Manufacturing technology of photovoltaic devices based on layered compositions and their properties

A. V. Umarov[1,2*], *D. K.* Djumabayev[1], *B. A.* Mirsalikhov[1], and *G. A.* Kasimova[1]

[1]Tashkent state transport university, Tashkent, Uzbekistan
[2]Tashkent University for Applied Science, Tashkent, Uzbekistan

Abstract. The paper considers the manufacturing technology and study of the mechanisms of operation and properties of layered electrical compositions, as well as the study of the possibility of obtaining effective photoelectric converters on their basis.

1 Introduction

The main reason for the delay in the large-scale application of solar converters is primarily due to the high cost of solar cell manufacturing technology. Therefore, in this issue, a special place is occupied by the creation of solar energy to generate cheap electricity on a commercial scale. For large-scale application of semiconductor photoelectric converters, it is necessary, on the one hand, to modernize their manufacturing technologies, and, on the other hand, to synthesize new materials based on various elements. That is the reason why researchers are continuing to research at an accelerated pace to improve technology and develop new materials based on various elements that are promising for the manufacture of solar cells.

Layered composites such as Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe), and their solid solutions CZTSSe are promising materials for the manufacture of solar photoconverters [1-4]. In terms of optical properties, they favorably differ from other compounds of this class. However, studies of the patterns of formation of layered compositions, studies of their electrical and optical properties, depending on the technological mode of production, have not been studied.

2 Objects and methods of research

For the production of prototype photovoltaic devices based on processed thin layers from chemical solutions, glass substrates / indium-tin oxide with a resistance of 4 ohms were used, which were sonicated in acetone or isopropyl alcohol for cleaning, then washed with distilled water and dried in a stream of hydrogen or directly in centrifuge boat. Later, indium tin oxide was spin-coated over the substrates at 1500 rpm into a poly(3,4-ethylenedioxythiophene) (PEDOT) buffer layer: 120 nm thick. Then, solutions were

---

*Corresponding author: abdusalom@inbox.ru applied over this layer, both by drop method and by centrifugation. saturated ZnPc/FA, ZnPc:I_2/FA, ZnPc:PTCDI/FA and ZnPc:I_2:PTCDI/FA. After drying thin layers at room temperature, some of them were thermally treated according to the data in Table. 2.3. Aluminum electrodes were deposited by thermal evaporation in high vacuum from molybdenum and/or tungsten boats. For evaluation purposes, the photovoltaic parameters were measured both immediately after the manufacture of the devices, and removing them from a high vacuum, as well as after exposure to room air for certain periods of time (2 hours -72 hours → 6 months).

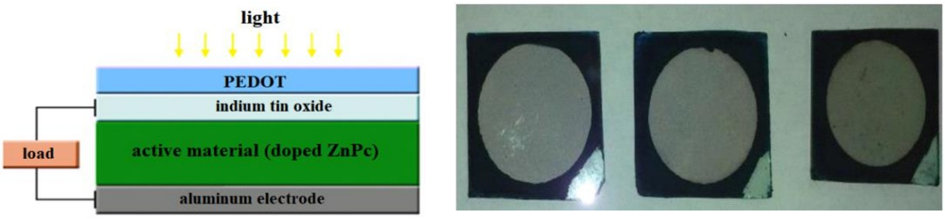

Fig. 1. Scheme of photocells glass/indium-tin oxide/poly(3,4-ethylenedioxythiophene) polystyrenesulfonates/zinc phthalocyanine/Aluminum (a) and images of three real devices with a given structure (b).

Initially, experimental studies were carried out on solar cells processed from solutions, with configurations: PEDOT / indium-tin oxide / zinc phthalocyanine / Aluminum and poly (3,4-ethylenedioxythiophene) / indium-tin oxide / zinc phthalocyanine / I_2 / Aluminum with various thicknesses (2.1-8 μm) active layers of zinc phthalocyanine are processed from solutions with a 98% FA concentration as a solvent. On fig. 1 shows a diagram of photocells and images of three real devices of this type.

