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The behavior of the optical characteristics of modified arsenic triselenide films

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Abstract: The influence of the level of modifier content on the behavior of the optical characteristics of thermally deposited films of arsenic triselenide chalcogenide glasses is investigated. A parallel shift of the absorption edge towards short wavelengths and a decrease in the slope of the exponential “tail” are observed. The increase in the slope of the Urbach energy dependence with an increasing modification level can be explained both by an increase in the concentration of metal-metal bonds, due to a deviation from stoichiometry, and by a transition through the value of the coordination number corresponding to the point of the topological phase transition. A simultaneous decrease in the band gap apparently indicates an increase in the defectiveness of the structure. In addition, it may indicate the presence of a higher concentration of trap states near the Fermi level, leading to a corresponding smearing in the “tails” of conductivity in chalcogenide glassy semiconductors (CGS).

Keywords: chalcogenide glasses, modifying impurity, absorption coefficient, Urbach energy, band gap

Introduction

Studying the influence of a modifying impurity on the optical properties of amorphous chalcogenide glasses in the As–Se system is important from the point of view of their use in optoelectronics (Avanesyan et al. 2022; Provotorov et al. 2021). The spectral dependence of optical absorption in amorphous semiconductors, as a rule, includes the following main regions:

1. Upper absorption region ($\alpha > 10^4$ cm^{-1}), in which the presence of interband transitions is assumed, and the absorption coefficient is determined by the following expression (Avanesyan et al. 2021):

$$\alpha(h\nu) = \frac{B\left(h\nu - E_g\right)^2}{h\nu}, \tag{1}$$

where B is a constant, ν is the frequency of optical vibrations, h is Planck’s constant, and E_g is the optical band gap. The latter is determined by the intersection of the tangent and the absorption curve in coordinates $\alpha(h\nu)^{1/2}$ with the axis of photon energy values $h\nu$.

2. Intermediate interval (1 cm^{-1}< α <10^4 cm^{-1}), in which parameter α depends exponentially on the photon energy, that is, the so-called “glassy” modification of Urbach’s rule is performed (Weinstein et al. 2001):

$$\alpha(h\nu, T) = \alpha_{\mathrm{gl}} \exp\left[\left(h\nu / E_{\mathrm{U}}\right) + \left(T / T_{\mathrm{o}}\right)\right], \tag{2}$$

where α_{gl} is a constant, E_{U} is a parameter (Urbach energy) which takes into account the degree of disorder present in the system and determines the width of the "tails" of the zones of localized states in the band gap, and T_{o} is the characteristic temperature. The temperature-independent logarithmic slope of the spectral response is given by:

$$1 / E_{\mathrm{U}} = \partial(\ln\alpha) / \partial(h\nu), \tag{3}$$

Expression (2) includes a shift of the absorption edge with increasing temperature to the long-wavelength region without changing the slope parameter E_{U}. The second term in the exponent (2) characterizes the linear temperature dependence of the absorption edge, which occurs in the temperature range from close to room temperature and above up to T_{g}. As some studies show, in the region of low temperatures there is a significant deviation from the linearity of the temperature shift of the optical edge. The parameter Eu, proposed by Weinstein et al. (Weinstein et al. 2001), characterizes the influence of static (i. e., "frozen" phonons) and dynamic (i. e., thermal phonons) order disturbances arising from the movement of atoms from the equilibrium state. At the same time, this parameter is also a characteristic of the energy length of the band "tails" of the density of states. It was found that the specified parameter is highly sensitive to changes in the structure and level of order, making it an ideal tool for obtaining information about structural changes in glass caused by various experimental conditions. Unfortunately, there is no unambiguous interpretation of the nature of the rule under discussion. There are usually three main factors that determine the value of the E_{U} parameter for glassy semiconductors (Sobolev 2012): a) the dominant type of the chemical bond, b) coordination number of the glass former, c) the size of atoms in the modifier sublattice.

3. Weak absorption in the "tails" of the zones with a low value of the coefficient $\alpha < 1$ cm^{-1}, whose shape of dependence and value are determined by the degree of purification, thermal history and sample manufacturing technology.

Experimental methods

The behavior of impurities in amorphous semiconductors raises two issues — one related to the nature of defects and the other, to the degree of disorder. In thermally deposited CGS films, the structure of which is more disordered than in bulk samples, the addition of modifier atoms occurs more easily. Films for optical measurements were prepared by vacuum deposition of the original CGS onto a glass substrate kept at room temperature. The degree of amorphism of the studied samples was controlled by the X-ray method. Optical absorption was measured using an SF-2000 and SF-56 spectrophotometer. The incident radiation was perpendicular to the surface of the layer under study.

