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INFLUENCE OF EuF_3 RARE- EARTH IMPURITY ON THE OPTICAL PROPERTIES AND SURFACE MORPHOLOGY OF $Se_{95}As_5$ CHALCOGENIDE GLASS- LIKE SEMICONDUCTOR

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The results of a comparative analysis of optical properties taking into account the structural features and morphology of the surface of films based on $Se_{95}As_5$ $(EuF_3)_x$ (x = 0.001-1 at.%) obtained by thermal evaporation on cold glass substrates in a vacuum of 10^{-6} mm Torr. Habe been presented. The effect of europium on the optical properties and morphology of the surface of $Se_{95}As_5$ films were studied. Taking into account the structural features of $Se_{95}As_5$, as well as the manifestation in them of EuF_3 in the form of ions, the observed features of the concentration dependence of the optical constants on the EuF_3, as well as the relief images observed by the AFM method, are explained. The width of the forbidden band of the material under study was determined using the Tautz model, and for all samples the band gap widths were determined whose values varied within 1.91÷ 1.95 eV. As can be seen, there is no significant change in the width of the forbidden band when an impurity is introduced.

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1. Introduction

Rare-earth fluorides form an important family of useful inorganic materials because of their use as key elements in optics, optoelectronics and the scope of magnets. In particular, rare-earth fluorides have a high intensity of radiation, are highly stable and durable at high temperatures and intense excitation energy, which makes them excellent starting materials for use in luminescence. Nanocrystals of complex three-component rare-earth fluorides (Se-As-LnF_3) attract special attention of researchers due to their unique optical properties, as components of optical telecommunications. Chalcogenide glass-like semiconductors (CGS) are less sensitive to the introduction of impurities into them. However, the study suggests the possibility of changing the spectrum of local states in the forbidden band in these materials by introducing impurity atoms. Films of chalcogenide glass-like semiconductors are used to create memory elements in microcircuits of reprogrammable permanent storage devices for computers, photosensitive media for recording optical information, and also as inorganic photo and electronic resistors in the manufacture of microelectronics products. Therefore, taking into account the above-mentioned features of the materials under study, the introduction of fluorides of rare-earth elements into chalcogenide semiconductors is of great practical importance. When the CGS is irradiated, a change in the refractive index, the transmission of the material, is observed, due to a shift in the absorption band. The shift occurs as a result of certain changes that occur in the structure of the CGS. The information recorded on the CGS is erased when heated to a temperature close to the softening point. In CGS, the effective interaction between localized electrons can have the

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character of attraction; this leads to their pairing, and hopping conductivity, as a rule, is not observed.

As an impurity, rare earth fluoride (EuF_3) is used in the work. The use of EuF_3 in the work is explained by the fact that the impurity mainly manifests itself as charged centers (Eu^{+3} and F^- ions) and should influence the concentration of U^- centers, according to the Anderson hypothesis [1]. On the other hand, EuF_3 in the forbidden band is formed by states due to their 4f states, as a result of which the optical width of the forbidden band is overlapped in energy by electronic transitions allowed for the REE ion, which leads to a change in its optical, photoelectric and electrical properties [2-5].

The effect of the EuF_3 impurity on the optical properties and on the surface relief of $Se_{95}As_5$ is studied. To understand the mechanisms of electronic processes, the optical width of the "forbidden band", the refractive index, and the extinction coefficient are determined, which are closely related to the atomic and electronic structure of the material and the energy spectrum of electronic states.

2. Experimental details

The samples were obtained by fusing elementary substances of special purity in vacuumed to 10^{-3} Torr. quartz cells. The synthesis was carried out at a temperature of 1200 K for 10 hours in a rotating furnace followed by cooling in the off-furnace mode with a holding time of at least 5 hours. The impurity concentration was used within 0.001 ÷ 1at%. Samples for measurements were films of thickness 0.5 μm ÷ 2 mm. The films were fabricated by thermal evaporation in a vacuum of 10^{-6} Torr. onto cold glass substrates. The optical transmission spectra were studied by the method of two-beam spectroscopy in the energy range 1 ÷ 2.8 eV, and the surface morphology of the films by AFM method. All experiments were carried out at room temperature.

