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The optical absorption of $Se_{95}As_5$ system doped by atoms of samarium

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During the investigation of optical properties of the $Se_{95}As_5$ chalcogenide vitreous semiconductor (CVS) structure containing impurity of samarium, it was established that there is a correlation between dependences of optical absorption factor (α), its photoinduced change (Δα), effective concentration of the charged defects (N_t) and the characteristic energy (E_0), corresponds to Urbach absorption on the concentration of entered atoms of rare earth impurity elements (Sm). It is shown, that absorption of light in the spectrum region corresponds to Urbach rule and in the weak absorption region, i.e. in the «tail» area is controlled by the charged defects (U^-–centers). It was established, that by changing the impurity atoms content it is possible to change the concentration of intrinsic charged defects that allows controlling the optical properties of CVS material.

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1. Introduction

Chalcogenide vitreous semiconductors (CVS) due to such unique physical properties as high transparency in the wide range of wavelength in infrared (IR) region, possibility to change refractive index and electron properties by different impurities introduction, low energy of phonon interaction and also simplicity of production technology of this material class makes them prospective for use in different devices of micro- and optoelectronics. However advantageous use of CVS for different purposes requires technology development of material production with given properties and comprehensive investigation of electron processes in progress.

We formulated in [1] the production method of crystal-resistant CVS of Se-As system including halogen impurities (Cl, Br) and investigated completely the processes of charge carrier transfer, as well as photo-electric and optical properties [2-7]. It is shown that by chemical composition change and impurity introduction one can change electron properties of CVS especially to produce CVS material with improved characteristics of charge carrier transfer.

The present paper deals with the investigation of CVS optical properties of $Se_{95}As_5$ system containing Sm rare-earth impurities.

The choice of rare-earth impurity as an investigation subject is connected with the fact that the material, both in structure and in electron properties is more stable and show – wide –band feature [1-7].

The choice of rare-earth impurity is due to the fact that CVS with rare earth element (REE) ions have been used for the production of telecommunication device light guide of near IR band. Besides 4f-electron state in rare-earth elements being more resistant in CVS system band gap creates local 4f levels due to 4f states of REE ions. It leads to the fact that optical band gap of REE doped CVS overlaps in energy a possible number of transitions resolved for REE ion (Sm). It is suggested that Sm impurities can be manifested as positively charged interstitial defects (U^--centers). By changing the U^-- centre concentrations one can control CVS electrical, optical and photoelectric properties that is very important for practical use.

2. Experimental technique and manufacturing of samples

Synthesis of CVS of the $Se_{95}As_5$ composition with samarium impurity was carried out by alloying the corresponding amounts of the chemical elements special cleanliness in the vacuum quartz ampoules at temperatures above 900°C in the rotating furnace, with the subsequent cooling at switching off furnace. The impurity was introduced during synthesis, at a concentration of about $3\times10^{19}\div 3\times10^{22}$ cm^{-3}.

The factor of optical absorption is investigated by the method of two-beam spectroscopy in the energy interval of 1 ÷ 2.8 eV.

The samples for were films of thickness of 0.5 μm ÷ 2 mm. The films were prepared onto the glass substrates by thermal evaporation in vacuum at 1.3×10^{-4} Pa .

3. Results and discussion

In Fig.1a there are presented CVS optical absorption spectra of $Se_{95}As_5$ composition with different content of Sm impurity. As it is seen from the figure the curves of spectral distribution of absorption factor for all the samples show the features peculiar to CVS materials i.e. dependence α(hυ) in the energy range of the incident photon 1.6÷2 eV obeys Urbach rule. At photon energy above 2 eV on exponential function is observed, but below 1.6 eV there was observed a “tail” absorption, i.e. photon absorption with the energy smaller than optical band gap but not obeying Urbach rule.

