

Electrical Characteristics of Nonlinear Polymer-Solid Solution Composite Resistors

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Abstract: *The varistor effect was observed in composites on the basis of a nonpolar polymer (polyethylene) and the $(\text{CuInSe}_2)_{1-x}(\text{CoSe})_x$ $x = 0.1$ chalcopyrite phase. It was found the influence of components of the composite to current-voltage characteristics in the value of the resistivity and dielectric permeability.*

Keywords: *solid solutions, diffractogram, polymer, semiconductor, current-voltage characteristics.*

1. INTRODUCTION

In recent years, has become more urgent question of creating materials that would simultaneously possess magnetic, optical and semiconductor properties [1-5]. For example, the introduction of atoms of transition elements with unfilled 3d-shell in ternary semiconductor type $A^I B^{III} C_2^{VI}$ and $A^{II} B^{IV} C_2^V$ results in new materials that combine both semiconducting and magnetic properties [1-4]. Introduction of the manganese atoms in the compound $A^I B^{III} C_2^{VI}$ made it possible to obtain materials with Curie temperature of 350 K. intensively also conducted research on the effect of manganese and iron atoms on the properties of ternary compounds $A^I B^{III} C_2^{VI}$ for creating high-performance solar energy converters. However, despite high values of efficiency $\sim 20.3\%$ of solar cells based film Cu (In, Ga) Se_2 as compared with other semiconductor materials, this value does not match the theoretically expected $\sim 30\%$ for this class of materials. Reasons for this are multi-component chemical composition, the lack of accurate data on many important fundamental parameters of materials, limited and contradictory information about the nature of their own growth defects in these semiconductors and their energy levels in the forbidden zone, determining the recombination processes. Of course, the further development of the physics of semiconductors with the chalcopyrite structure can be an important step in improving technology and efficiency values approaching \sim to the theoretical 30%. Currently, the most promising compound semiconductor, which can be used for solar cells and compete with silicon and gallium arsenide is a ternary compound type CuInSe_2 [1].

CuInSe_2 -semiconductor with a band gap of 0.96 eV belongs to the group of diamond semiconductors $A^I B^{III} C_2^{VI}$ which are characterized by the presence of a chalcopyrite structure. Great interest in CuInSe_2 and solid solutions based on it due to the fact that the complex electron energy spectrum and anisotropy of the optical properties allow you to create based on chalcopyrite crystal light emitting diodes, photo detectors, solar cells, coherent and incoherent sources of polarized radiation. In the present paper presents the results of experimental studies of the electrical conductivity of solid solutions on the basis of $(\text{CuInSe}_2)_{1-x}(\text{CoSe})_x$ $x = 0.1$ (SS-solid solutions) in a constant electric field.

One of the effective methods used to modify polymers with the aim to obtain their necessary properties is to employ various fillers. Moreover, two and multiphase composite materials can also be used, in particular, composites based on the polymer filler system (semiconductors, ferroelectrics, etc., can be used as fillers) that exhibit varistor, posistor, and piezoresistor properties [6-8]. These properties are linked with the formation of a potential barrier at the phase interface, i.e., on the interface between the particles of the polymer and filler. The formation of various properties of composites and parameters of the potential barrier formed at the phase interface strongly depend on the structure and electro physical parameters of the particular individual phases and on the phenomena at the polymer–filler interface. Therefore, the variation of the composite composition is promising for the creation of novel more effective materials with the necessary complexes of properties for various domains of engineering. Note that, nowadays, nonlinear resistors on the basis of composite materials are widely used for the protection of equipment of automation, microelectronics, and electrical

engineering from lightning or switching surges. The mode of functioning of composite nonlinear resistors is based on their property of changing the resistance under the action of various external factors, such as the temperature, mechanical stress, electric voltage, and so on. In this connection, the development of low voltage nonlinear varistors (resistors) with various combinations of composite materials is a topical problem.

2. METHODS

CuInSe₂ ternary compounds were synthesized from ultrapure elements (indium In-000 brand, high purity selenium 17-3, electrolytic copper). Synthesis of the samples was performed in a vertical furnace evacuated (~ 0.1 Pa) in quartz ampoules follows: the oven temperature was raised at 800 C / hour to 700° C and the vials were held at this temperature for 2 hours, then the temperature was raised to 1050 - 1100° C. The synthesis process was continued for 8 hours to bring to a state of synthesized samples, as close as possible to equilibrium, they were annealed at 600°C for 500 hours. To obtain the desired semiconductor resistors previously been milled in a ball mill with porcelain balls to the size of the granules 60 μm or less. Resistors were obtained from a homogenous mixture of the components by hot pressing at 180°C and a pressure of 15 MPa. Contents of the components vary over a wide range (respectively, 15-40% dispersant and 85-60% PP). The resulting film composite varistor is cooled by quenching in water. With this method of cooling of the film are more elastic. The sample thickness was 150 μm. Measuring 6 mm diameter electrodes were made by applying silver paste samples.