3. Result and discussion

Figure 1 shows the spectra of the optical absorption coefficient of $Se_{95}As_5$ with different EuF_3 impurity content. Similar spectra are possessed by all CGS materials. As can be seen, the curves of the spectral distribution of the absorption coefficient exhibit features inherent in CGS materials, i.e. the dependence α (hυ) in the region of the energy of the incident photon is 1.6 ÷ 2 eV obeys the Urbach rule, at energies higher than 2 eV a power dependence is observed, and below the energy of 1.6 eV is the "tail" absorption, i.e. absorption of photons with energies less than the optical width of the forbidden band, but not obeying the Urbach rule. To determine the optical width of the band gap, we used the Tautz model [6], which is often used in processing experimental data in CGS [7]. The widths of the forbidden band are determined for all samples, the values of which vary within 1.91÷ 1.95 eV. As can be seen from figure 2, there is no significant change in the width of the forbidden band when the impurity is introduced.

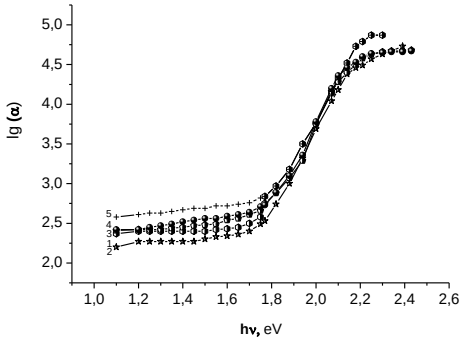


Fig. 1. Spectra of the optical absorption coefficient of $Se_{95}As_5$ containing EuF_3 (0.01÷1 at.%) at room temperature: 1-$Se_{95}As_5$, 2-$Se_{95}As_5$ $(EuF_3)_{0.01}$, 3-$Se_{95}As_5$ $(EuF_3)_{0.10}$, 4-$Se_{95}As_5$ $(EuF_3)_{0.25}$, 5-$Se_{95}As_5$ $(EuF_3)_{1.00}$

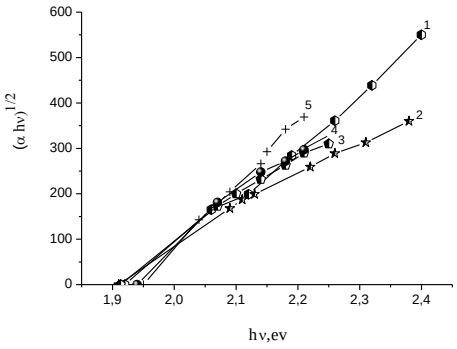
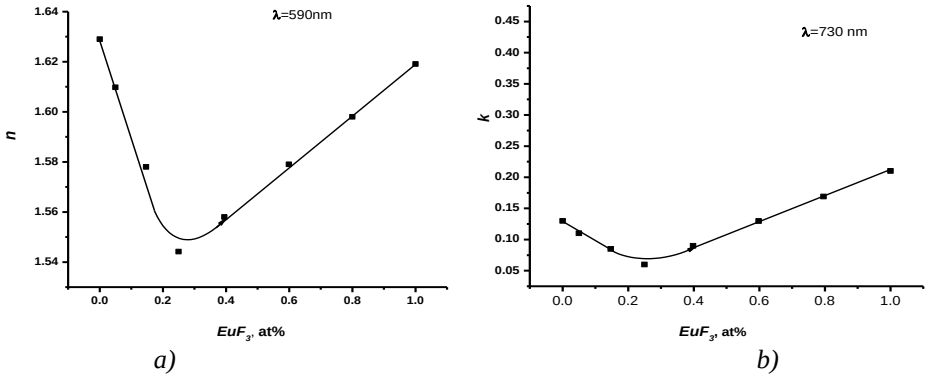


