

PHOTOELECTRIC PROPERTIES OF AMORPHOUS SOLID SOLUTIONS OF Se-S SYSTEM

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The paper contains the photoconductivity measuring results of film samples of $\text{Se}_{100-x}\text{S}_x$ ($x=0;5;10;20;30;40;50$) system, the wave length in interval $0,38\div 1,00$ μm . The photoconductivity change in the dependence on system composition $\text{Se}_{100-x}\text{S}_x$ is explained in model limits of intrinsic charged defects in noncrystalline semiconductors and their change, i.e. they presence of D^+ and D^- defects in forbidden band forming from initial neutral defects D^0 that is connected with change of short range ordering configuration character.

INTRODUCTION

The photoelectric phenomena present themselves the strong method of semiconductor investigation and they are directly connected with light energy absorption [1].

In reference the sulfur and solid solutions of Se-S system are too little studied materials among chalcogens and chalcogenides. The selenium on forbidden gap value and melting point are between tellurium and sulfur. This gives possibility to change its physical parameters in wide limits under sulfur influence. As it is seen in [2] the change of sulfur content in Se-S system leads to change of photoconductivity maximum from pure sulfur up to photoconductivity maximum of pure selenium (from 4,7 up to 7,0 μm). This is revealed in strength changes, constants of crystal lattices, in its elementary cells, glass-transition temperature and dielectric constant, forbidden gap and other parameters of Se-S system.

The physical properties of Se-S system are investigated in series of works [4-11]. In work [4] the technique of film obtaining ($x=0,15; 0,42; 0,60; 0,8; 0,9; 1$) is described. The optical characteristics of films by $40\div 80$ μm thickness are measured in spectral range $16\div 5$ μm and absorption peaks at 235, 255, 360 and 455 cm^{-1} are observed. The photo-darkening effect caused by photo-crystallization is revealed at radiation by ruby laser. The optical absorption and conductance of Se-S system in solid and liquid states are measured in work [5]. As the author of work [6] shows the absorption boundary shifts from 2,2 eV for pure selenium up to 2,4 eV for alloy of 40% S composition that is observed in [7]. In work [8] IR transmission spectrums of glassy Se containing 0; 2,5; 5 at.% S, Te, As or Ge and also pure Se in range $400\div 600$ cm^{-1} are studied. The author connects the new absorption bands in the case of introduction of sulfur and tellurium in Se with formation of ring molecules of Se_3S_5 or Se_5Te_3 types correspondingly.

In work [9] it is shown that $\text{Se}_x\text{S}_{1-x}$ alloys rich of Se are characterized by high viscosity and form glasses in wide interval of compositions at solidification. The glass-transition temperature T_g decreases and achieves 273K at $x=0,7$ at increase of sulfur content.

As authors of [10] show though Se and Te have properties which are analogical to chalcogenide ones, they contain the structural units with molecular properties and they are considered as the separate group.

The structural model of binary system presents itself the continuous grid in which the coordination "rule 8-N" for both components at any their relation, is carried out. The hetero- and homo-polar bonds are possible between atoms.

The hexagonal crystalline Se consists in helical chains built parallel to each other. The chemical bond inside the

chains has covalent character and is very strong one and bond between chains is the weak one of Van-der-Waals one. In liquid phase we consider that the chains are oriented occasionally. At rapid alloy cooling the viscosity becomes very high one and before the chains disorientate the glassy state appears.

The tellurium addition in liquid selenium alloy leads to chain shortening as Se-Te chain is weaker than Se-Se and crystallization at cooling simplifies. When S is added to alloy the reversal thing happens, i.e. Se-S bond is stronger than Se-Se one. The amorphous selenium presents itself the mixture of molecules (closed annuluses) and polymer chains. The sulfur, selenium and tellurium have the coordination number which is equal to 2. The average mole energies of the bond decrease and values of melting point and strength increase in S, Se and Te series. This shows that the more the bonding force between atoms in the chain the less the bond between the chains.

X-ray investigations of Se-S system structure [11] show that regulation of S atoms in structure of Se matrix takes place up to $\sim 28\%$ S distorted it and when S content in the system achieves 50% the phase transition by structure takes place.

The transformations on the chalcogenide base are widely used in optoelectronics in the different electric circuits for different chains. The search of new materials is required for widening of spectral sensitivity interval and photosensitivity maximum of the given transformers. In the given work the photosensitivity of solid amorphous solutions of $\text{Se}_{100-x}\text{S}_x$ ($x=0;5;10;20;30;40;50$) system is studied with this aim.

