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TECHNOLOGICAL AND ELECTROPHYSICAL PARAMETERS OF ZnO VARISTOR WITH IMPURITIES

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Abstract- The article describes the electrical properties of the intercrystallite boundary and mechanisms of conductivity in a ZnO varistor with impurities. The study shows the properties of the reagents used in the synthesis of the ZnO varistor, as well as the composition of the substances used to provide the varistor effect. The article also presents the energy diagrams of the crystallite boundary in the ZnO varistor, the equivalent circuit diagram and the energy diagram of micro varistors, respectively. It has been established that conductivity is possible during physical processes both at the intercrystallite boundary and through a potential barrier. And the dependence of conductivity on frequency and temperature was shown. It turned out that in the low-frequency region, the electrical conductivity increases monotonically, and then strongly increases with increasing frequency. In this case, the electrical conductivity σ changes according to the law $\sigma \approx f^{0.8}$. The resulting dependence $\sigma \approx f^{0.8}$ indicates a hopping mechanism of charge transfer over states localized in the vicinity of the Fermi level [1-2]. Dependence of conductivity on temperature, it can be said that the charge transfer in the varistors under study is carried out by hopping conduction of electrons with a variable hopping length over localized states lying in a narrow energy band near the Fermi level. These states in a varistor can be created by extended defects, intercrystallite boundaries and dislocations.

Keywords: ZnO, Varistors, Impurities, Potential Barrier, Crystallite, Reagents, Non-Linearity, Electrical Conductivity, Frequency, Temperature.

1. INTRODUCTION

It is known that that semiconductor materials are of great importance for power engineering due to their non-linear conductivity. The use of such materials provides attenuation of harmful voltage waves, which can be amplified during power surges on high voltage lines and half stations. It should be noted that SiC and ZnO materials with symmetrical current-voltage characteristics are mainly used for this purpose in modern electrical engineering. The material based on these elements (at operating voltages) as a dielectric has a high resistance. With a sharply decreasing resistance, it has a conductive property, i.e., varistor property. If we connect such an element, for example, a transformer, in parallel to our protective device, then the sharply rising waves will decrease, and the device will not detect high transient voltages [3].

Numerous experimental results show that the formation of the varistor effect in these materials is directly related to the presence of a potential barrier at the boundaries of the crystallite-amorphous phase [2]. Such a structure of ZnO causes bipolar conductivity in the specified material and the ability to change the resistance sharply at certain voltages. Note that such a characteristic as an electric current leakage largely depends on the uniformity of the distribution of alloying elements, which in turn determines height of the potential barrier [4]. On other hand, the observed sensitivity to the presence of oxygen atoms is a factor that has a certain effect on the dielectric permeability of ceramics. In fact, the detected dependence of the specified characteristic on the ratio of grain size to the thickness of the depleted layer is actually dependent of the oxygen absorption mechanism [5]. Additional evidence importance structural state of the ceramics, is especially dispersion of the phase components, are the results [6].

Indeed, the observed low breakdown voltage values for varistor sintered at higher temperatures are due to grain growth and a decrease at number of grain boundaries between the inner electrodes. In addition to the number of boundaries between phases, the thickness of the layer acquires a certain value. Based on this, an increase at layer thickness should contribute to an increase in the breakdown voltage [7]. Another problem of multi-phase varistor is the leakage current. The selection of the optimal structural state of the ceramics makes it possible to effectively decrease it. An example is the increase in the stability of secondary spinel particles $Zn_{2.33}Sb_{0.67}O_4$ during cooling of ceramics. Another factor by optimize state of structure is location insulating phase between the skeleton of bismuth-containing phases, which helps to reduce leakage current of the varistor by about two orders of magnitude [8].

As in [6, 7], at [9, 10] the importance a dispersion of the structural components is emphasized. Thus, for ceramics consisting of the main ZnO phase and oxides of rare earth elements the grain size significantly depends on the sintering temperature. An increase at sintering temperature by only 200°C is accompanied by an increase grain size up to 6 times and a decrease at nonlinearity coefficient by 2-2.5 times.