Experimental distribution of optical band gap in glass-like material is more complex than in crystals. First of all this is because in mentioned materials beyond the boundary of conduction band and valence band there was rather high concentration of local electron states due to light absorption in the absence of phonon effects. Therefore optical band gap has been determined conventionally in the frame of Tauc model [8], used previously for experimental data treatment in CVS [9], i.e. we consider that light absorption in the energy region above 2 eV is related to the electron states in non-localized states (transitions "band-band"), density of states valence band and band conduction having parabolic distribution. By applying

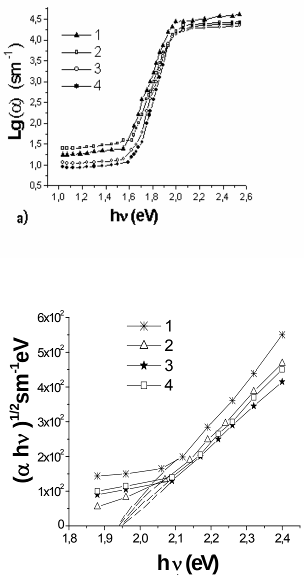
$$\alpha(h\upsilon) = A(E_g - h\upsilon)^p / (h\upsilon)^m n(h\upsilon) \qquad (1)$$

there has been constructed a plot of the dependence $\alpha(h\upsilon)$ on the incident light energy. The result are given in Fig. 1b, where p=2, m=1, $n(h\nu)$ refractive is the index, and A – is constant. The width of band gap is about $E_g \approx 1.95$ eV for all samples and does not depend on concentration of the samarium impurity.

The absorption factor to fitting the Urbach rule in the intermediate region of spectrum, i.e. in the photon energy region of 1.6 ÷ 2 eV, is

$$\alpha = \alpha_0 \exp [- (E_g - h\upsilon)]/E_0 \qquad (2)$$

where E_0 is the characteristic energy, which characterizes steepness (smear degree) of the edges and carries information on the root-mean-square rejection of internuclear distances in vitreous matrix [9].



b)

Fig. 1 The spectra of optical absorption factor (a) and dependences of αhν on the energy of falling radiation (b) of $Se_{95}As_5$ system doped by samarium. 1- 0 , 2 -1,.5 ×10^{20} cm^{-3} 3 – 1,.8 ×10^{22} cm^{-3} , 4 -3 ×$10^{22c}m^{-3}$.

The values of characteristic energy (E_0) for all samples are determined from exponential region, which results are presented in fig. 2a as dependence on the concentration of Sm impurity.

In [10] by utilization the model of casual field created by charged atoms chaotically distributed in space for characteristic energy the formula

$$E_0 = 2.2\, W_B\, (N_t a_B^3)^{2/5} \qquad (3)$$

where $W_B = e^2/2\varepsilon a_B$, a_B - is the Bohr radius in substances, ε-is the dielectric permittivity, N_t- is the effective concentration of the charged defects. Taking the dielectric permittivity value equal to ε=6.58 [11], the concentration of the charged defects (N_t) are calculated by the formula (3) and the obtained results are presented in Fig. 2a. As seen from Fig. 2a, b, with increasing concentration of entered Sm impurity atoms of up to 1.5×10^{20} cm^{-3}, the value of characteristic energy and concentration of the charged defects increases and further increase of impurity atoms concentration results in the decreasing of E_0 and N_t.

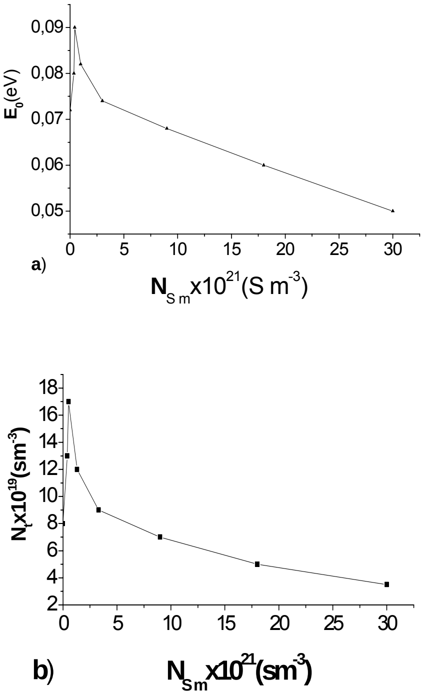


Fig. 2 Dependence of characteristic energy (a) and concentration of the located states (b) in $Se_{95}As_5$ system on the composition of samarium impurity.

