

Deposition and optical absorption studies of Cu–As–S thin films

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Abstract. Cu–As–S thin films were deposited using the thermal evaporation technique. Optical transmission spectra of $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin films were measured within the temperature range 77...300 K. Temperature behaviour of absorption edge inherent to $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin films was studied. Temperature and compositional dependences of optical parameters in Cu–As–S thin films have been analyzed. It has been revealed that the energy pseudogap decrease and Urbach energy increase with the copper content increase take place in Cu–As–S thin films. The influence of order-disorder processes on optical properties of Cu–As–S thin films has been discussed.

Keywords: thin film, thermal evaporation, optical absorption, energy pseudogap, Urbach energy.

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1. Introduction

Due to their specific electrical and optical properties chalcogenide glasses take an important place among the non-crystalline materials. It is shown that the chalcogenides possess semiconducting properties, has found wide practical applications as an efficient material for optical data recording, holography, integrated optics [1]. In the recent years, the chalcogenides proved to be promising elements in manufacturing of optical lenses, prisms, plane-parallel plates and other parts of optical system that operate in the visible and infrared spectral regions. This is due to high values of refraction indexes as compared with classical optical glasses and to the wide range of transmittance.

Glasses and composites of Ag(Cu)–As–S system are perspective materials for creation of solid electrolytes, electrochemical sensors, electrochromic displays, *etc.* [2]. Among silver-containing chalcogenides, the Ag–As–S ternary system takes a remarkable place [3, 4]. Recently, we have reported about the structure [5], electrical conductivity [6], and optical absorption [7] in superionic Ag_3AsS_3 – As_2S_3 glasses and composites. In Ref. [8], we have presented the results of deposition of $(\text{Ag}_3\text{AsS}_3)_{0.6}(\text{As}_2\text{S}_3)_{0.4}$ thin films by using rapid thermal evaporation. Typical Urbach behaviour of optical absorption edge is observed for $(\text{Ag}_3\text{AsS}_3)_{0.6}(\text{As}_2\text{S}_3)_{0.4}$ thin film [9, 10]. Analysis of compositional dependences of the Urbach absorption

edge parameters for $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ ($x = 0.3, 0.6, 0.9$) thin films was performed in [11]. The influence of laser and e-beam irradiation on structural and optical properties of $(\text{Ag}_3\text{AsS}_3)_{0.6}(\text{As}_2\text{S}_3)_{0.4}$ thin film was analyzed in [12].

It should be noted that physical properties of Cu–As–S glasses were extensively studied (*e.g.*, [13, 14]), whereas only some papers were devoted to the properties of Cu–As–S thin films. Thus, physical-and-chemical interactions in amorphous thin films of As_2S_3 –copper system were investigated using the methods of resistometry, ellipsometry, microscopy and chemical dissolution in [15]. Optical properties of copper-containing thin films of Cu–As–S–Se system were studied in [16]. In [17], preparation of undoped and Cu-doped As_2S_3 thin films by using the chemical bath deposition method was reported as well as their structural, optical and electrical properties were presented. It was shown that the optical band gap decreases from 3 to 2.34 eV due to doping the Cu in As_2S_3 film [17].

This work is aimed at studying the deposition process, investigation of the optical transmission spectra, analyzing the absorption edge as well as the temperature and compositional studies of optical parameters inherent to Cu–As–S thin films.

2. Experimental

Cu–As–S thin films were prepared using rapid thermal evaporation from the corresponding material at near 1350 °C in vacuum ($3 \cdot 10^{-3}$ Pa) with a VU-2M setup. Structural properties of thin films were studied using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). SEM image in Fig. 1 demonstrates the surface of $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film. The EDX technique was used for determination of the chemical composition of Cu–As–S thin films. The thickness of Cu–As–S thin films was evaluated to be 0.5...1.5 μm .

The optical transmission spectra were studied in the interval of temperatures 77 to 300 K by using the MDR-3 grating monochromator; the UTREX cryostat was used for low-temperature studies. From the optical transmission spectra, the spectral dependences of the absorption coefficient were obtained [18].

3. Results and discussion

The optical transmission spectra of $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film measured within the temperature range 77...300 K are shown in Fig. 2. With the temperature increase, a red shift of the short-wave part of the transmission spectrum as well as the interferential maxima have been observed. Besides, a typical decrease of transmission in the interferential maxima with temperature has been revealed. The absorption edge spectra of $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film calculated from the transmission spectra have been presented in Fig. 3. It is seen that the absorption edge spectra within the range of their exponential behaviour in $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film are described by the Urbach relation [19]

$$\alpha(h\nu, T) = \alpha_0 \cdot \exp\left[\frac{\sigma(h\nu - E_0)}{kT}\right] = \alpha_0 \cdot \exp\left[\frac{h\nu - E_0}{E_U(T)}\right], \quad (1)$$

where E_U is the Urbach energy, σ – steepness parameter of the absorption edge, α_0 and E_0 are the coordinates of convergence point of the Urbach absorption edge. The α_0 and E_0 values for $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film as well as for As_2S_3 thin film are given in Table 1.