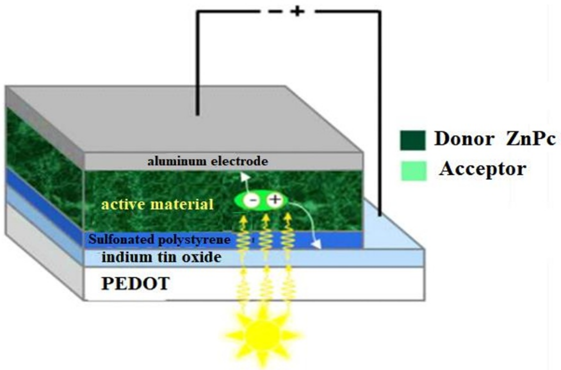

Fig. 2. Scheme of a photocell treated with a solution of PEDOT / indium-tin oxide / zinc phthalocyanine: PTCDI / Al as a layered composition.

Further experimental studies were carried out on samples obtained on the basis of layered compositions of poly (3,4-ethylenedioxythiophene)/ indium tin oxide/zinc phthalocyanine: PTCDI/Al and PEDOT/ indium tin oxide/zinc phthalocyanine: PTCDI: I_2/Al. The scheme of photocells of the “layered composition” type is shown in fig. 2.

In the course of research, due to the fragility of aluminum electrodes, after several measurements, the contacts were damaged (Fig. 3), which made further measurement of photoelectric parameters impossible. To solve this problem, an experimental verification of the following assumptions was proposed:

- Improvement of contacts by heat treatment of samples in vacuum, at different temperatures, in hydrogen atmosphere and in inert atmosphere.
- Cold welding of conductive metal wires with aluminum electrodes.
- Use of conductive adhesives (containing metal powder as a dispersive phase) as a contact element between conductive foils and aluminum electrodes.

Fig. 3. Photocell surface image with damaged aluminum electrode

Experimental studies have shown that the heat treatment of samples (Fig. 4) improves the contacts between the aluminum electrodes and the layered composition. However, even after the heat treatment of the samples, the risk of structural damage remained particularly high.

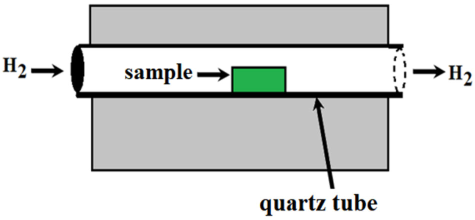

Fig. 4. Scheme of installation for heat treatment of samples

Another series of experimental studies showed that the use of conductive adhesives (containing metal powder as a dispersive phase) as a contact element between conductive foils and aluminum electrodes is an effective solution to the problem under consideration. An adhesive containing silver powder "Contactol" was used as a binding element. The use of this adhesive in the short term does not affect the photovoltaic parameters and the reliability of the devices. Cold welding of conductive metal wires with aluminum electrodes has yet to be applied in future research.

3 Results and their discussion

Figure 5 shows the effect of applied voltage on electric current through a layered PEDOT/Indium-Tin Oxide/Zinc Phthalocyanine/Aluminum composition with both an embedded and non-embedded ZnPc/FA layer. These structures clearly show the straightening behavior in the dark, which is enhanced by the incorporation of iodine. The active surface of ZnPc is about 1.5 cm^2, the layer thickness is about 5 µm. The void concentration in ZnPc is 1.02×10^{11} cm^{-3}, and in indium-tin oxide it is 2.7×10^{20} cm^{-3}. By applying a negative voltage to the Al electrode, the current strength was measured at various voltage values in the range from 0 V to 10 V at room temperature. From a study of the effect of voltage on the forward bias electric current of PEDOT/indium tin oxide/zinc phthalocyanine structures with both interstitial and non-embedded ZnPc layer, we observe asymmetric behavior and improvement in electrical conductivity after iodine incorporation into the ZnPc layer.

