high temperature, which is used for silver baking. The diffusion of silver through the black layer is facilitated at this temperature.

4. Conclusions

Zinc oxide varistors with electrodes created by the electrodeposition of copper have leakage current in 3 – 4 times is less than leakage current for varistors with silver electrodes created by the silver baking. The reason of it is a thermal influence on zinc oxide-based ceramics at creation of silver electrodes.

The investigation of current–voltage characteristics at high electric current for ceramic samples with different thickness has shown absence of the transition layer between ceramics and copper electrode, which gives a negative effect on varistor CVC and, hence, on its protective ratio U_{100}/U_{10}^{-3}.

Data of raster electronic microscopy show the well defined border between ceramics and the copper electrode. The transition layer is not observed visually and a good contact between ceramics and copper takes place.

The tearing strength for copper electrode, created by electrochemical way on the surface of zinc oxide-based ceramics, is equal to $(8.21\pm3.03)\times10^6$ newton·m^{-2} and is close to magnitude $(7.15\pm2.17)\times10^6$ newton·m^{-2} for the silver electrode.

For ZnO varistor ceramics the copper electrodes created by electrochemical way do not yield to the silver electrodes created by silver baking.

Acknowledgements

The authors are very grateful to Mr. T. Stewart for the data of electronic microscopy.

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