In X-ray diffraction analysis of samples held at room temperature C_uK_α-emission by setting Diffraktometr D8 Advance. Electrical conductivity was measured by the probe compensation method. Measuring parameters held constant current. While measuring the voltage drop across the probes were carried out in two directions of the current. As used compensator DC potentiometer R348. Relative measurement error composes 2%.

3. RESULTS AND DISCUSSION

From the analysis of the phase diagram of established [9] that the solubility in FeSe system (CuInSe₂)_{1-x}(CoSe)_x is equal to 10% of the diffraction pattern (Fig. 1) shows single-phase solid solution (CuInSe₂)_{1-x}(CoSe)_x (x = 0.1). Figure 1 shows that the crystal structure of the compound refers to the ordered structure of chalcopyrite, which follows from the presence of the typical reflections of the type (112), (220/204), (116/312), (316/332).

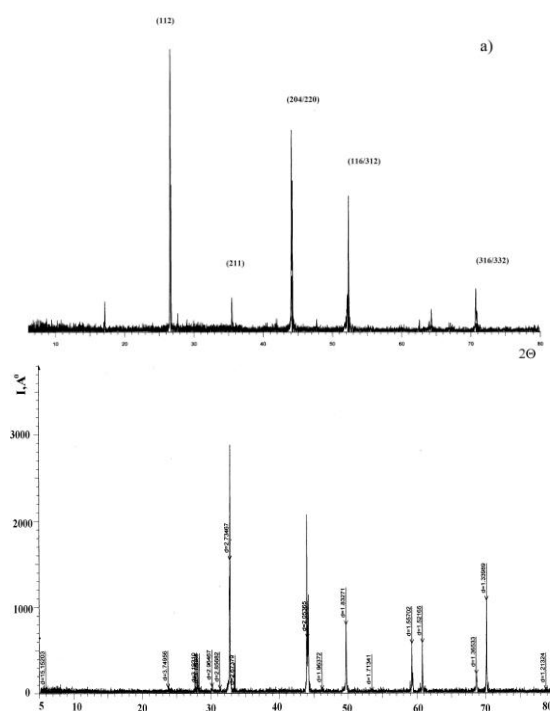


Fig1. Diffractogram

a- CuInSe₂; b- (CuInSe₂)_{1-x}(CoSe)_x(x=0.1)

For all samples, we analyzed the I-V characteristics and resistivity as functions of the volumetric concentration of the filler (SS). Measurements were taken at $T = 293$ K.

The experimental results are presented in Figs. 2 and 3. Figure 1 shows that the dependence of the resistor current on the applied voltage is nonlinear for all samples.

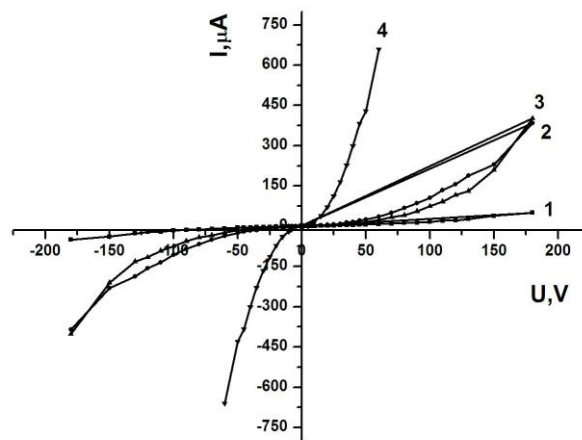


Fig2. Current -voltage characteristics of the composites with different concentration of solid solution

90mol%CuInSe₂ + 10mol %CoSe.

1-15%SS+85%PE; 2-1-20%SS+805%PE;

3-25%SS+75%PE; 4-40%SS+60%PE

(Fig.2) CVC is highly linear, namely, the sharp growth (2-3 orders) of electric current's value with increasing of applied voltage is observed. This is an important factor for the creation of composite varistors, and the voltage dependence of samples' electrical conductivity has the exponential character, the opening voltage of varistor is changed in the range of (8-10) V. An increase in the percentage of filler increases the current value depending on the voltage. This is due to the fact that, with increasing percentage of filler properties of the composite is determined by properties of the filler. Because of this, in the composite electrical current №4 applied voltage is more than in the other samples.

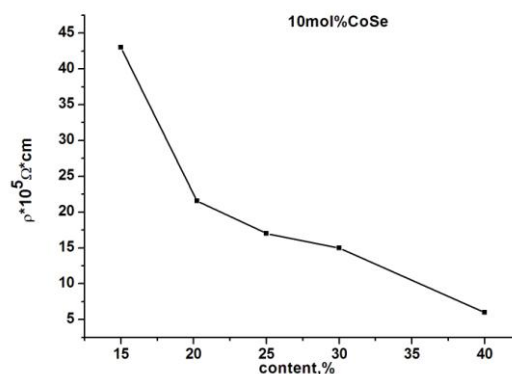


Fig3. Dependence of the resistivity of the composite on the filler percentage CuInSe₂-10mol%CoSe (at 50 V)