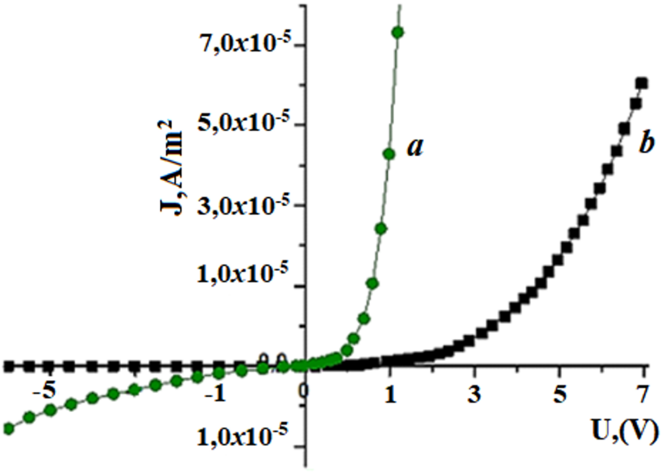

Fig. 5. Effect of applied voltage on electric current through PEDOT/indium tin oxide/zinc phthalocyanine/Aluminum and PEDOT/indium tin oxide zinc phthalocyanine:I_2/Al layered composition.

It is noted that at low values of direct voltage, the current changes with voltage according to a linear law, and at high values of voltage, the dependence of current density on voltage has an exponential character. The dynamic resistance Rd is determined experimentally by the linear slope of the characteristic shown, according to the dependence:

$$R_d = \frac{\Delta U}{\Delta J} \qquad (1)$$

As a result of the introduction of iodine into the ZnPc layer, the dynamic resistance of the composition PEDOT/indium tin-tin phthalocyanine zinc decreased from $R_d=3.8 \cdot 10^4$ Ohm·m^2 to a value of $9 \cdot 10^3$ Ohm·m^2. To determine the mechanism of current transport through the structures under study, the direct branches of the studied characteristics were reconstructed on a logarithmic scale (Fig. 6). Two linear slopes are observed, which confirm the different mechanisms of transport of electric charge carriers when different forward voltages are applied. The exponential dependence at higher voltages can be explained by the formation of a space charge region between Al and ZnPc. We observe that when voltages are applied above 0.6 and 1.0 V at room temperature, the so-called Schottky barrier effect disappears.

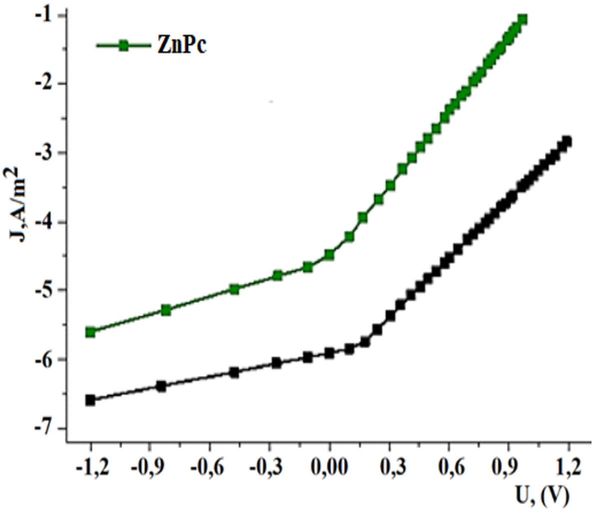

Fig. 6. Influence of applied voltage on electric current through logarithmic-scale straight-leg layered composition of PEDOT/Indium Tin Oxide/Zinc Phthalocyanine with doped and undoped ZnPc layer.

For forward bias, the slopes in the voltage range up to approximately 1 V indicate that the value of m is on the order of unity, which describes an ohmic conduction mechanism. The current density in the region of ohmic conduction is described by the equation:

$$J = p_0 e\mu \frac{u}{d} \qquad (2)$$

where the concentration of thermally generated voids (p_o) is determined by the equation [5]:

$$p_0 = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]. \qquad (3)$$

where (E_F - E_v) is the distance of the Fermi energy level from the edge of the valence band, N_v is the density of states in the valence band. Substituting (3) into (2), we obtain the electric current density:

$$J = N_v e\mu\left(\frac{u}{d}\right)\left[\frac{-(E_F - E_v)}{kT}\right]. \qquad (4)$$

According to publications [6-11], the Nv value for ZnPc is about 10^{27} m^{-3}, which corresponds to approximately one electronic state per molecule. On fig. Figure 7 shows the dependence log(J/U)=f(10^3/T) in the ohmic region for iodine-embedded and non-embedded ZnPc layered compositions. Fig. 7 indicates a single level of the electron trap with energy E_t above the edge of the valence band.