One of the factors that distinguishes ZnO ceramics from a varistor is the wide variation in its basic electrophysical parameters due to the introduction of a small number of impurities into them. It should be noted that one of the most promising areas for the development of protective devices and elements is the creation of two-phase and multiphase composite materials based on a ceramic varistor [5], [11-19].

2. METHOD OF ANALYSIS

For the manufacture of varistors, a ceramic charge of the composition (mol.%) $96.5ZnO + 0.5Bi_2O_3 + 0.5Co_3O_4 + 0.5MnO_2 + 0.5B_2O_3 + 1Sb_2O_3 + 0.5ZrO_2$ in an amount of 100 g is weighed and crushed in a ball mill to a particle size of 60 microns or less [20]. Then, granules are prepared from this mixture, which are pressed under a force of 40-ton force to obtain samples in the form of washers 10 mm high and 20 mm in diameter. After that, the samples are placed in an electric furnace for synthesis: heating to a temperature of 900°C is carried out at a rate of 150°C/h, and to a temperature of 1250°C at a rate of 200°C/h.

The properties of the reagents used and the composition of the varistor samples are shown in Tables 1 and 2. Synthesis of pressed washers takes place in atmospheric air, and the washers are annealed at a temperature of 1200°C for 2 hours.

After turning off the oven, the samples are cooled for 7-8 hours. These surfaces are vacuum deposited with a thin layer (3-4 mm) of aluminum to provide electrical contact. The height of the intergranular barrier φ_0=0.8 eV in ZnO oxides with surface-active ions (Bi, Co, Mn). The addition of ZnO to these ions complicates its structure.

Table 1. Properties of reagents used [20]

Properties	ZnO	Bi_2O_3	Co_3O_4	Sb_2O_3	MnO_2	Ni_2O_3	CrO_3	H_3BO_3
Quan.of main component,mas. %	99.96	99.97	99.97	99.96	99.95	99.3	99.93	9.96
Degree of dispersion, µm	0.3	5-10	0.5-2	0.2-1	0.3-3	0.5-4	0.5-2	0.5-3
Density 10^3 kg/m^3	5.6	8.9	5.68	5.2	5.18	7.45	4.98	3.2
Melting points,°C	1975	817	1805	655	1785	1957	break	break
Cation radius, mm	0.074	0.098	0.072	0.090	0.080	0.069	0.052	-
Type of electrical conductivity	N	p	p	p	p	p	p(Cr_2O_3)	p

Table 2. Composition of varistor samples [20]

Ingredient	Sample No. 1		Sample No. 2		Sample No. 3	
	mol%	Quantity in 500 g	mol%	Quantity in 500 g	mol%	Quantity in 500 g
ZnO	97	91.6	96.5	90.76	95.5	89.577
Bi_2O_3	0.5	2.7	0.5	2.69	0.5	2.6845
Sb_2O_3	1	3.4	1	3.368	1	3.359
Co_3O_4	0.5	1.398	0.5	1.392	0.5	1.3887
B_2O_3	0.5	0.41	0.5	0.404	0.5	0.403
MnO_2	0.5	0.51	0.5	0.502	0.5	0.4955
Cr_2O_3	-		0.5	0.878	0.5	0.876
Ni_3O_2	-	-	-	-	0.5	0.522
SiO_2	-	-	-	-		0.692

For example, when trivalent Ca is added to ZnO, adsorption surfactant centers are formed. The resulting this structure can localize free electrons [Ca^{3+}-O_2^-] Numerous experimental results show that the potential crystal barrier in ZnO stabilizes only in the range of 350-400°C, regardless of the type of impurity. In general, it is necessary to determine the mechanism of physical processes in bipolar conduction devices, to ensure the use of varistor materials for various purposes, and the stability of their properties [21-24].