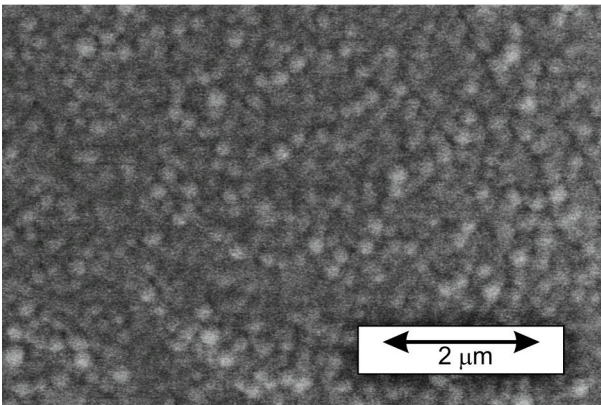


Fig. 1. SEM image of the $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film.

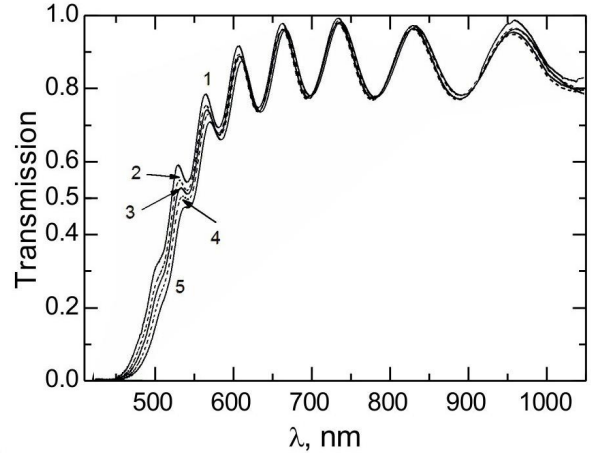


Fig. 2. Optical transmission spectra of the $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film at various temperatures: (1) 77, (2) 150, (3) 200, (4) 250 and (5) 300 K.

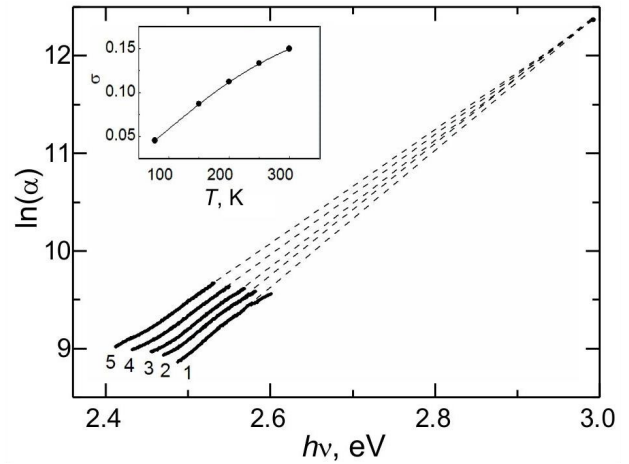


Fig. 3. Spectral dependences of the absorption coefficient of $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film at various temperatures: (1) 77, (2) 150, (3) 200, (4) 250 and (5) 300 K. The insert shows the temperature dependence of steepness parameter σ .

Table 1. Parameters of the Urbach absorption edge and EPI for $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin films.

Film	As_2S_3	$\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$
E_g^α (eV)	2.570	2.450
E_U (meV)	109.4	172.5
α_0 (cm^{-1})	$5.34 \cdot 10^4$	$2.30 \cdot 10^5$
E_0 (eV)	2.754	2.990
σ_0	0.264	0.221
$\hbar\omega_p$ (meV)	30.2	64.6
θ_E (K)	351	749
$(E_U)_0$ (meV)	57.2	146.3
$(E_U)_1$ (meV)	114.7	291.6
$E_g^\alpha(0)$ (eV)	2.529	2.530
S_g^α	15.1	13.6

As a rule, such Urbach behaviour of absorption edge is associated with exciton (electron)-phonon interaction. In our case, the temperature behaviour of the absorption edge in $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film is explained by electron-phonon interaction (EPI). The EPI parameters are obtained from the temperature dependence of steepness parameter for the absorption edge (see insert in Fig. 3) using the Mahr equation [20]

$$\sigma(T) = \sigma_0 \cdot \left(\frac{2kT}{\hbar\omega_p} \right) \cdot \tanh\left(\frac{\hbar\omega_p}{2kT} \right), \quad (2)$$

where $\hbar\omega_p$ is the effective phonon energy in the single-oscillator model describing the EPI, and σ_0 is a parameter related to the EPI constant. Parameters $\hbar\omega_p$ and σ_0 for $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film are given in Table 1. It should be noted that for $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film $\sigma_0 < 1$, which is the evidence for strong EPI [21]. Besides, in the $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film, as compared to the As_2S_3 one, EPI is enhanced (which corresponds to a decrease of the σ_0 -parameter), and the energy $\hbar\omega_p$ of effective phonon that takes part in absorption edge formation increases (Table 1).