The homogeneous solutions at crystallization of which the series of solid solutions settle down, form in melted state between sulfur and selenium. Taking into consideration that behaviors of sulfur and selenium have more similarities, we can suppose that they are able to form the mixed molecules of Se-Se, Se-S, S-S type.

The selenium, sulfur and solid solutions on their base are close to chalcogenide glasses by their physical properties. However, as it is known Se is semiconductor whereas S is good isolator. Consequently, the solid solutions on their base should lead to the change of their parameters from semiconductor up to isolator.

Nowadays it is established that one can directly change the electric properties of chalcogenide glassy semiconductors by change of chemical composition and also by introduction of impurities. More over the change of the concentrations of charged defect centers (U^+ are centers) in semiconductors that allows us to control by their electric, optic and photoelectric properties.

The photoconductivity in semiconductors is directly connected with photon absorption in substances as a result of which the current carriers form.

THE OBTAINING TECHNOLOGY AND EXPERIMENT TECHNIQUE

The selenium by B₅ purity and pure stick sulfur suspended with accuracy up to 0,0001g are taken for obtaining of solid solutions selenium-sulfur.

The vibration method is used for better alloy homogenization. The ampoules during three hours are treated by shaking at temperature 280°C, i.e. on 60°C higher than selenium melting point.

The samples for measurement have structures of "sandwich" type and present themselves the layers of 3mkm thickness prepared by thermal evaporation in vacuum at residual pressure 10⁻⁶ millimeter of mercury. The polished glass substrates on which previously the bottom electrode from aluminum is marked are used as substrates. The semitransmitting film from aluminum evaporated in vacuum on the layer of investigated material serves as top electrode. The film chemical composition is taken the similar as in joint hinge. The sample temperature is controlled with the help of thermocouple.

The spectral dependence of stationary photoconductivity is measured by incident photon energy in 1,0÷3,2 eV interval. The measurements of photo- and dark currents are carried by charge amplifier Y5-11. The data of stationary photoconductivity are normalized on photon constant number at each energy value.

THE EXPERIMENTAL RESULTS AND THEIR DISCUSSIONS

The photoconductivity spectrums of the given solid solutions are taken on installation including the adjustable source of current, monochromator, lighting unit, and amplifier-electrometer.

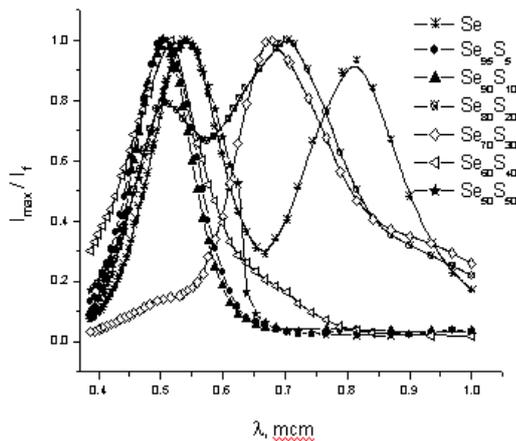


Fig.1. Photoconductivity spectrums of Se-S film system in darkness.

The generation process of free charge carriers under radiation influence is in the base of photoconductivity [1]. In simple case the radiation in intrinsic semiconductor excites the valence electrons in conduction band where they are in free state and can participate in charge transfer process; the holes appearing in valence band also make contribution in conductivity. The electron excitation by light into conduction band takes in impurity semiconductor of n-type. Analogically

one can excite electrons from valence band on acceptor centers forming the mobile holes in semiconductors of p-type. In both cases of impurity conductivities in crystal the free current carriers of only one sign generate.

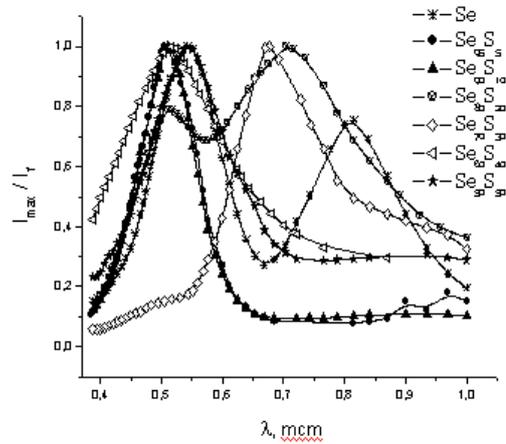


Fig.2. Photoconductivity spectrums of Se-S film system with lighting.