Fig. 3a, b, c shows the dependences of optical absorption factors of the $Se_{95}As_5$ CVS on the concentration of the entered samarium atoms in the power dependence region (Fig. 3a), in the Urbach region (Fig. 3b) and in the "tail" region, i.e. when energy of a photon is lower, than Urbach absorption (Fig. 3c). It is clearly seen, that the dependence of optical absorption factor on the concentration of Sm atoms both in Urbach, and in the "tail" region almost repeats the dependence for E_0 and N_t.

However, in the Urbach region the impurity of Sm strongly influence the value of optical absorption factor. As seen from Fig. 3a the influence of Sm impurity on the value of optical absorption factor in the region of power dependence, i.e. at photon energies exceeding 2 eV differs from above mentioned regions; the factor of optical absorption decreases up to 3×10^{21}sm^{-3} of the samarium contents, i.e. there is "blooming" of the sample, and the further increase of concentration of the Sm atoms results to gradual increase of the factor, i.e. "fogging" of the sample. The above-mentioned facts of influence of rare impurity elements on the optical properties of $Se_{95}As_5$ prove the complex character of influence of a given impurity on their structure and electron properties.

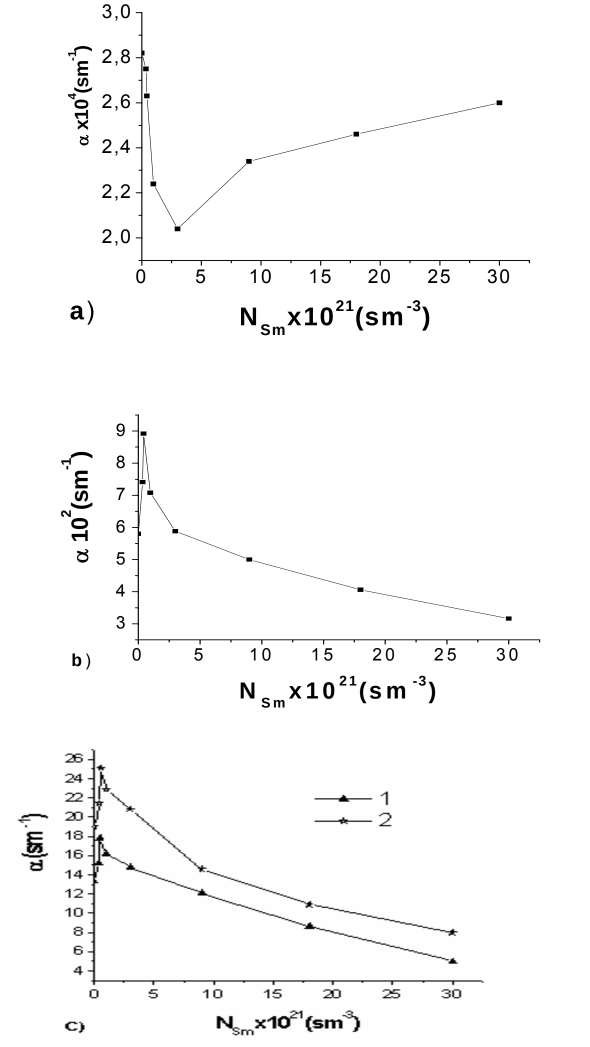


Fig. 3 Dependence of optical absorption factor on the composition of samarium impurity in the power dependence region (a), in the region of Urbach absorption (b), in the energy region lower than Urbach absorption (c).1-at illumination, 2 – in darkness.