Results and discussion

Fig. 1 shows the spectral characteristics of the absorption coefficient α of As_2Se_3 films obtained by vacuum deposition for different levels of modifying impurity (Pb) content. The data obtained indicate a parallel shift of the absorption edge with increasing Pb content, a shift of the spectrum towards shorter wavelengths, and a decrease in the slope of the exponential tail with increasing modifier content. In this case, the highest slope corresponded to undoped CGS. The intermediate value of the absorption coefficient complies with Urbach's rule, which is usually associated with a superposition of electron transitions from the "tails" of the valence band to the states of the extended conduction band. There is a simple correlation between the apparent band gap and the width of the valence band "tail" E_{o} (Vainshtein et al. 2000):

$$E_{\mathrm{g}} = E_{\mathrm{go}} - cE_{\mathrm{o}}, \tag{4}$$

where E_{go} is the maximum band gap for an infinitesimal tail width, and c is a constant.

If the width of the Urbach tail varies with impurity concentration (or temperature), extrapolating the Eu energy edges to the high energy region for different amounts of impurities gives an intercept

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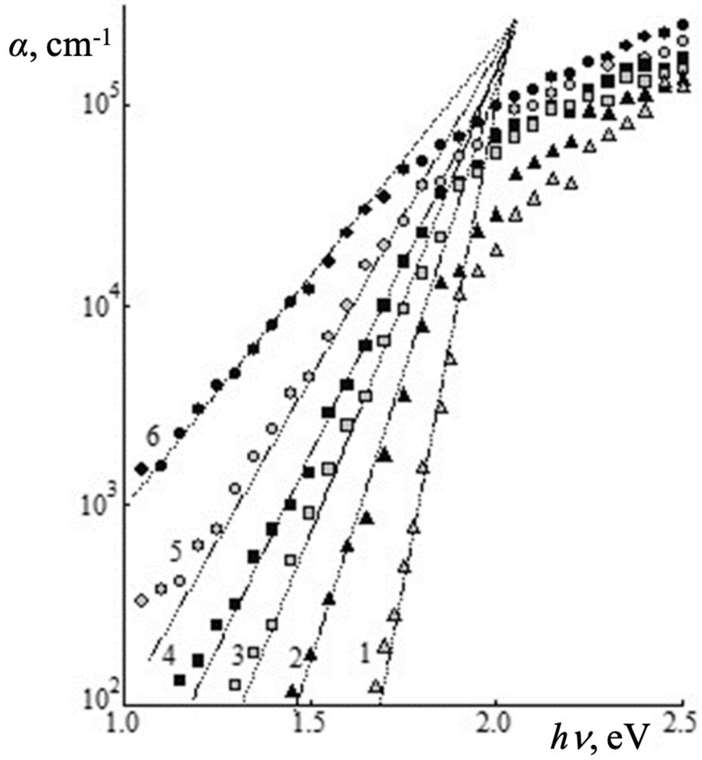

Fig. 1. Absorption spectra of As_2Se_3<Pb> films with different levels of modifier content: 1 — undoped sample, 2 — 1.5 %, 3 — 3.2 %, 4 — 4.1 %, 5 — 6.4 %, 6 — 10.5 at. % Pb

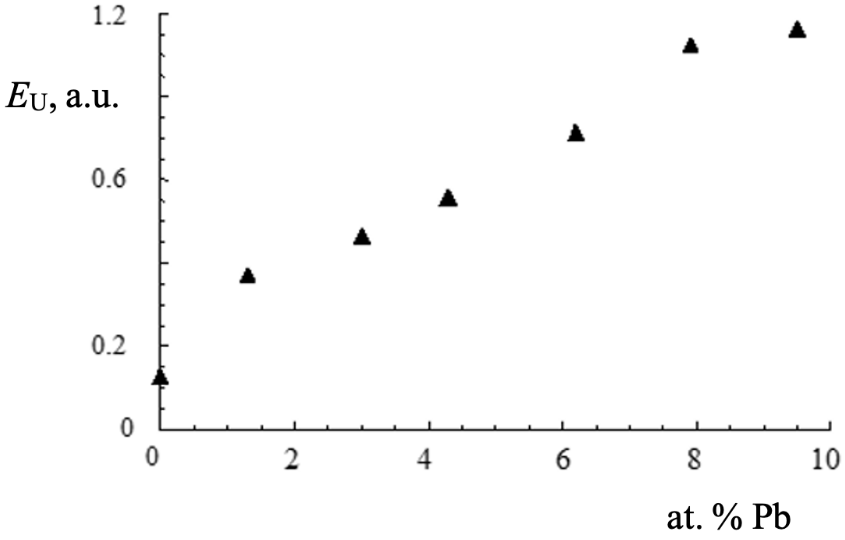

Fig. 2. Dependence of Urbach energy on the percentage of the modifier for As_2Se_3 <Pb>

corresponding to the value of E_{go}. Fig. 2 shows the dependence of the Urbach energy E_U on the level of modification of the samples of the CGS under study. Two areas of increasing E_U value can be noted. As the modifier content increases, the slope of the dependence becomes steeper. The observed increase in E_U values, as shown by previous studies, can be explained by two reasons, namely: a) an increase in the concentration of metal-to-metal bonds due to a deviation from stoichiometry, b) a transition through the value of the coordination number corresponding to the point of topological phase transition. The observed expansion of the Urbach "tail" may be associated with an increase in disorder during the formation of new structural elements in combination with modifier atoms in addition to the existing structural disorder.