The measuring results of photoconductivity of amorphous film samples of Se_{100-x}S_x (x=0;5;10;20;30;40;50) system are presented on Fig.1. It is seen that maximums of their spectral characteristics change with composition change of Se-S system. The analogous results with lightening are presented on fig. 2. As it is seen the lighting leads to shifting of spectral photoconductivity characteristics in the dependence on composition of Se-S system samples.

As it has been mentioned above the photoconductivity is connected with absorption. The photoconductivity changes in the dependence on composition of Se-S system and their absorption coefficient are presented on figures 3-9.

It is known that photon flow penetrating in semiconductors decrease with penetration into semiconductor volume by the law: $F(x) = F_0^{exp}(-\alpha x)$ where F_0 is photon flow penetrating through semiconductor surface; $F(x)$ is photon flow on x depth from surface; α is absorption coefficient. The value reversal to absorption coefficient $1/d$ defines the depth on which the photon flow takes place. The coefficient α depends on absorption mechanism, ΔE semiconductor forbidden gap, wave length of incident radiation and is velocity measure of photon strength decrease in penetration process in semiconductor.

The absorption coefficient in intrinsic semiconductor is equal to zero for photons with energy less than forbidden gap. The absorption coefficient strongly increases for photons with energy exceeding ΔE . The absorption coefficient achieves the big enough value in short wave region, i.e. the radiation in this region takes place on very small depth. The absorption coefficient in long wavelength spectrum region decreases on several orders and the penetration depth increases in several times.

The dependence of light absorption coefficient on wave length influences on the type of spectral characteristics and maximum position. The difference of light absorption mechanism by them essentially influence on material spectral characteristics.

The change and shift of spectral characteristics maximum can be carried out with the help of different factors

and also changing the material composition. This is related to sensitivity of material photoconductivity.

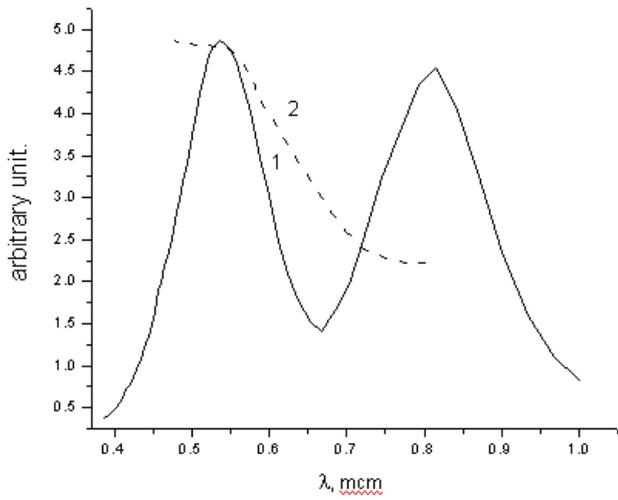


Fig.3. Photoconductivity (curve 1) and absorption coefficient (curve 2) of Se films.

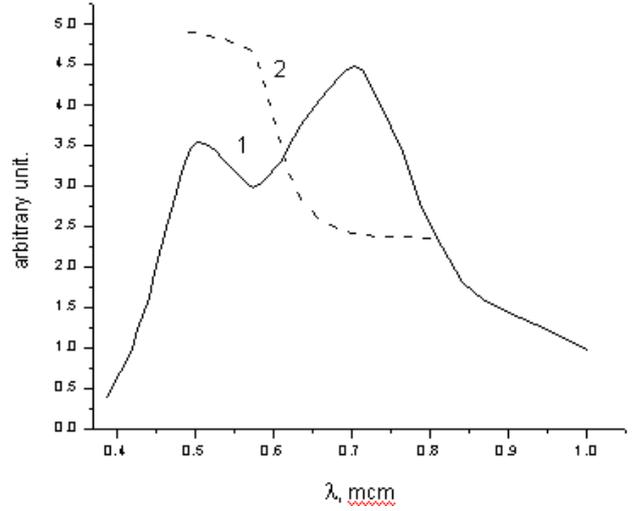


Fig.6. Photoconductivity (curve 1) and absorption coefficient (curve 2) of $Se_{80}S_{20}$ films.