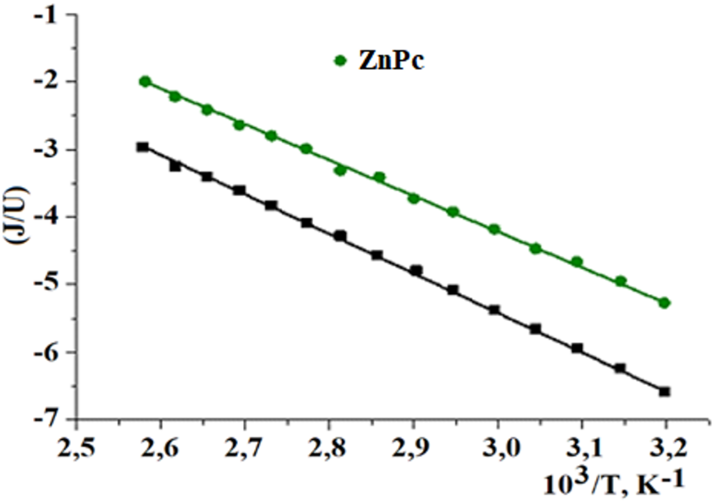

Fig. 7. Dependence log(J/U) = f(10^3/T) in the ohmic region of the composition PEDOT/indium tin oxide zinc phthalocyanine with and without interstitial ZnPc layer.

From the slopes of the characteristics in Fig. 7 the value (E_F-E_v) is determined and the intersection at (1/T)=0 on the current axis will give us the value of the product (μN_v) between mobility and void concentration. These values are presented in Table 1.

Table 1. Electrical parameters E_F, μ and po of a layered composition of PEDOT/Indium Tin Oxide/Zinc Phthalocyanine with and without embedded ZnPc layer.

Options	indium tin oxide/ zinc phthalocyanine/Aluminum	zinc phthalocyanine/Aluminum doped indium tin oxide/I_2
$E_F\ (eV)$	0.53	0.42
$\mu (cm^2/V \cdot s)$	$1.2 \cdot 10^{-2}$	$9.2 \cdot 10^{-1}$
$p_0\ (cm^{-3})$	$5.4 \cdot 10^{11}$	$6.5 \cdot 10^{12}$

It can be seen from Table 1 that, as a result of doping, p_0 increases by one order of magnitude, and z by about two orders of magnitude, which can be explained by the fact that, on the one hand, iodine acts as an electron acceptor, and, on the other hand, it contributes to the rearrangement of ZnPc molecules in the treated layers, facilitating the transfer of charge through them. With direct polarization (Fig. 5), when voltages above 1 V are applied, a quadratic dependence of the current density on voltage is observed, which is described by a power law in the form

$$J \sim U^m \qquad (5)$$

By calculating the value of the m-index (the m-index has values ≥ 2), it can be found that the conduction mechanism is a space charge-limited current. The numerical value of this index indicates the presence of band gap traps, which depends on the sample temperature and the bias direction. The current density in this region is described by the relation [12, 13]:

$$J = \frac{9}{8}\varepsilon\mu\theta\frac{U^2}{d^3} \qquad (6)$$

Where ε and μ are the electrical permittivity and mobility of charge carriers of zinc phthalocyanine, and θ is the ratio of free charges to trapped charges and is described by the expression:

$$\theta = \frac{N_v}{N_{t(s)}}\exp\left(-\frac{E_t}{kT}\right) \qquad (7)$$

where N_t is the concentration of traps whose energy level is located in the band gap at an energy distance E_t from the lower edge of the valence band. Then the current density will look like:

$$J = \frac{9}{8}\varepsilon\mu\frac{N_v}{N_{t(s)}}\frac{U^2}{d^3}\exp\left(-\frac{E_t}{kT}\right) \qquad (8)$$

Fig. 8 shows the dependence $(J/U^2) = f(10^3/T)$ in the region of the electrical conductivity mechanism limited by the space charge. This relationship is a straight line. From the slope and from the intersection with the current axis, the values of E_t and $N_{t(s)}$ were estimated, which are given in Table 2. Substituting the obtained values of E_t and $N_{t(s)}$ into E_q. (7) makes it possible to calculate the trap velocity θ [14, 15]. The obtained values are presented in table 2. As expected, we found that the introduction of iodine increases the concentration of traps in the processed thin layers while reducing their energy level. We assume that, along with iodine compounds, oxygen compounds present in the treated thin layers also act as traps.