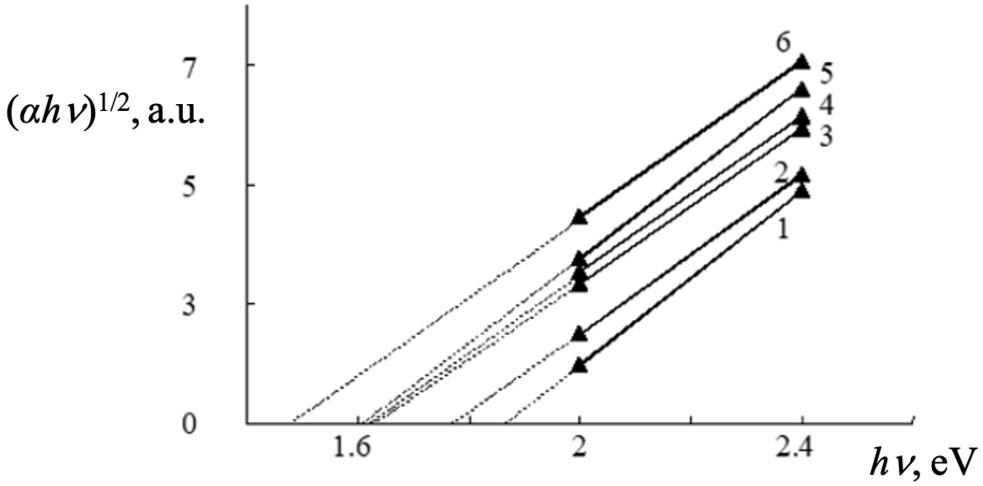

Fig. 3. Tauc plot for modified As_2Se_3<Pb> films (linear approximation):
1 — 0, 2 — 1.5, 3 — 3.2, 4 — 4.1, 5 — 6.4, 6 — 10.5 at. % Pb

Fig. 3 shows the corresponding dependences in Tauc coordinates (Tauc 1968) for As_2Se_3 film structures.

The optical band gap E_g was determined by extrapolating the linear dependence of the optical absorption edge from the $\alpha^2(h\nu)$ curves. The data obtained show a decrease in this parameter proportional to the percentage of impurities. The decrease in E_g with increasing Pb content is in satisfactory agreement with the results of studies on the effect of doping on the optical properties of CGS obtained by other authors. The difference in the value of the band gap apparently indicates a greater defectiveness of the structure and, probably, a greater concentration of trap states near the Fermi level, which leads to a corresponding smearing in the "tails" of CGS conductivity. Following the fact that the Pb–Se bond energy is greater than the As–Se one, we can conclude that the concentration of As–As bonds increases with increasing modifier content. The noted behavior of the Tauc plots can be determined by the formation of new structural units of the PbSe type, which accompanies the introduction of the modifier and reduces the optical band gap compared to the original matrix.

The structure of As_2Se_3 is usually represented using a statistical model based on structural units — clusters of the AsSe, $AsSe_2As$, $AsSeAs_2$ and $AsAs_3$ types. The AsSe compound is dominated by molecular fragments As_2Se_3 and As_4Se_4 with the presence of homobonds between arsenic atoms. These bonds lead to a noticeable decrease in the binding energy in the AsSe lattice compared to stoichiometric As_2Se_3. Under these conditions, the formation of new clusters based on impurity atoms (for example, PbSe) does not contradict the structural model. Apparently, both factors contribute to the observed behavior of the E_U parameter. The increase in the slope of the E_U dependence may be associated with a topological phase transition to a layered structure. According to available data, the energy states near the valence band of the As_2Se_3 material mainly include the p-orbitals of chalcogen lone pairs (low-energy region of the reflection region), and the high-energy maximum zone belongs to the pσ orbital of the chalcogen atom. The p and s As orbitals contribute to both sides of the reflectance spectrum peak.

Conclusions

The conducted studies show that the addition of a modifier significantly modifies the fundamental reflection spectrum of CGS based on the As–Se systems, lowering the low-energy branch and raising the high-energy side of the spectral reflection curve. These changes indicate an increase in the role of bonding orbitals compared to the contribution of orbitals belonging to lone electron pairs. It has been established that the key physical and, in particular, optical characteristics of chalcogenide glasses are closely related to the presence of LEP in chalcogens involved in the formation of the upper part of the valence band of the semiconductor. Chalcogenide lone pair semiconducting materials are important due to their prospective applications in thermoelectrics, phase change memories, topological insulators, etc. At a low percentage of Pb, one can expect a stronger influence of impurity on intermolecular interactions since delocalization of lone pair electrons reduces the energy of valence states and contributes to stabilization of the entire structure.

Conflict of Interest

The author declares that there is no conflict of interest, either existing or potential.

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