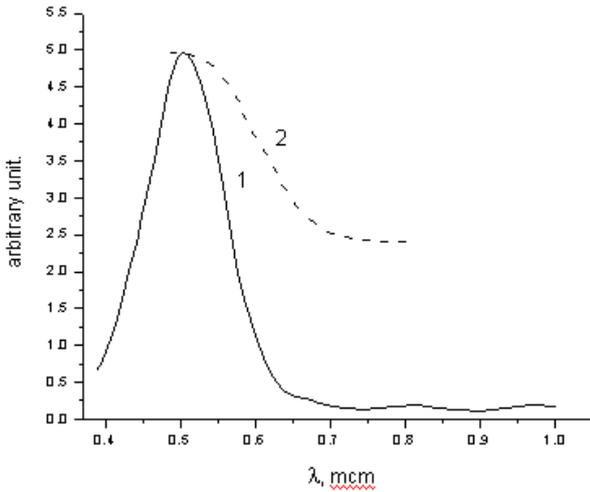


Fig.4. Photoconductivity (curve 1) and absorption coefficient (curve 2) of $Se_{95}S_5$ films.

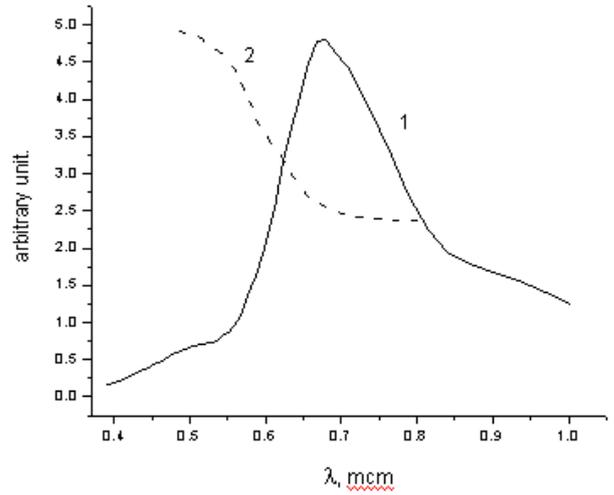


Fig.7. Photoconductivity (curve 1) and absorption coefficient (curve 2) of $Se_{70}S_{30}$ films.

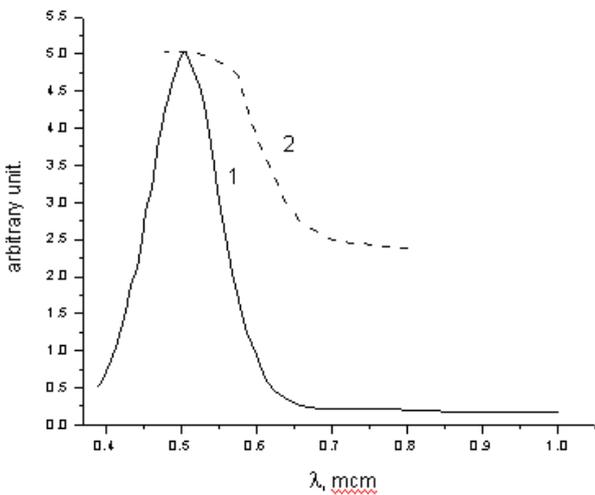


Fig.5. Photoconductivity (curve 1) and absorption coefficient (curve 2) of $Se_{90}S_{10}$ films.

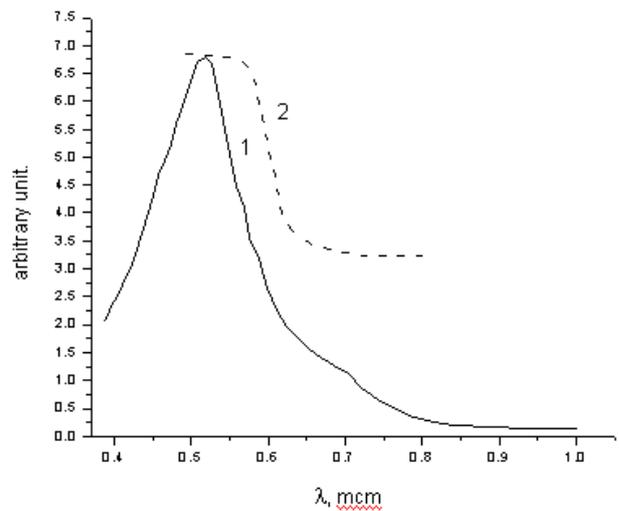


Fig.8. Photoconductivity (curve 1) and absorption coefficient (curve 2) of $Se_{60}S_{40}$ films.

