ELECTROPHYSICAL CHARACTERISTICS OF THE NEAR-SURFACE LAYER OF SEMICONDUCTOR CERAMICS FOR ZnO VARISTORS

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Electrophysical properties of near-surface layer of ZnO varistor ceramics forming during high-temperature annealing in oxidizing gaseous atmosphere are studied. Microstructure of near-surface layer and its electrical properties have features which are determined by an increased concentration of oxygen at surface of pressed ceramic billets in comparison with bulk during annealing. From the data of electron raster microscopy of cross-chipping of varistors, it is defined that the average value of thickness of near-surface layer is 40 µm. It is found that the specific resistivity value of near-surface layer is $5.3 \cdot 10^{12}$ Ω·cm. The electrical capacitance of near-surface layer is calculated from capacitance measurement data for varistors containing such layer under two electrodes and without layers. It is shown that the electrical capacitance of near-surface layer exceeds that of varistor by more than an order. Conclusion is made that the near-surface layer gives a weak contribution to dielectric properties of ZnO varistor ceramics. However contribution of this layer to electrical conductivity of ceramics in pre-breakdown region is significant.

Keywords: varistor, zinc oxide ceramics, near-surface layer, electric resistivity.

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1. Introduction

Zinc-oxide varistors are used in devices for limiting the overvoltage on electrical circuits, electronic equipment and schemes [1-5]. Volt-current characteristics (VCC) of ZnO varistors in the range of electric currents of $(10^{-3}–1)$ A·cm^{-2} exhibits high nonlinearity. At low strengths of electrical field (in the region of Ohm's law) varistor resistance is high (of order of 10^{10}-10^{12} Ω·cm) while in region of reversible electrical breakdown their resistance is low (of order of 10^2 Ω·cm) [6, 7]. At parallel connection with load, varistors prevent overvoltage on it [8, 9]. Protective properties of varistors are determined by the coefficient of protection $k_{pr} = U_{100}/U_{0,001}$, where U_{100} and $U_{0,001}$ are voltages on varistor at currents 100 A·cm^{-2} and 1 mA·cm^{-2}, respectively. In this case protection effectiveness will be the greater the closer to one will be the value of k_{pr} [10] that correlates with greater nonlinearity of varistor properties. The protection coefficient is an important parameter of varistors. Its value significantly depends on such factors as homogeneity of ceramic microstructure and electrical conductivity of ZnO grains which limits the current through punched potential barriers (upper part of varistor VCC) [11]. Therefore high-temperature annealing is most important stage in manufacture of varistors.

At this stage the granular structure of zinc-oxide varistor ceramics is formed and potential barriers responsible for nonlinearity of varistor VCC arises at ZnO grain boundaries [12-15]. However, it should be borne in mind that physical-chemical processes occurring during annealing of ZnO varistor ceramics are largely determined by the gaseous atmosphere composition [16]. This suggests a difference of electrophysical properties for internal and near-surface regions of varistors. The impedance of near-surface layer connected serially with ceramic bulk in electrical circuit should influence on linear and nonlinear properties of varistors. Such layer has black color in contrast to bulk of green color and in further will be called a black layer.

The purpose of this paper is to determine thickness, electrical resistance and electrical capacitance of the black layer which is formed in ZnO varistor ceramics during high-temperature annealing in oxidizing atmosphere.

2. Samples and experimental procedure

The studied samples of zinc-oxide ceramics for commercial varistors of composition 97,5 mol.% ZnO, 0,5 mol.% Bi_2O_3, 1,0 mol.% Sb_2O_3, 0,5 mol.% Co_3O_4, 0,5 mol.% MnO_2 are disk-shaped. They were annealed in air for 1 hour at 1520 K in accordance with the standard technology of varistor manufacturing.

The data of electronic raster microscopy of cross-chipped of annealed varistor disks performed with REM-106I microscope (SELMI, Ukraine) were used for measuring of thickness of the studied black layer.

Capacitance measurements were performed on "L and C high-frequency meter E7-9" at the frequency of 600 kHz. Studied samples initially had a black layer under each of two electrodes. After the measurements electrode surfaces of the samples were grinded for removing the electrodes and black layer. Then electrodes again were created directly on ceramic material and the measurements were repeated. Thus electrical capacitances of varistor samples containing black layer on both electrode surfaces and capacitances of samples without black layer were measured.

Copper was used as electrodes. Copper electrodes were applied to the bases of varistor disks by the electrochemical method according to [17].

The electrical resistance of the black layer was defined from the calculated dependence of varistor sample resistivity on inverse thickness of the sample with using data [16] of measurements of VCC for commercial ZnO varistors in the region of Ohm's law before and after removing the black layer.