When choosing various functional varisters made of semiconductor ceramic materials (for example, ZnO, SiC), it is necessary to take into account their crystalline conductivity, band gap, electrical conductivity of electric charges, and potential amplitudes at the interface between amorphous and crystalline phases. Consider the process of moving charge carriers in ZnO, which differs from a number of other semiconductor materials.

The process of moving electric charges in polycrystalline semiconductor ceramics based on ZnO is divided into two groups:
- the movement of electrons through a potential barrier.
- along the border of a potential barrier.

The first mechanism is the conversion of electrical carriers from crystallites to crystalline ones, and the second mechanism is breakthrough displacements. Despite the differences in voltage ranges and types of materials, the only working element of all ceramic varistors with a fuzzy structure is the crystallite boundary.

At present, ZnO-based varistors are widely used in high voltage technology to limit the increase in voltage (current) caused by various reasons. The non-linearity (β) of the current-voltage (U_{op}) of ZnO-based cells varies in the range of 50-70. This high non-linearity makes ZnO varistors indispensable compared to other semiconductors [20]. The ZnO varistors are connected in series and placed in a dielectric coating. One of the most important factors in the application of varistors is the stability of their parameters. To do this, electro thermal wear of the varistor is carried out: under the influence of an electric field, the barriers are heated to 403-423 K, and then cooled to room temperature. To protect them from the environment, the surface of the electrodes is varnished.

This process is repeated until the varistor opening voltage (U_{op}), non-linearity factor (β) and resistance (ρ) to the opening voltage stabilize. It is important that the varistor settings are protected from moisture in order for them to remain stable. The last operation of varistors is to place electrodes on their surface. The process is carried out as follows: the surface of the elements is chemically cleaned, silver pastes are placed on the surface and fired. To protect the electrodes from the environment, their surface is polished. ZnO is a semiconductor compound and is type A^2 B^6 [5].

The corresponding parameters of SiC, its band gap is larger than that of other semiconductors. Therefore, the non-linearity of the original ZnO must be greater after its opening voltage, since its coefficient of non-linearity is smaller. However, despite the band gap, due to the lack of oxygen during the firing process, the stoichiometry of ZnO is distorted and therefore has an n-type semiconductor. A very thin insulating region is formed among the ZnO crystallites, which ensures the formation of the varistor effect. The ZnO varistor, with a cross section of 1 cm^2, has a constant amplitude of several kA and can withstand high voltage surges up to the operating voltage [13, 14].

When studying the transport characteristics of inhomogeneous materials, an important role is given to the analysis of the dispersion of the dielectric parameters of the material (dielectric permittivity, dielectric losses, etc.). The dependences of the effective values of the permittivity and the dielectric loss factor on frequency are sensitive to the relationship between the electrical parameters of the dispersed phase and the matrix, as well as to the shape of the inclusions and their orientation in an external electric field [21]. Despite the wide range of applications in various fields of physics and chemistry [13, 15, 22], theoretical studies of the dispersion of the permittivity of heterogeneous media are hindered for a number of reasons, among which the following should be noted.

Analytical calculations of the effective parameters of multi component systems, which are of independent importance and are an integral part of the theory of dispersion of inhomogeneous dielectrics, are in themselves a complex mathematical problem that can be solved only in individual cases. The frequency dependence of the dielectric parameters, namely, the components of the complex permittivity, is a characteristic of the material and is determined for each substance not only by the properties of the material's molecules, but by the presence and composition of impurities [13, 16, 20]. Note that the addition of ZnO with additives of various composition directly affects their crystal structure and physical properties. Therefore, the determination and comparison of structure-sensitive physical properties and crystal structure, which are important for semiconductors, is one of the important issues [17-19], [22], [25].