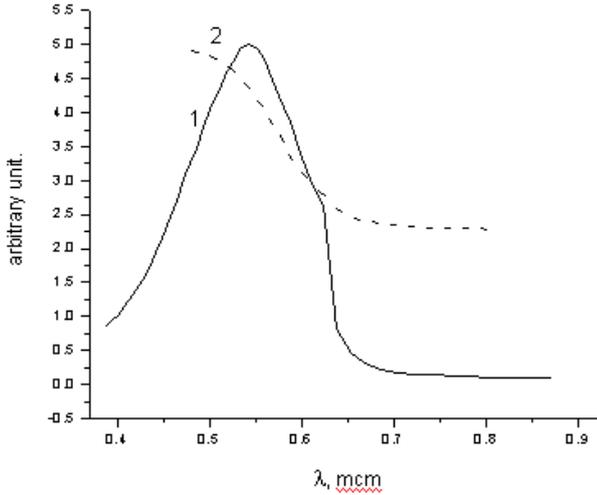


Fig.9. Photoconductivity (curve 1) and absorption coefficient (curve 2) of Se₅₀S₅₀ films.

From above mentioned it is clear that the photoconductivity can appear only at excitation by short-wave excitation when photon energy exceeds the some threshold value. This is either the energy distance between extremums of conduction band and valence band in the case of intrinsic photo-effect or the distance between extremums of any band and donor or acceptor level in the case of impurity photo-effect. The threshold frequency of photoconductivity and also spectral dependence of semiconductor photosensitivity is mainly defined by its optical properties.

In work [12] by study of dependence of absorption coefficient of Se-S system is defined that $\alpha \sim f(\hbar\omega)$ dependence below the strong absorption region is obeyed to exponential law. The region of exponential change of α with $\hbar\omega$ increase is called Urbah's "tail" [13]. Such dependence is known in crystalline chalcogenides of alkali metals, CdS and trigonal selenium. This phenomenon is also observed in chalcogenide and silicate glasses [13,14]. The several mechanisms: the variations of crack thickness caused by strength fluctuations; the widening of band edge indicated by intrinsic electric fields has been supposed for explanation of such exponential dependence. It is said that [15,16] the absorption edge reflects the appearance of state tails in the crack as a result of angle fluctuations and bond lengths. The another authors consider [17] that the electron transitions between localized states in tails of bond edges are the reasons of tail appearance and it is supposed that the strength of such states exponentially coincides with photon energy.

In [17] the existence of correlations between inclination of Urbah "tail" and coordination number or valency is shown. It is shown that materials with weaker coordination (higher valency) easily form the ideal amorphous grid with less quantity of defects and spaces.

The dependence $\alpha \sim f(\hbar\omega)$ is obeyed to Urbah rule in exponential region.

$$\alpha = \alpha_0 \exp[-(E_g - h\nu) / E_0], \quad (1)$$

where E_0 is characteristic energy which characterizes the edge tilt and has the information on quality of standard deviation of interatomic distances in glassy materials [18].

E_0 values defined from $\alpha \sim f(\hbar\omega)$ exponential dependence of Se-S system firstly strongly increase and later do more moderately with S content increase.

Nowadays the fact is established that the more electron properties of chalcogenide and chalcogen glassy semiconductors is explained by the presence of charged defects D^+ and D^- . These defects form from initial neutral defects D^0 by the following reaction:



And can be intrinsic impurity defects.

It is supposed that electric, photoelectric and optical properties on non-crystalline semiconductors are controlled by charged defects. The following formula is obtained using the model of random field formed by chaotically distributed atoms for characteristic energy [19]:

$$E_0 = 2,2W_B (N_t a_B^3)^{2/5}, \quad (3)$$

where $W_B = e^2 / 2\epsilon a_B$, a_B is Bohr radius in substance, ϵ is dielectric constant; N_t is effective concentration of charged defects.

It is known that for Se the dielectric constant is $\epsilon = 6,6$ and for sulfur is $\epsilon = 3,69$. Taking into consideration the linear decrease of dielectric constant with composition we calculate the concentrations of charged defects for different compositions of Se-S system by formula (4). The results show that the concentration of charged defects decreases with increase of S content. Probably this is connected with decrease of linear chains in the system the ends of which are the defect centers. Besides Se-S bond is stronger than Se-Se one that influences on concentrations of defects.