Electrical capacitances of black layers were calculated from the data of capacitance measurements for varistor samples before and after removing the black layer.

3. Results and discussion

Internal regions of varistor ceramics are formed by ZnO single crystals (main phase) and crystallines with structures of pyrochlore $Zn_2Bi_3Sb_3O_{14}$, spinel $Zn_7Sb_2O_{12}$ and bismuth oxide Bi_2O_3 embedded in three-dimensional network of Bi-enriched amorphous phase [2]. In view of increased oxygen content the black layer is characterized by higher (3-5 times in comparison with bulk) content of spinel phase, tendency to reduce the pyrochlore phase, and insignificant amount or absence of free Bi_2O_3 [16]. Cobalt Co^{+2} dissolved in bulk of ZnO grains passes into Co^{+3} state on crystal surface leading to blackening of the near-surface region of the ceramic [16]. Accordingly microstructures of internal and near-surface regions differ as shown in Fig. 1.

In Fig. 1 the black layer on varistor disk surface is visually observed. The bulk part of varistor disk has lighter color. The black layer thickness is different for different points of the surface. The average thickness of black layer is 40 μm. Taking into account that the minimal thickness of studied varistor samples is about 1 mm, the following ratio can be accepted:

$$2L_l / L << 1 \qquad (1)$$

where L_l = 40 μm and L ≥1 mm are thickness of black layer and studied samples, respectively.

a   b

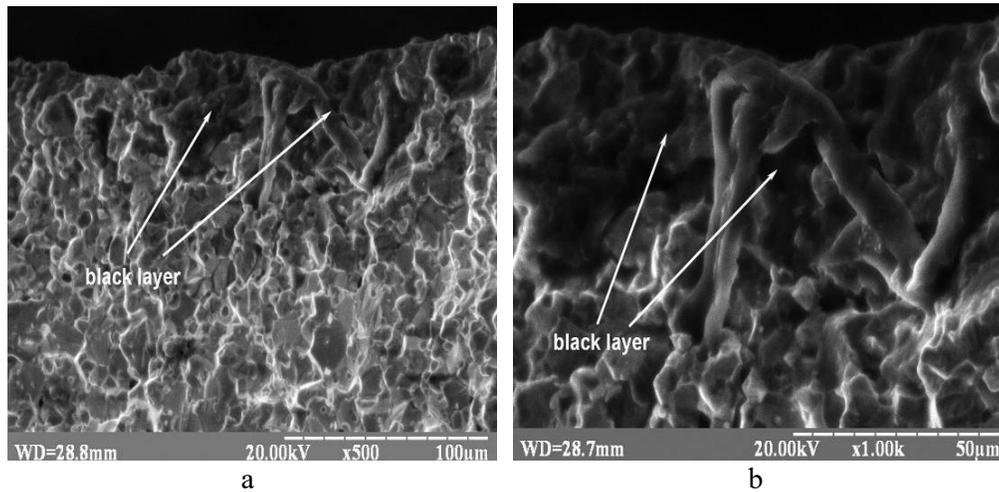**Fig. 1. SEM images of cross-chipped of ZnO varistor disk annealed in air at magnification of: a) ×500; b) ×1000**

An equivalent electrical circuit for a varistor sample containing the studied layer under two electrodes can be represented in a general case by the series connection of impedances as shown in Fig. 2.
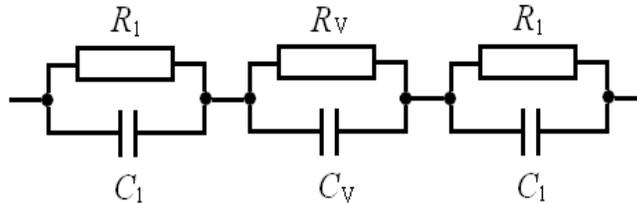

Fig. 2. Equivalent electrical circuit of sample of ZnO varistor ceramics with black layer under two electrodes: S_l and R_l – electrical capacitance and active resistance of black layer, respectively; C_v and R_v - electric capacitance and active resistance of bulk part of studied sample (ceramics), respectively.

At constant current or at very low frequencies the equivalent electrical circuit (Fig. 2) is a serial connection of resistors R_l and R_v: $R = 2R_l + R_v$, where R is varistor sample resistance. In this case the specific electrical resistivity ρ of varistor sample, taking into account relation (1), is determined by the following expression:

$$\rho = \rho_v + 2\rho_l \frac{L_l}{L} \qquad (2)$$

where ρ_v is specific electrical resistance of bulk part of sample; ρ_l is specific electrical resistance of thestudied black layer.

