

SOME ELECTROPHYSICAL CHARACTERISTICS OF ZINC OXIDE BASED VARISTORS

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ABSTRACT

The present work is devoted to studying the temperature influence on current -voltage characteristics and electrical conductivity of the ZnO based varistors. It is shown, that observable nonlinearity of voltage- current characteristics (VCC), exponential temperature dependences of electric conductivity and nonlinearity factor and also reduction of researched opening voltage of varistors are conditioned by the zinc oxide grains boundaries. The hysteresis on VCC in all temperatures interval is observed at that the width of the hysteresis loops is increased by temperature growth, that is explained by existing of the dipole moments of inserted oxide impurities of Co, Mn type and etc.

1. INTRODUCTION

Now with development of the microelectronic technology and the big integrated circuits, for protection of power supply systems and electric circuits from the overvoltage the requirement for different kinds of the accident protection devices, including on the basis of varistors, is continuously increased [1-3]. It is connected by the varistors nonlinear characteristics that allow them to be long time under the working voltage and to protect sufficiently the electrical lines from overvoltages.

In turn the varistors properties are very sensitive to theirs production conditions, that can influence on theirs grains size, thickness and intercrystalline phases physical properties [4-7]. Particularly, an important problem connected with the varistors production perfection is influence of the ambient temperatures on varistors electrical properties.

In the present work the research of temperature dependence of the zinc oxide based varistors electric properties is carried out.

2. EXPERIMENT, RESULTS AND DISCUSSIONS

For varistors preparing the oxides with cleanliness of 99,9 % have been used. The ZnO based varistors with impurities of CoO, BiO₃, MnO₂, ZrO₂ and others oxides have been made on standard ceramics technology. Samples have been synthesized at T=1500°C in an air atmosphere. The densely sintered samples have been covered by silver electrodes. For all samples the VCC and electric conductivity measured in a direct current mode at various temperatures are investigated. Results of experiments are presented on fig. 1-4, from which the following are visible: 1) the volt-ampere characteristic in the investigated temperatures interval has nonlinear character. The value of current through the varistor increases for 4 order and also 3-4 characteristic areas are observed on I=f (U) curves; 2) with growth of heating temperature the I = f (U) curves are displaced in the low electric voltage area, in addition the value of varistors opening voltage (classification voltage) decreases (fig.4); 3) dependence of electric conductivity σ from electric field intensity has exponential character (fig.2); 4) in the all temperatures interval the hysteresis on I=f (U) curves is observed (fig.4)..

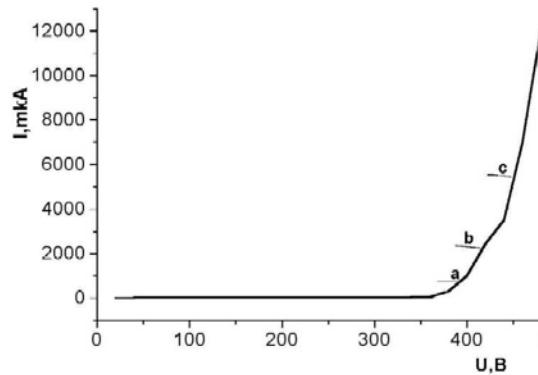


Fig.1. Volt-ampere characteristic of varistor at the room temperature

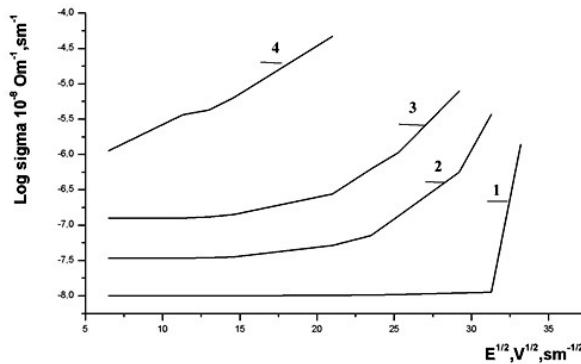


Fig.2. Dependence of electric conductivity of varistor from the electric field intensity.
1 - 295 K; 2 - 383K; 3 - 420K; 4 - 463K.

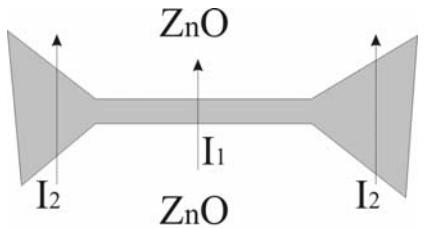
Note that during the formation of varistors electric properties the follows plays a special role: 1) continuous conductivity through potential barriers of intercrystal borders (an intercrystal barrier layer); 2) conductivity lengthways of intercrystal borders without participation of crystal grain [8]. According to works [4,6,10] potential barrier layers represents the contacts between two adjacent grains of zinc oxide. In turn, the reason of these barriers formation is modulation of semiconductor's power zones by a field of the charged impurities and defects adsorbed at the intercrystal borders.