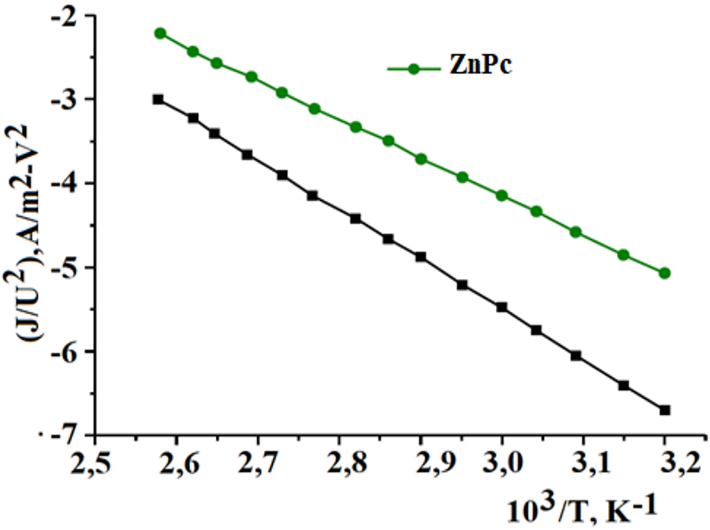

Fig. 8. Dependence $(J/U^2)=f(10^3/T)$ in the region of load limiting current spatial distribution of layered composition PEDOT/indium-tin oxide/zinc phthalocyanine with embedded and non-embedded ZnPc layer.

The dependence of the electric current on the applied reverse bias voltage, shown in fig. 9 show that there is also information about the change in the electrical properties of the layered composition after incorporation. B under reverse bias conditions, the order of magnitude of the

Table 2. Electrical parameters E_t, $N_{t(s)}$ and θ of a PEDOT/composition of indium tin-tin-zinc phthalocyanine with a layer of interstitial and non-interstitial ZnPc in the space charge-limited current region

Options	indium tin oxide/ zinc phthalocyanine/Aluminum	zinc phthalocyanine/Aluminum doped indium tin oxide/I2
$E_t\,(eV)$	0.68	0.62
$N_{t(s)}\,(cm^{-3})$	$2.2 \cdot 10^{14}$	$1.3 \cdot 10^{16}$
θ	$1.15 \cdot 10^{-6}$	$1.05 \cdot 10^{-8}$

The dependence of the electric current on the applied reverse bias voltage, shown in fig. 9 show that there is also information about the change in the electrical properties of the layered composition after incorporation. B under reverse bias conditions, the order of magnitude of the electric current strength is much lower than the direct current strength in the region, indicating a limitation of its space charge, which can be explained as a Schottky or Poole-Frenkel type of conduction [16]. The general equation [17] describing the reverse current density looks like this:

$$J = A^{**}T^2 \exp\left(-\frac{\Phi_s}{kT}\right)\exp\left(\frac{\beta_s U^{1/2}}{kTd^{1/2}}\right), \tag{9}$$

where $A^{**} = 1.25 \cdot 105\ A \cdot m^2 \cdot K^2$ is the Richardson constant, Φ_s is the height of the Schottky barrier at the boundary of the injection electrode, β_s is the Schottky field weakening coefficient.