Fig. 4a, b shows the spectral distribution of optical absorption factor of the $Se_{95}As_5$ CVS structure containing 3×10^{20} cm^{-3} of Sm without illumination and under the strongly absorbed light with photon energy of ≈ 2 eV (Fig. 4a) and the dependence of photoinduced change of the optical absorption factor on the concentration of Sm atoms (Fig. 4b). As seen, additional illumination influences the obtained optical results and this could be explained by the introduction of "lightweight" elements to film volume, before the introduction of oxygen to compounds of rare-earth elements, i.e. formation of new chemical compounds of AsO, SeO. Such explanation is not comprehensible to our investigation as technological process and preparation regimes of samples exclude the introduction of oxygen to the film structure. Independence of band gap width of the $Se_{95}As_5$ CVS compositions on the concentration of entered samarium atoms proves that the impurity atoms influence, basically, the electronic states located inside the band gap and near the edges of the conduction band. The set of the observed experimental facts allows stating the number of reasons regarding the influence of rare-earth atoms of Sm on the optical properties of $Se_{95}As_5$.

The below-mentioned experimental facts prove the connection between the optical absorption factor and the charged defects:

- Dependence of optical absorption factor of the $Se_{95}As_5$ CVS on the concentration of the entered samarium atoms, in Urbach (Fig. 3b) and in "tail" region (Fig. 3c), i.e. in the region of weak absorption;
- Observation of "photoblooming" in the "tail" region, i.e. decrease of the optical absorption factor under action of stimulating light from the intrinsic absorption region (Fig. 4a) and dependence of photoinduced change of the optical absorption factor on the concentration of entered atoms of Sm (Fig. 4b);
- Observation of correlation between the dependences of optical absorption factor, values of the characteristic energy (E_0) corresponding to Urbach absorption, concentration of the charged defects (N_t) on the concentration of the entered atoms of samarium (Fig. 2, 3)

The origin of exponential region (Urbach absorption) in the absorption spectrum it is not fully explained. However, now it is universally recognized that Urbach absorption is directly connected to the structural disorder [19]. Analyzing the experimental facts concerning optical properties, authors of work [22] have come to the conclusion, that the characteristic energy of the Urbach absorption E_0 is the parameter that determines the degree of disorder and is dependent on such factors as dominant type of chemical connection, coordination number of vitrificator and the size of atoms in sublattice of the network modifier. The parameter of disorder (E_0) in chalcogenide glasses is lower than in others vitreous materials and that, apparently, is due to the greater covalence in them.

According to [18], the origin of Urbach absorption is due to fluctuation of the electrostatic type potential. Detailed calculations of the absorption factor and its dependence on the external electric field were carried out in [19] for the case of smooth fields of electrostatic type and in [20] the transitions with participation of phonons were taken into account. According to [20] tail in absorption is defined by the Frank-Kiddush's effect in the internal electrostatic absorption factor only in the "tail" region, i.e. in this region takes place the "photoblooming".

The "blooming" also has been observed in As_2Se_3 CVS films e[12], modified by complex compounds of rare earth elements and whose origin is probably connected to spatial fluctuations of concentration of the charged defects or impurity [21].