From above-stated it is follows that electric properties of the zinc oxide based ceramics are determined by the value of current, which passes through consequence chains of contacts between the adjacent grains of ZnO [7]. For each such contact it is conditionally possible to allocate two components of a direct current (fig.3a).

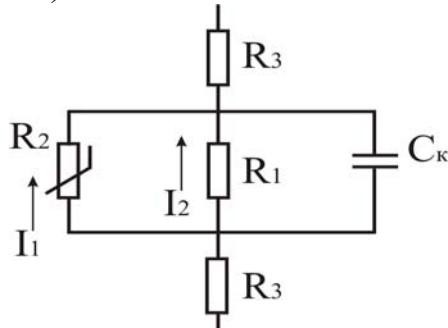
On fig. 3a the phase between nodes of zinc oxide is shaded. As such phase there can be a layer enriched with bismuth and antimony [9]. From figure 3a it is visible, that the component of current I_1 passes through the borders areas where adjacent grains of ZnO closely abuts to each other. Thickness of contacting layer can make about $(30-40)\text{\AA}$. In this borders area the energy barrier is formed that responsible for high nonlinear part of ceramic's VCC. Other component of current I_2 is determined by resistance of borders area where adjacent grains ZnO are separated by a thick layer of the internodes phase. For I_2 the weak nonlinear $I=f(U)$ dependence is specific.

Considering above - stated, it is possible to present the equivalent circuit of separate contact between the ZnO grains as shown on fig. 3b. On this circuit R_3 is resistance of ZnO grain, R_1 is resistance of the intergrains phase, C_k is geometrical capacity of contact of two ZnO grains, R_2 is nonlinear resistance of contact area of through which the current I_1 passes.

In view of above-stated experimentally observable specific areas on fig.1,2 can be explained as follows. As it is shown from fig. 1,2 at low values of the applied voltage the value of an electric current is small and makes microamperes, thus the value of electric conductivity is accordingly equal $10^{-6}\text{-}10^{-8} \text{ Ohm}^{-1}\text{cm}^{-1}$.



a)



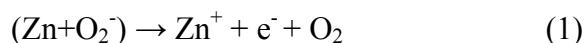
b)

Fig.3. Schematic representation of ZnO grain contact area (a) and its equivalent electric scheme (b).

These data show that at initial moment of time the varistor behaves as dielectric which has the high resistance (R₁). This resistance is caused by presence of potential barriers between adjacent ZnO grains. At low values of an electric field the value of this resistance high enough, it plays the basic role and limits value of a current through the varistor. As a result of it at low values of an external field weak dependence I=f(U) (part "a", fig.1) is observed. With growth of the applied voltage the current value is determined by resistance R₂ which has nonlinear character. With increase an applied voltage the value of this resistance sharply decreases and falls up to 10-100 Ohm. As a result of it there is simultaneously a growth of conductivity on 2-3 order and accordingly of current through the varistor (parts b,c). Besides as is obvious from fig.2, the number of specific areas and their activation energy is decreased, also at temperature 190°C and above the varistors conductivity has the ohmic character.

Experimentally observable temperature dependences of an electric current, electric conductivity, classification voltage and nonlinearity factor also are confirming factors which show a determining role of grains border on transit of current carriers through the varistor.

The matter is that a condition (unsoundness) of a surface and volume of zinc oxide crystal grains are strongly connected to presence of excess atoms of zinc. As a rule, excess atoms of zinc occupy the internodes of a lattice and, disposed the electrons, become the donors. Growth of electric conductivity can be explained by that with rise in temperature the height of intercrystal potential barriers strongly decreases. The reason for this can be as growth of the current carriers number due to ionization of traps, as well as change of a charging condition of oxygen on the grains borders, namely, decomposition of an unstable superficial condition between internodes cations Zn⁺ and chemisorbed oxygen (Zn+O₂⁻) by reaction



From the equation (1) it is visible, that as a result of this reaction the electrons concentration increases. It in turn, according to figures, results to reduction height of intercrystal potential barrier, to growth of sample conductivity and, as consequence, to reduction of VCC steepness. As a result it turns out observable reduction values of nonlinearity factor and classification voltage.

Basically according to [11] at temperatures higher than 400°C the conductivities of crystal grains and borders of grains are leveled and as a result it the nonlinear characteristic of the varistor disappears.

Exponential character dependence of electric conductivity from intensity of an electric field (fig. 2) is well described by effect and formula of Pool-Frankel

$$\sigma = \sigma_0 \exp \frac{e^{3/2} E^{1/2}}{kT(\pi\epsilon\epsilon_0)^{1/2}} \quad (2)$$

where σ_0 is conductivity at a weak electric field, ϵ is dielectric permeability of the varistor, ϵ_0 is electric constant, k is Boltzmann constant, E is intensity of an electric field, T is absolute temperature.