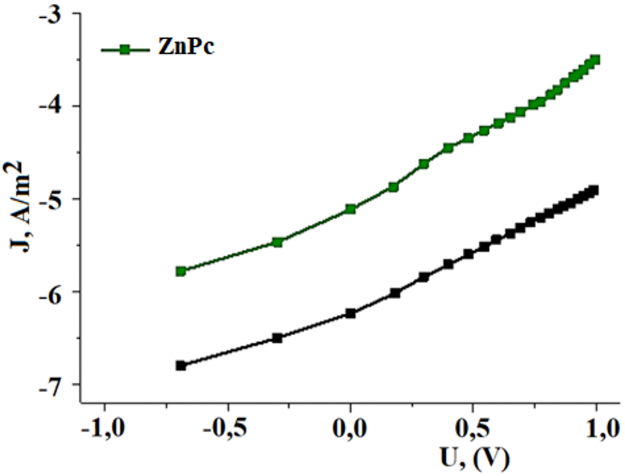

Fig. 9. Dependence of the electric current on the applied voltage of the reverse branch on a logarithmic scale a of the layered composition PEDOT/indium-tin oxide/zinc phthalocyanine with embedded and non-embedded ZnPc layer

For the Poole-Frenkel emission, which is a decrease in the barrier field at the interface of the injection electrode, the current-voltage dependence is given by the equation:

$$J = J_0 \exp\left(\frac{\beta_s U^{1/2}}{kTd^{1/2}}\right) \qquad (10)$$

where J_0 is the current density at low voltages and β_{PF} is the barrier reduction factor due to the Poole-Frenkel field. The two coefficients β_s and β_{PF} are related by the equation $2\beta_s=\beta_{PF}=(e^3/\pi\varepsilon\ )^{1/2}$. Substituting the value of the dielectric constant for ZnPc (ε_r=3.4) $\varepsilon=3.07\cdot10^{-11}$ F/m, the theoretical values of the coefficients at low and high voltages $\beta_{PF}=3.6\cdot10^{-5}$ eV $m^{1/2}$ $V^{-1/2}$ and $\beta_s=1.8\cdot10^{-5}$ eV $m^{1/2}$ $V^{-1/2}$. To find the experimental values of these coefficients, the dependence log $J=f(U^{1/2})$ was plotted. This dependence is illustrated in Figure 10 and indicates two pronounced linear sections, according to which the values of the coefficients β_s and β_{PF} were estimated, which are given in Table 3.

Thus, the experimental results indicate that, in the region of high voltages, the conduction mechanism is controlled by radiation in the space charge region formed at the metal-ZnPc interface. In the region of low voltages, the values of β_{PF} differ from the theoretical values of the Poole-Frenkel coefficient. The change in the coefficient β_{PF} in the region of low voltages can be explained by the uneven penetration.

Table 3. Barrier reduction factor (β_{PF}) for PEDOT/indium tin oxide zinc phthalocyanine layered composition with and without interstitial ZnPc layer

Coefficient	indium tin oxide/ zinc phthalocyanine/Aluminum		zinc phthalocyanine/Aluminum doped indium tin oxide/I2	
	$U<1V$	$U>1V$	$U<1V$	$U>1V$
$\beta_{PF} eV\, m^{1/2} V^{-1/2}$	$1\cdot10^{-5}$	$1.8\cdot10^{-5}$	$2.2\cdot10^{-5}$	$1.8\cdot10^{-5}$

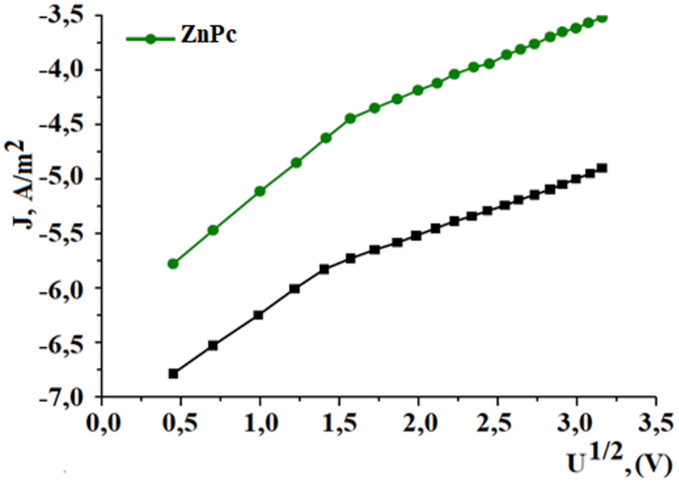

Fig. 10. Dependence $logJ = f(U^{1/2})$ of PEDOT composition/indium tin oxide zinc phthalocyanine with and without intercalated ZnPc layer.