Expression (2) determines the direct dependence $\rho \sim 1/L$ shown in Fig. 3.

As follows from expression (2) and Fig. 3, the black layer contribution to varistor resistivity will increase with varistor thickness decreasing.

The specific electrical resistance of the black layer is determined using expression (2) at substituting the measured values of corresponding physical quantities.
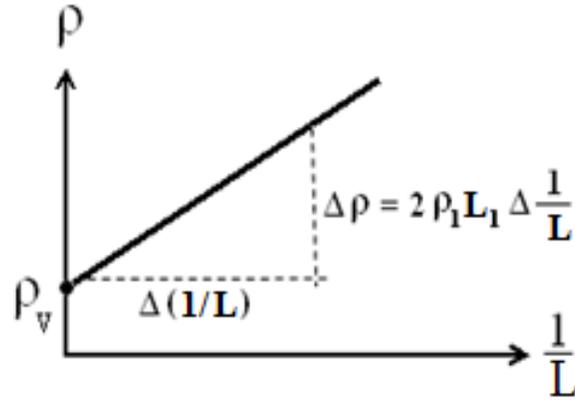
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Fig. 3. Calculated dependence of specific electrical resistivity of ZnO varistor with black layer on electrode surfaces on inverse thickness of the varistor.

Values ρ and ρ_v for ZnO varistor samples in the region of Ohm's law can be found from data of measurements of VCC for commercial ZnO varistor given in [16].

According to these data, the resistivity of varistor sample with the black layer under two electrodes is $4.0 \cdot 10^{10}$ $\Omega \cdot$cm. For a varistor with removed black layer the resistivity is significantly lower – $3.5 \cdot 10^{7}$ $\Omega \cdot$cm. The initial thickness of varistor sample, according to [16], is 0.98 cm.

Value ρ_l calculated with using expression (2) is approximately $5.3 \cdot 10^{12}$ $\Omega \cdot$cm.

The large value of quantity ρ_l can be explained by higher intergranular potential barriers in black layer in comparison with varistor bulk [16].

At capacitance measurements at high frequencies the amplitude value of variable voltage applied to a sample is small (not more than 5 V) and capacitance conductivity (Fig. 2) exceeds active conductivity. In this case the equivalent electrical circuit shown in Fig. 2 is a serial connection of capacitances C_l and C_v. Taking into account relation (1), electrical capacitance of the black layer can be found from measured at high frequencies capacitances of varistor samples as:

$$C_l = \frac{2C_2}{\dfrac{C_2}{C_1} - \dfrac{L_1 S_2}{L_2 S_1}} \tag{3}$$

where C_2 and C_1 are electrical capacitances of varistor sample without black layer and with black layer under two electrodes, respectively; L_1 and L_2 are thicknesses of varistor sample with black layer under two electrodes and without black layer, respectively; S_2 and S_1 are areas of electrodes of varistor sample without black layer and with black layer on two electrode surfaces, respectively.

It follows in particular from (3) that at the initial absence of the black layer (in this case its thickness $L_l = 0$ and $C_1 \to \infty$) $C_2/C_1 = (L_1 S_2)/(L_2 S_1)$.

Table 1 shows results obtained from capacitance measurements for samples of ZnO varistor ceramics before and after removing the black layer by grinding.

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Table 1

L_1, mm	S_1, cm^2	L_2, mm	S_2, cm^2	C_1, pF	C_2, pF	C_l, pF	ε_l
0,92	2,34	0,73	2,40	2295	3684	23567	421
3,82	5,30	3,38	5,20	1533	1749	109153	861
9,80	4,00	9,20	4,74	691	895	54338	568

The values of relative permittivity ε_l of the black layer were calculated using values of its thickness L_l which previously was found from data of scanning electron microscopy (Fig. 1).

As can be seen from Table 1, the electrical capacitance of the black layer much exceeds the capacitance of the sample itself that contains such layer on two electrode surfaces. This suggests that a black layer does not influence noticeably on nonlinear properties of varistor ceramics. Really, according to data of [16], the VCC for samples with the black layer and without it coincide starting from current densities 10^{-3} A·cm^{-2}.

4. Conclusions

According to data of raster electron microscopy, it is defined that the average thickness of a black layer formed on ZnO varistor ceramics during its high-temperature annealing is 40 microns. Structure and electrical properties of such layer differ from bulk due to different formation conditions.

From the calculated dependence of the electrical resistance of a varistor in the region of Ohm's law on inverse thickness of the varistor the specific resistivity of its black layer is determined. The value of specific electrical resistivity of black layer is $5.3 \cdot 10^{12}$ Ω·cm that is approximately two orders higher than that of varistor sample.