Thus, as a result of investigations of optical properties of Se_{100-x}S_x system it is established that the correlation between dependences of coefficient of optical absorption (α), effective concentration of charged defects characteristic energy (E_0) corresponding to Urbah absorption on S content in composition of Se-S system, exists. It is shown that light absorption in spectrum region where Urbah rules are carried out is controlled by charged defects. It is established that one can change the concentration of intrinsic charged defects by the change of S content and by this one can control the optical and photoelectric properties of Se-S properties.

As results presented on fig. 3-9 show that light absorption character changes in the dependence on Se-S system composition at photoconductivity character.

The destruction of ideal structure of non-crystalline solid state takes place in systems including the atoms with unshared electron couples. Often the electron couple at bond opening stays on the one of fragments, i.e. the heterolytic bond takes place. Moreover the one positively and one negatively charged defect centers in short range ordering region appear. The energy which is necessary for bond opening compensates because of existence of unshared electron couple of atoms being in nearest surrounding and the number of chemical bonds stays constant. Thus, the structural disorder takes place in homogeneous glasses of

stoichiometric composition along with strength oscillations and existing topological order of different type. The last one reveals in the form of positively and negatively charged defect centers as in the case of point defects in the crystals. As a result the defects the formation reactions of which are characterized by the least change of free energy, dominate.

Note that in our case the material synthesis, sample preparation and conditions of their measurements are similar for $Se_{100-x}S_x$ ($x=0;5;10;20;30;40;50$) system. We obey to "rule 8-N" principle at the synthesis of solid solutions of different compositions of $Se_{100-x}S_x$ system. The character bond energies for Se-Se, S-S, Se-S are different as the bond energy between atoms of binary amorphous compounds for different configurations of short range ordering are different ones. The electron structure of $Se_{100-x}S_x$ ($x=0;5;10;20;30;40;50$) system samples will change in the

dependence on character change of short range ordering, that is seen from presented figures 3-9. It can be explained by structural differences of investigated samples of Se-S system samples with sulfur content increase.

The obtained data can be explained with the help of model of charged intrinsic defects in non-crystalline semiconductors [20-24]. It is known that the change in non-crystalline semiconductors of coordination number, atom type surrounding by the given atom, bond lengths (interband distance) and valence angles with composition change of investigated samples leads to short range ordering change in them. This leads to change of their physical properties. The non-crystalline samples of Se-S system consist of closed and linear atom chains and their relations change in the dependence on their composition that leads to character change of short range ordering in them [25].

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Se-S SİSTEMİNİN AMORF BƏRK MƏHLULLARININ FOTOELEKTRİK XASSƏLƏRİ

İşdə dalğa uzunluğunun 0.38÷1.00 mkm intervalında $Se_{100-x}S_x$ ($x=0;5;10;20;30;40;50$) sisteminin nazik nümunələrinin fotokeçiriciliyi ölçülmüşdür. $Se_{100-x}S_x$ sisteminin tərkibdən asılı olaraq fotokeçiriciliyinin dəyişməsi onlarda məxsusi yüklü defektlərin olması modeli əsasında izah olunur. Bu defektlər qadağan olunmuş zonanın daxilində neytral D^0 defektindən D^+ və D^- defektlərinin yaranması ilə bağlıdır. Bu tip defektlər atomların düzülüş quruluşunun dəyişməsi, yəni yaxın nizamlı düzülüşün dəyişməsindən asılıdır.

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ФОТОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА АМОΡФНЫХ ТВЕРДЫХ РАСТВОРОВ СИСТЕМЫ Se-S

Работа содержит результаты измерения фотопроводимости пленочных образцов системы $Se_{100-x}S_x$ ($x=0;5;10;20;30;40;50$) в интервале длин волн 0,38÷1,00 мкм. Изменение фотопроводимости в зависимости от состава системы $Se_{100-x}S_x$ объясняется в рамках модели собственных заряженных дефектов в некристаллических полупроводниках и их изменением, т.е. наличием в запрещенной зоне дефектов D^+ и D^- , образующихся из исходных, нейтральных дефектов D^0 , что связано с изменением характера конфигураций атомов и ближнего порядка.

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