Fig. 2. Dependence of $\alpha(h\nu)$ on the energy of the incident radiation for $Se_{95}As_5$ with EuF_3: 1-$Se_{95}As_5$, 2-$Se_{95}As_5$ $(EuF_3)_{0.01}$, 3- $Se_{95}As_5$ $(EuF_3)_{0.10}$, 4- $Se_{95}As_5$ $(EuF_3)_{0.25}$, 5- $Se_{95}As_5$ $(EuF_3)_{1.00}$

By now, it is generally accepted that Urbach absorption is directly related to the structural disorder present in the system, which is also confirmed by experiments on the study of light absorption in radiation-damaged materials [5]. For CGS materials, a typical representative, which is $Se_{95}As_5$, a more suitable model of static random fields, apparently, is the Coulomb field. The reason for this, first of all, is that most electronic properties of CGS materials are controlled by defects having negative effective correlation energy (U^-centers), the existence hypothesis first proposed by Anderson [1]. Defects of this type arise due to a violation of the ground state of the chemical bond, i.e. the coordination numbers, valances and charge of the atom change.

Figure 3 shows the dependences of the refractive index n (Figure 3a) and the extinction coefficient k (Fig. 3b) of $Se_{95}As_5$ on the concentration of EuF_3. It can be seen that the influence of the EuF_3 impurity on the values of the coefficients n and k is nonmonotonic: up to a concentration of ~ 0.25 at%, the values of n and k decrease, and further their growth is observed. According to [8], the CGS materials of the type, for example, arsenic selenide, to which the CGS compositions of $Se_{95}As_5$ can be attributed, have a less labile and more rigid structure, resulting in the formation of ordered microregions with high coordination number, separated from each other by regions with a lower atomic density. Such a difference in the arrangement of atoms leads to the fact that the microscopic density (ρ) near the boundary of the microregion with a high coordination number is less than within the region itself, which makes it possible to interpret the results obtained within the framework of the Penn model developed for materials containing small pores [9-11]. From Fig. 4, which shows the width of the Penn band $Se_{95}As_5$ as a function of the EuF_3 concentration, it is seen that the low impurity concentration (up to 0.25 at%) increases, while the high one gradually decreases it, which indicates the complexity of the influence of the impurity on the concentration of localized states in the mobility gap. Judging from the graphs in Figures 3 and 4, we can state that a small concentration of impurity molecules EuF_3 decreases and a high concentration increase the density of localized states in the mobility gap of the material under study. To explain the results obtained, attention should be paid to the structural features of the arrangement of atoms and the energy spectrum of electronic states in $Se_{95}As_5$, as well as the changes occurring in them when introducing impurities of REE fluorides. For this purpose, the effect of the EuF_3 impurity on the relief and surface properties of $Se_{95}As_5$ has been investigated. In Fig. 5 shows the ASM 3D image of the relief of the $Se_{95}As_5$ CGS composition (a) and $Se_{95}As_5(EuF_3)$ (x = 0.01; 0.1 at.%) (b, c). The AFM study of the relief shows that the relief of the samples varies greatly when the impurity of the rare-earth compound EuF_3 is introduced into the initial $Se_{95}As_5$composition. The relief of the $Se_{95}As_5$ samples containing EuF_3 is gradually smoothed out. As can be seen, from Fig. 5 (c) the surface becomes even smoother with increasing EuF_3 content. This gives us reason to judge that EuF_3 at a high content (0.25-1 at. %) leads to the formation of a homogeneous surface of the sample. It can be seen that the surface of the composition $Se_{95}As_5$ and $Se_{95}As_5(EuF_3)_x$ (x = 0.01; 0.1 at.%) is different, that is, structural changes occur.



a) *b)*

Fig. 3. Dependences of the refractive index (a) and the extinction coefficient (b) of $Se_{95}As_5$ on the concentration of EuF_3 (N_{EuF3} = 0.9 x 10^{19} ÷ 1.9 x 10^{20} cm^{-3}).