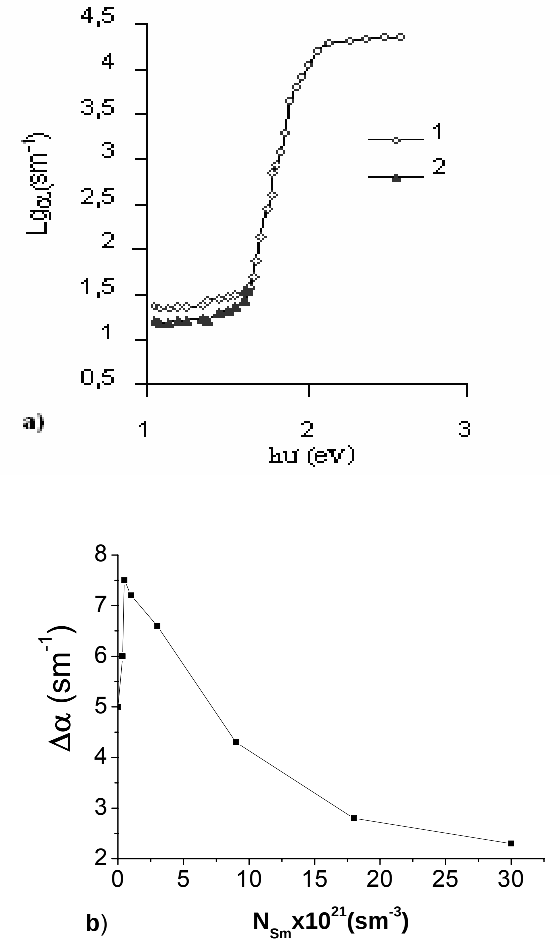


Fig. 4 a) Dependence of optical absorption factor on the radiation energy of the $Se_{95}As_5$ system with impurity of $3\times10^{20}sm^{-3}$ (1), the same dependence at illumination (2) b) Dependence of photoinduced change of the optical absorption factor for $Se_{95}As_5$ system on the amount of samarium impurity.

In paper [23] two groups of materials were distinguished by structural features, and on flexibility of structure. One group includes those materials where the structural matrices contain bridging connections and are more mobile owing to what type of disorder regions occur without infringement of the continuity of the grid. The second group of materials possesses more rigid structure. Introduction in such system of various modifiers results in the formation of the ordered regions of the average order, i.e. micro-area with high coordination number. Thus, between various regions there are potential barriers whose heights are determined by the charged centers. If one accepts, that the entered samarium atoms are Sm^{3+} ions and they basically are positioned in regions with increased coordination number (i.e. the degree of structural disorder and heterogeneity of distribution of the charged centers, and also the height of the potential barriers are high) this should lead to the increase of the parameters: absorption factor, concentration of the charged centers and characteristic energy that was really observed at small concentration - up to 1.5×10^{20} cm^{-3} of Sm (Fig. 2,3). At high concentration of Sm^{3+} impurity ions being allocated by all matrices and due to chemical activity drawing to them the ends of selenium circuits promote the structural reorganization resulting in the formation of disordered grid and simultaneously form connections between the various micro-areas. On the other hand, according to the model of the charged defects, the presence of Sm^{3+} ions should lead to the change of concentration of the intrinsic charged defects: the decrease of D^+ and the increase of D^-. Joint influence of the specified factors results in the reduction of characteristic energy of the Urbach absorption and concentration of the charged defects controlling Urbach absorption owing to what there is "blooming" of the material that is observed at the high concentration of Sm impurity (Fig. 2, 4). The observation of "photoblooming" only in the weak absorption region, and, also, the appearance of a maximum in dependence of photoinduced change of the optical the absorption factor on the concentration of entered Sm atoms at 1.5×10^{20} cm^{-3} (Fig. 4b), i.e. at concentration where the optical absorption factor and concentration of the charged defects possess the maximum value once again testify that absorption of light in the specified region of the spectrum is due to the transitions between bands and states of D^+ , D^- whose concentration at photoexcitation goes down in comparison with the equilibrium one.

4. Conclusions

It was established, as a result of investigation of optical properties of the $Se_{95}As_5$ CVS structure containing impurity of samarium, that there is a correlation between the dependences of optical absorption factor (α), its photoinduced change (Δα), effective concentration of the charged defects (N_t) and the characteristic energy (E_0) corresponding to Urbach absorption on the concentration of entered impurity atoms of the rare earth elements (Sm). It is shown that absorption of light in the region of the spectrum, which is due to the Urbach rule, and in the weak absorption region, i.e. in "tail" region is controlled by the charged defects (U^- - centers). It is established that by changing the impurity atoms content it is possible to change the concentration of intrinsic charged defects that allows to control the optical properties of the CVS material.

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