It is found that the electrical capacitance of the black layer calculated from capacitance measurements of varistor samples is more than an order higher than that of sample itself that contains such layer.

Due to the large capacitance connected in series with the capacitance of varistor bulk, the black layer makes a weak contribution to dielectric properties of ZnO varistor. However, due to high electrical resistivity contribution of such layer to electrical conductivity of a varistor in the pre-breakdown region is significant.

References

1. **Gupta, T.K.** Application of zinc oxide varistors / T.K. Gupta // Journal of the American Ceramic Society. – 1990. – Vol. 73, N 7. – P. 1817 – 1840.

2. **Li, J.-L.** Microstructure and electrical properties of rare earth doped ZnO-based varistor ceramics / J.-L. Li, G.-H. Chen, Ch.-L. Yuan // Ceramics International. – 2013. – Vol. 39, N 3. – P. 2231 – 2237.

3. **Poosimma, P.** Stability of zinc oxide varistors / P. Poosimma // A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences. – 2014.

4. **Zhao, H.** Improving age stability and energy absorption capabilities of ZnO varistors ceramics / H. Zhao, J. Hu, Sh. Chen, Q. Xie, J. He // Ceramics International. – 2016. – Vol. 42, N 15. – P. 17880 – 17883.

5. **Bai, H.** Influence of Bi-Co-O synthetic multi-phase on electrical properties of the Zno-Bi$_2$O$_3$-MnO$_2$–SiO$_2$ varistors / H. Bai, Y. Sun, Zh. Xu, R. Chu, G. Li // Materials Letters. – 2017. – Vol. 209. – P. 115 – 117.

6. **Rabab, S.** Influence of zinc oxide particle size and surface properties on the electrical, optical and cytotoxicity characteristics of zinc oxide discs / S. Rabab // Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy. – University Sains Malaysia. – 2015.

7. **Ivon, A. I.** Grain resistivity in zinc oxide and tin dioxide varistor ceramics / A. I. Ivon, A. B. Glot, R. I. Lavrov, Zh.-Y. Lu // Journal of Alloys and Compounds. – 2014. – Vol. 616. – P. 372 – 377.

8. **Martzloff, F. D.** Surge-Protective Devices / F. D. Martzloff, L. M. Levinson // In book: Electronic Ceramics: Properties, Devices, and Applications (Electrical and Computer Engineering) / Ed. by L. M. Levinson. – New York, 1988. – P. 275 – 305.

9. In-situ quantitative measurement of electric fields in zinc oxide thin films using electrostatic force microscopy // Jan Harloff. – University of Pennsylvania, School of engineering and applied science. – December, 1995. – 85 p.

10. **Dmitriev, M. V.** The use of OPN to protect the insulation of 6-750 kV overhead lines (Применение ОПН для защиты изоляции ВЛ 6-750 кВ) / M. V. Dmitriev. – S. Peterburg.: Politech. University, 2009. – 92 p.

11. **Bartkoviak, M.** Nonlinear currents in Voronoi networks / M. Bartkoviak, G. D. Mahan // Physical. Review B. –1995. – Vol. 51, № 16.P. 10825 – 10832.

12. **Meshkatoddini, M. R.** Metal oxide ZnO-based varistor ceramics / M. R. Meshkatoddini // In book: Advances in Ceramics – Electric and Magnetic Ceramics, Bioceramics, Ceramics and Environment / Ed. By C. Sikalidis. – InTech, September 2011. – pp. 329 – 356.

13. **Clarke, D. R.** Varistor Ceramics / D. R. Clarke // Journal of the American Ceramic Society. – 1999. – Vol. 82, № 3. – P. 485 – 502.

14. **Beynet, Y.** ZnO-based varistors prepared by spark plasma sintering / Y. Beynet, A. Izoulet, S. Guillemet-Fritsch and at. // Journal of the European Ceramic Society. – 2015. – Vol. 35, № 4. – P. 1199 – 1208.

15. **Katkov, V. F.** Electrical conductivity and structure of the near-surface region of oxide-zinc ceramics / V. F. Katkov, A. B. Glot, A. I. Ivon // Neorg Materials. – 1989. – V.25, №2. – P. 526 – 528.

16. Patent 98937 Ukraine. Method of forming a metal layer on ceramics / R. I. Lavrov, I. M. Chernenko, A. I. Ivon. – 2012. – Bul. № 13.

17. **Lavrov, R. I.** Comparative characteristics of silver and copper electrodes on ZnO varistor ceramics / R. I. Lavrov, A. I. Ivon, I. M. Chernenko // Journal of the European Ceramic Society. – 2003, Vol. 24, № 9. – P. 2591 – 2595.