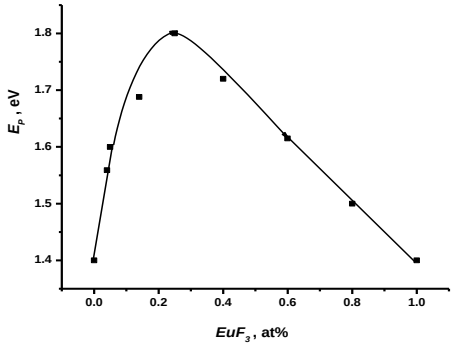
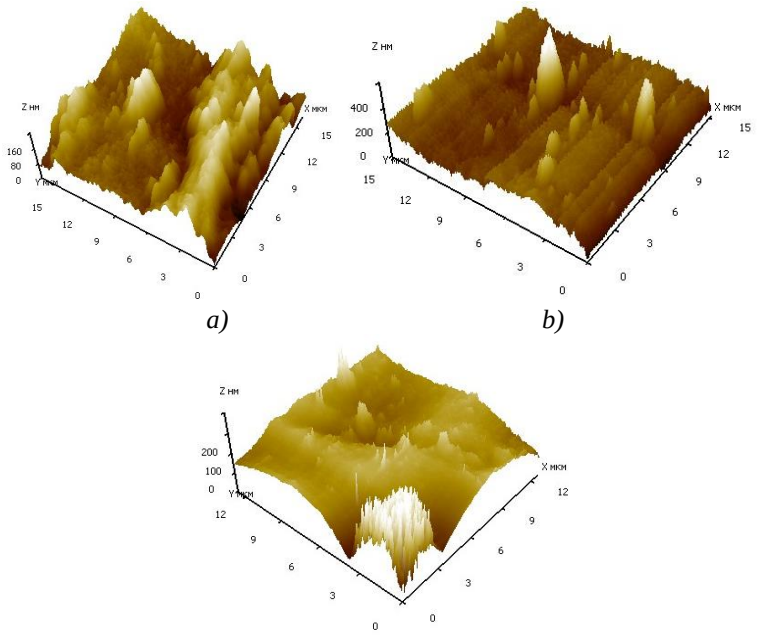


Fig. 4. Dependence of the width of the Penn zone of the $Se_{95}As_5$ on the concentration of the EuF_3 molecules (N_{EuF3} = 0.9 x 10^{19} ÷ 1.9 x 10^{20} cm^{-3}).

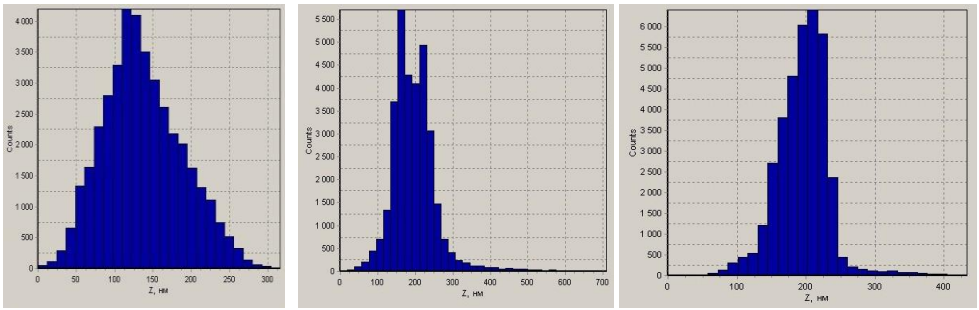


a) *b)*

c)

Fig. 5. AFM 3D image of the relief of $Se_{95}As_5$ (a), $Se_{95}As_5(EuF_3)_{0.01}$ (b), $Se_{95}As_5(EuF_3)_{0.1}$ (c).