Note that in formation of intercrystal borders between atoms an important role plays also interaction between the zinc oxide and impurity atoms. In work [9] by means of electron-diffraction researches it is shown, that as a result of these interactions the continuous phase inclusions and also a continuous number of interchanging solid solutions are formed, which well described by formula Zn_{1-x}SbxO ($x=0,1\%$ mol.).

A principal cause of an observable hysteresis on I=f(U) curves (fig.4), apparently, is presence the own dipole moments of impurity atoms (Co, Cr, Mn etc.) contained in the varistor.

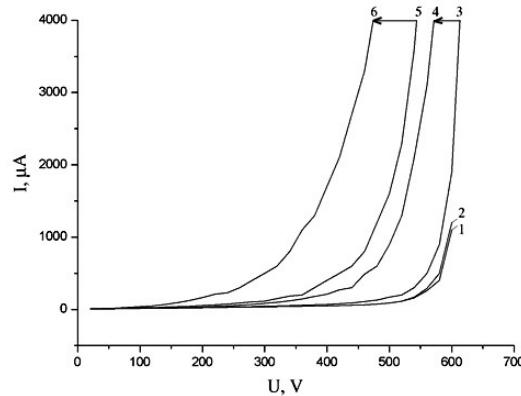


Fig.4. Volt-ampere characteristic of varistor at the various temperatures:
1-2 - 295K; 3-4 - 323K; 5-6 - 373K.

The dipole moments of superficial conditions of two contacting surfaces at absence of an external electric field at first time are chaotic oriented. Therefore transitions between contacting adjacent grains are complicated by the Coulomb repulsion. With growth of the applied voltage (in a forward direction) there is an orientation of the majority dipole moments along a direction of electric field intensity. At VCC reverse, apparently, not all dipole moments have time for off-orientation. Therefore there is an observable hysteresis on curves I=f(U). Expansion of hysteresis loops with temperature increasing, apparently, is connected by that under action of temperature the off-orientation of the dipole moments oriented under action of an electric field is occurs, and their chaotic distribution increase that is confirmed by the experimental fact, namely by the expansion of hysteresis loop.

3. CONCLUSIONS

Thus, the analysis of the obtained results allows making the following conclusions:

1) The reason of high resistance of the varistor (10^8 Ohm) at low values of an external voltage is presence of potential barriers on the borders between the ZnO grains which are formed during synthesis of the varistor;

2) Observable nonlinearity VCC of researched samples allows assuming that electric conductivity and also other important parameters, such as nonlinearity factor and classification voltage, are conditioned by borders of zinc oxide grains. With growth of

temperature and intensity of an electric field the height of intercrystal barriers is reduced and by that influence of a transitive layer on electric properties of the varistor strongly decreases.

3) Observable hysteresis phenomenon is connected to action of two factors, namely, orientation of the dipole moments with growth of electric field intensity and their off-orientation with increase of annealing temperature.

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ZnO ƏSASINDA VARİSTORLARININ BƏZİ ELEKTROFİZİKİ XARAKTERİSTİKALARI

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Məqalə sink oksidi əsasında hazırlanmış varistorların voltamper xarakteristikalarına və keçiriciliyinə temperaturun təsirinin tədqiqinə həsr olunmuşdur. Göstərilmişdir ki, voltamper xarakteristikasının qeyrixətliliyi, elektrik keçiriciliyinin və qeyrixətlilik əmsalının eksponensial asılılığı və klassifikasiya gərginliyinin azalması tədqiq edilən nümunələrdə sink oksid dənələrinin sərhədi ilə müəyyənləşir. Temperaturun bütün intervalında voltamper xarakteristikasında histerezis müşahidə edilmişdir. Temperaturun yüksəlməsi histerezis əyrisinin eninin böyüməsinə səbəb olmuşdur. Bu hal daxil olunan Co, Mn aşqarlarının dipol momentləri ilə bağlıdır.

НЕКОТОРЫЕ ЭЛЕКТРОФИЗИЧЕСКИЕ ХАРАКТЕРИСТИКИ ВАРИСТОРОВ НА ОСНОВЕ ZnO

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Данная работа посвящена изучению влияния температуры на вольтамперные характеристики и электропроводности varисторов на основе оксида цинка. Показано, что наблюдаемая нелинейность вольтамперной характеристики, экспоненциальная зависимость электрической проводимости и коэффициента нелинейности, а также уменьшение классификационного напряжения исследуемых образцов обусловлены границами зерен оксида цинка. Во всем интервале температур наблюдается гистерезис на вольтамперных кривых, причем с увеличением температуры ширина гистерезисной петли увеличивается, что объясняется наличием дипольных моментов вводимых примесных оксидов типа Co,Mn и др.