It should be noted that the study of electrical conductivity is one of the main methods used to determine the purity of materials, mainly metals and emiconductors. In addition, electrical conductivity makes it possible to clarify the dynamics of current carriers in a macroscopic object, the features of their interaction with each other and the object with other objects.

The mechanism of electrical conductivity in dielectric materials is more complex than in semiconductor materials. This is due to the fact that the movement of electric charge carriers (electrons, holes) in these materials is hindered by various factors, for example, defects in the crystal lattice, including deep and shallow traps of energy levels in its band gap, scattering of the lattice crystal from thermal vibrations, etc. d. available [19]. Figure 1 shows the conductance as a function of frequency.

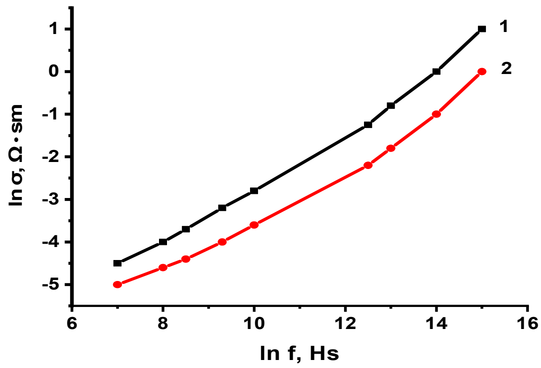

Figure1. Dependence conductivity from frequency (ZnO with impurities)1-303 K, 2-344 K [21]

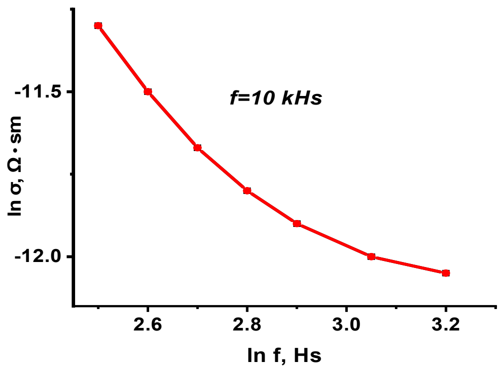

Figure 2. Conductivity versus temperature at f=10 kHz (ZnO with impurities) [21]

Figure 1 shows that in the low-frequency region, the electrical conductivity increases monotonically, and then increases strongly with increasing frequency. In this case, the electrical conductivity σ changes according to the law $\sigma \approx f^{0.8}$. The dependence $\sigma \approx f^{0.8}$ obtained indicates a hopping mechanism of charge transfer over states localized in the vicinity of the Fermi level [18]. Note that at the temperatures under study, the $\sigma=F(f)$ dependence has the same character [21]. Figure 2 has shown the temperature dependence of conductivity at f=10kHz.

It can be seen from the experiments and Figure 2 that the conductivity decreases with the temperature dependence. Note that the frequency dependence of the dielectric parameters, namely, the components of the complex permittivity, is a characteristic of the material and is determined for each substance not only by the properties of the material's molecules, but by the presence and composition of impurities [21].

3. CONCLUSIONS

The article describes the electrical properties of the intercrystallite boundary and mechanisms of conductivity in a ZnO varistor with impurities. It has been established that conductivity is possible during physical processes both at the intercrystallite boundary and through a potential barrier. And the dependence of conductivity on frequency and temperature was shown. It was found that the frequency dependence of the dielectric parameters is a characteristic of the material and is determined for each substance not only by the properties of the molecules of the material, but by the presence and composition of impurities. ZnO ceramic varistors with all these advantages, proven in experiments, are synthesized with polymers to produce high-quality composites for the energy field and are successfully applied [11-19].

NOMENCLATURES

1. Symbols / Parameters

β: Coefficient non-linearity

U_{op}: Opening voltage

φ: Height of the intergranular barrier

ρ: Resistance

σ: Electrical conductivity

f: Frequency

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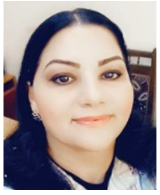

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