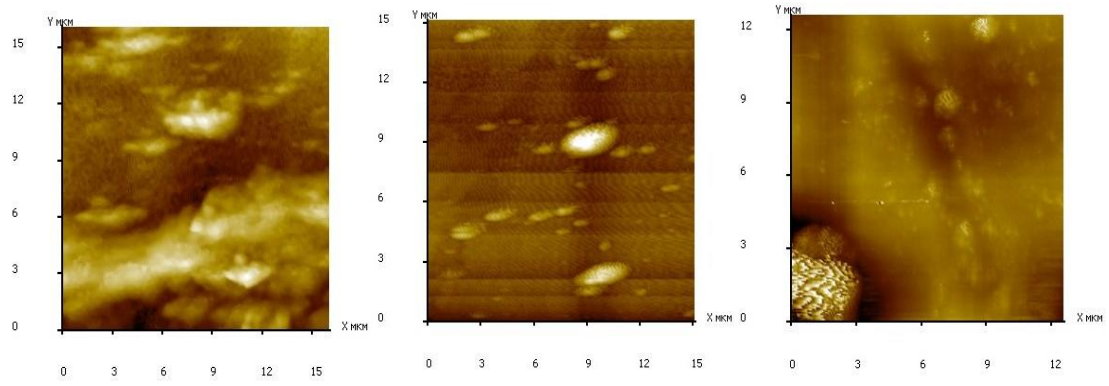
The histogram of the surface heterogeneity (Fig. 6) shows that the introduction of EuF_3 into the $Se_{95}As_5$composition smoothes the relief of the sample. It is also shown that the rms roughness of the surface of the sample $Se_{95}As_5$ is 50-250 nm, $Se_{95}As_5$ $(EuF_3)_{0.01}$ is 100-300 nm, and for $Se_{95}As_5$ $(EuF_3)_{0.1}$ is 150-250 nm.



a) *b)* *c)*

Fig. 6. The histogram of the values of the image elements and the rms surface roughness of samples of the structure of $Se_{95}As_5$ (a), $Se_{95}As_5$ $(EuF_3)_{0.01}$ (b), $Se_{95}As_5$ $(EuF_3)_{0.10}$ (c)

Figure 7 shows the AFM 2D images of the relief of a sample of $Se_{95}As_5$ and samples containing EuF_3 in various percentages. From figure 7 that with an increase in the EuF_3 content, the relief of the sample changes markedly. This picture is a consequence of the fact that at low content of EuF_3 appears as ions Eu^{3+}, F^- and fills the existing voids. This eliminates the inhomogeneities associated with the density deficit, and also reduces the concentration of broken bonds, which leads to a decrease in the density of localized states in the mobility gap associated with charged defects (U^- centers). This leads to a decrease in the fluctuations of the electrostatic potential. The latter factors lead to a decrease in the refractive index and extinction coefficient (Fig. 3), and also to an increase in the width of the Penn zone (Fig. 4). At high concentrations of EuF_3, the Eu^{3+} and F^- ions are distributed throughout the matrix, and new local states are formed in the $Se_{95}As_5$ mobility gap associated with the Eu^{3+} and F^- ions, leading to an increase in the fluctuations of the electrostatic potential. This leads to a gradual increase in the refractive index and extinction coefficient (Fig. 3), as well as to a decrease in the width of the Penn zone (Fig. 4).



a) *b)* *c)*

Fig.7. AFM 2D images of the relief of the $Se_{95}As_5$ (a), $Se_{95}As_5$ $(EuF_3)_{0.01}$ (b), $Se_{95}As_5$ $(EuF_3)_{0.10}$ (c)