At a low content of filler, due to large thickness of polymer interlayer between the filler particles, the magnitude of the potential barrier is high (see form. 1). The dependence of the tunneling resistance R on the magnitude of the potential barrier has an exponential form. Therefore, the probability of tunneling of carriers through a thick barrier is low, and the contribution of the tunneling conductance will be negligible. Consequently, the resistance of the composite will be determined, basically, the resistance of the polymer. At further increase in the percentage of filler, the thickness of polymer interlayer between the filler particles decreases, the average number of contacts between the particles increases, continuous chains begin to be formed and, consequently, the magnitude of the potential barrier decreases, and, according to formula 2,

$$\varphi = \frac{e^2 n_d b^2}{2\varepsilon_n \varepsilon_0} \quad (1)$$

$$R \sim \exp\left(\frac{\varphi}{kT}\right) \quad (2)$$

the value of tunneling resistance decreases exponentially.

As a result, the tunneling probability of carriers through the potential barrier will increase exponentially, the conductivity of the composite increases and, consequently, its resistivity decreases.

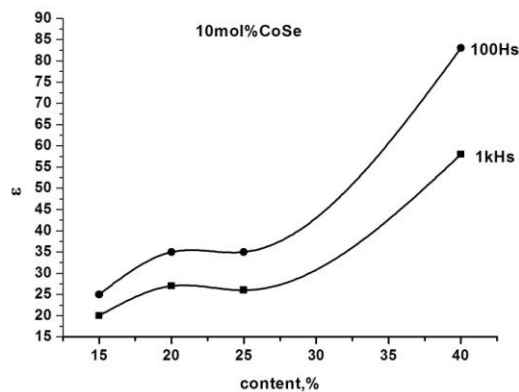


Fig4. Dependence of dielectrically permeability on semiconductor content

The observable growth of composite dielectric permeability can be imagined as follows. First, the dielectric permeability of filler almost on 1,5 orders is more than the dielectric permeability of polymer, therefore the contribution of ceramics in change of composite dielectric permeability much more, than polymer. Secondly, with increase of filler content its particle settle down to each other more densely, thickness of polymeric layers between the filler particles decreases, and it in turn leads to growth of a local field on these layers and, thereby, to increase of polarizability of these layers and therefore to increase of composite dielectric permeability.

As it is shown from figure, divergences between the calculated and experimental values of dielectric permeability take place. At that, the higher the filler content in composition the more this divergence. Evidently, this divergence is caused by that the two-phase system consisting of the continuum with dielectric permeability ε_1 and the filler particles with dielectric permeability ε_2 statistically distributed in the continuum is considered in Maxwell-Wagner model, and influence of polymer layers polarizability is not considered. Therefore values of composite dielectric permeability, obtained on experimental data higher than values calculated on Maxwell-Wagner model [6].

4. CONCLUSION

The technology of producing composite resistors on the basis of semiconductor materials and polymers will allow creating different low-voltage and low power-consuming composite varistors for using in microelectronics and other areas of science and technology.

The analysis of the experimental results again confirms that the mixture of polymer and filler is not completely mechanical; there are interphase interactions between them.

Influence of components contents of a composite on volt-ampere characteristics, on electric conductivity (specific resistance value) is revealed.

Revealed that, With increase of filler content its particle to each other more densely, thickness of polymeric layers between the ceramics particles decreases, and it in turn leads to growth of a local field on these layers and, thereby, to increase of polarizability of these layers and therefore to increase of composite dielectric permeability.

REFERENCES

- [1] Koutsa T., Mikina J.M. Modern problems of the semiconductor energy. Mir, 307, (1988) (in Russia)

- [2] Bodnar I.V., Rud V.U. Photoelectric properties of Schottky barrier In/n-CuInSe₂, Journal of Applied Spectroscopy. 73 (4), 502 (2006) (in Russia)
- [3] Hacıyev T.M., Babaev A.A., Magamedova Dj.X., Hohlachev P.P. Properties film CuInSe₂, obtained by the methods and selenization kvazirovannyh precipitation, Inorganic materials. 44 (12), 1436 (2008). (in Russia)
- [4] Shklovskiy B.I., Efros A.L. The electronic properties of doped semiconductors. M., Nauka, (1979) (in Russia)
- [5] Mott N., Devis E. Electronic Processes in Non-Crystalline Materials, M: Mir, (1974). (in Russia)
- [6] Souza F. I., Gomes J. W., Bueno P. R. Mater. Chem. Phys. 80, 512 (2003). (in Russia)
- [7] Geil P. H., Polymer Single Crystals. Wiley, New York, 1963; Khimiya, Moscow, (1968) (in Russia)
- [8] R.Dj., N.M. Allazova, Babanli M.B. Study of CuInSe₂-FeSe, News of Baku State University, N1, 20 (2005) (in Russia)

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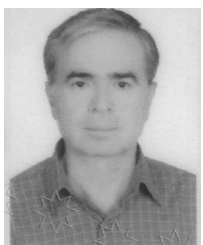


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