The experimental values of the coefficient β_{PF} in the region of high voltages are in complete agreement with the calculated theoretical values.

References

1. Siebentritt S., and Schorr S. Kesterites-a challenging material for solar cells. Progress in Photovoltaics: Research and Applications, Vol. 20(5), pp.512-519. (2012).
2. Li J., Ma T., Wei M., Liu W., Jiang G., and Zhu C. The Cu2ZnSnSe4 thin films solar cells synthesized by electrodeposition route. Applied Surface Science, Vol. 258(17), pp.6261-6265. (2012).
3. Khalkar A., Lim K. S., Yu S. M., Patole S. P., and Yoo J. B. Effect of growth parameters and annealing atmosphere on the properties of Cu2ZnSnS4 thin films deposited by cosputtering. International Journal of Photoenergy, (2013).
4. A. V. Umarov, B.A. Mirsalixov, D. K. Djumabayev, F. X. Xusnuddinov. Development and Research of Layered Composite Materials Based On Cu2ZnSnS (Se)4 for solar cells. International Conference San Francisco, CA, ICNTET-2022-1300, p.4222299 (2023).
5. Montani R. A., and Bazan J. C. Electronic conductivity and chemical diffusion coefficient of cadmium-doped cuprous iodide. Solid state ionics, Vol.46(3-4), pp.211-216. (1991).
6. Zeyada H. M., and El-Nahass M. M. Electrical properties and dielectric relaxation of thermally evaporated zinc phthalocyanine thin films. Applied Surface Science, Vol.254(6), pp.1852-1858. (2008).
7. Riande E., and Díaz-Calleja R. Electrical properties of polymers. CRC Press. (2004).
8. Kao K. C. Electrical conduction and breakdown in insulating polymers. In Proceedings of the 6th International Conference on Properties and Applications of Dielectric Materials (Cat. No. 00CH36347) (Vol. 1, pp. 1-17). IEEE. (2000).
9. Braik, M., Dridi, C., Ali, M. B., Ali, A., Abbas, M. N., and Errachid, A. Investigation of structural, optical and electrical properties of a new cobalt phthalocyanine thin films with potential applications in perchlorate sensor. Synthetic Metals, 209, 135-142. (2015).
10. Margrupov M.A., Umarov A.V., Saidkhodzhaeva K.Sh., Kasimov G.A. Study of the density of filler surface layer modified by polyacrylonitrile heat treated. Plasticheskie Massy: Sintez Svojstva Pererabotka Primenenie, Vol. 2, pp. 26–27. (1995).
11. Ibadullayev A., Teshabayeva E., Kakharov B., and Nigmatova D. Composite elastomeric materials filled with modified mineral fillers. In E3S Web of Conferences, Vol. 264, p. 05006. (2021).
12. Shah M., Sayyad M. H., and Karimov K. S. Electrical characterization of the organic semiconductor Ag/CuPc/Au Schottky diode. Journal of Semiconductors, 32(4), 044001. (2011).
13. E. Teshabayeva, A. Ibadullayev, U. Chorshanbiev, and M. Vapayev, Modification of composite elastomeric materials for polyfunctional purposes, AIP Conference Proceedings Vol. 2432, 030082 (2022).
14. M. A. Lampert, P. Mark, Current Injection In Solids. New York: Academic Press, (1970).
15. Rodrigues A. M. Extraction of Schottky diode parameters from current-voltage data for a chemical-vapor-deposited diamond/silicon structure over a wide temperature range. Journal of Applied Physics, Vol. 103(8), 083708. (2008).

16. F.Yakuphanoglu. Electronic and Photovoltaic Properties of Al/Psi/Copper Phthalocyanine Photodiode Junction Barrier. In: Sol Energy Mater Sol Cells. Vol.91 (2007).
17. Z. Ahmad, M.H. Sayyad, Extraction of Electronic Parameters of Schottky Diode Based On An Organic Semiconductor Methyl-Red, Physica E, Vol. 41, (2009).