Thus, the effect of EuF_3 on the optical properties of $Se_{95}As_5$ is related to the changes that occur in the atomic structure and the energy spectrum of electronic states, and is described in the Penn model [9-10]. Assuming that EuF_3 manifests itself in the form of Eu^{3+} and F^- ions, in small quantities, mainly filling existing voids, eliminates the inhomogeneities associated with the density

deficit in these areas [12]. And thanks to the chemical activity they promote the formation of bonds, as a result of which the concentration of broken bonds decreases, accompanied by a decrease in the density of localized states in the mobility gap, connected by charged defects (U^- centers) [3]. At high concentrations of EuF_3, the ions Eu^{3+} and F^- are distributed over the entire matrix, and new local states are formed in the $Se_{95}As_5$ mobility gap associated with Eu^{3+} and F^- ions, leading to an increase in the fluctuations of the electrostatic potential. This behavior of EuF_3 leads to a nonmonotonic change in the refractive index and extinction coefficient, as well as the width of the Penn zone, depending on the concentration of the impurity molecules EuF_3. The obtained results are satisfactorily explained taking into account the structural features of the $Se_{95}As_5$ CGS, which is characterized by the presence of ordered microregions at the boundary of which the continuity of the grid is violated, which leads to the formation of a surface with microinhomogeneities. Impurity ions Eu^{3+} and F^- due to chemical activity form bonds between different microregions, reduce the degree of heterogeneity.

4. Conclusions

Taking into account the structural features of the CGS of the Se-As system, as well as the manifestation in them of EuF_3 in the form of ions, the observed features of the concentration dependence of the optical constants on the EuF_3 content, as well as the relief images observed by the AFM method, have been explained. The CGS Se-As system is characterized by the presence of ordered microregions with a high coordination number at the boundary, which breaks the continuity of the grid, and micro-regions with a lower atomic density arise.

The Eu^{3+} and F^- ions, at low contents, mostly fill empty spaces in the region of reduced density, reducing the degree of heterogeneity and at the same time, because of the chemical activity, create connections between the various micro regions. At high concentrations, these ions, distributed throughout the matrix, create new charged defects, and thus the fluctuation of the electrostatic potential increases. The noted features lead to the observed dependences of the optical constants on the concentration of EuF_3.

References

[1] P.W. Anderson, Phys. Rev. Lett. **34**(15), 953 (1975).
[2] A.I . Isayev, S.I .Mекhtiyeva, A.K. Rzayev, Turkish J. of Physics **22** , 263 (1998).
[3] A.I. Isayev, S.I. Mekhtieva, N.Z. Jalilov, R.I. Alekperov, Solid State Communications **149**(1-2), 45 (2009).
[4] A. I. Isayev, S. I. Mекhtiyeva, N. Z. Jalilov, R. I Alekperov, V. Z. Zeynalov, Optoelectron. Adv. Mat. **8**, 368(2007).
[5] Ya.G. Klyava, Fiz.Tverd.Tela **27**, 1350 (1985).
[6] J. Tauc, The optical properties of solids. Ed.F. Abeles, North Holland: Amsterdam (1970).
[7] K. D. Tsendin, Electronic Phenomena in Glassy Chalcogenide Semiconductors, Nauka, St.-Petersburg (1996) [in Russian].
[8] A.I. Popov, Semiconductors and Semimetals, **78**, 51(2004).
[9] J. Jounopulosa, J. Lyukowski, Physics of hydrogenated amorphous silicon. Issue. 2: Electronic and vibrational properties. Moscow, Mir (1988)
[10] A. I. Isaev, S. I. Mekhtieva, S.N.Garibova, R.I.Alekperov, V. Z. Zeynalov, Fiz. Tekh. Poluprovodn **45**, 1026 (2011) [Semiconductors 45, 993 (2011)]
[11] Tanaka Keiji, Nonlinier Optics in Glasses: How can we analyze? Czech Rep.: Pardubice (2006).
[12] S. N. Garibova , S.I. Mekhtiyeva, A.S. Huseynova, M. A. Ramazanov, Chalcogenide Letters **14**(6), 223 (2017).