For spectral characterization of the exponential absorption edge, we used the energy pseudogap E_g^α taken at $\alpha = 10^4 \text{ cm}^{-1}$ (Table 1). The temperature dependences of the energy pseudogap E_g^α and Urbach energy E_U for the $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film are presented in Fig. 4 and can be described by the following relations [22, 23]

$$E_g^\alpha(T) = E_g^\alpha(0) - S_g^\alpha k \theta_E \left[\frac{1}{\exp(\theta_E/T) - 1} \right], \quad (3)$$

$$E_U(T) = (E_U)_0 + (E_U)_1 \left[\frac{1}{\exp(\theta_E/T) - 1} \right], \quad (4)$$

where $E_g^\alpha(0)$ and S_g^α are the energy pseudogap at 0 K and some parameter, respectively; θ_E is the Einstein temperature corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators, $(E_U)_0$ and $(E_U)_1$ are constants. The obtained $E_g^\alpha(0)$, S_g^α , θ_E , $(E_U)_0$, and $(E_U)_1$ parameters for $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film as well as for As_2S_3 thin film are listed in Table 1, and the temperature dependences of E_g^α and Urbach energy E_U calculated from Eqs. (3) and (4) are shown in Fig. 4 as solid and dashed lines, respectively.

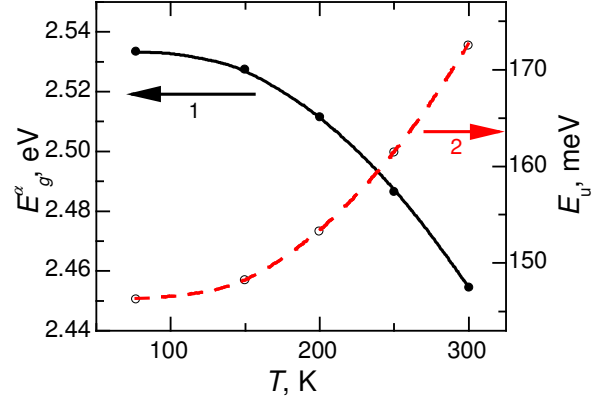


Fig. 4. Temperature dependences of the energy pseudogap E_g^α ($\alpha = 10^4 \text{ cm}^{-1}$) (1) and Urbach energy E_U (2) of the $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film.

It should be noted that the absorption edge of $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film is characterized by the high value of the Urbach energy E_U (Table 1). The Urbach energy E_U represents the influence of different type of disordering on absorption edge and is described by the equation [24]

$$E_U = (E_U)_T + (E_U)_X + (E_U)_C = (E_U)_T + (E_U)_{X+C}, \quad (5)$$

where $(E_U)_T$, $(E_U)_X$ and $(E_U)_C$ are contributions of temperature, structural and compositional disordering into the Urbach energy E_U , respectively. It should be noted that the first term in the right-hand side of Eq. (4) represents the sum of structural and compositional disordering, and the second one represents temperature disordering. In As_2S_3 thin film, only these two contributions (temperature and structural) influence on the absorption edge and determine the Urbach energy. In addition, the contribution of structural disordering into the Urbach energy E_U of As_2S_3 thin film is equal to 52%. With introduction of copper atoms into Cu-As-S thin films, the compositional component of disordering appears. Thus, in the $\text{Cu}_{0.1}\text{As}_{2.1}\text{S}_{3.1}$ thin film the contribution of sum of structural and compositional disordering into the Urbach energy is equal to 85%.

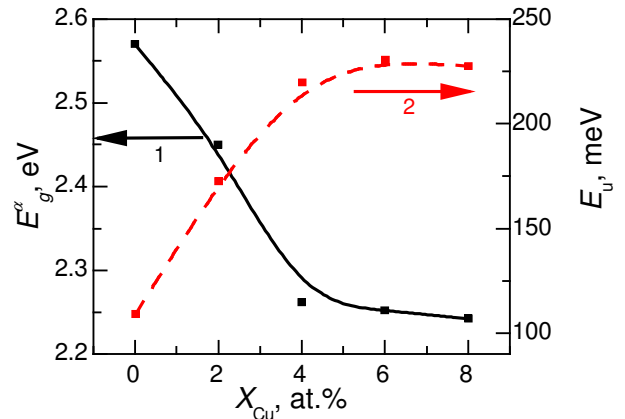


Fig. 5. Dependences of the energy pseudogap E_g^α ($\alpha = 10^4 \text{ cm}^{-1}$) (1) and Urbach energy E_U (2) on the copper content for Cu-As-S thin films.

Table 2. Energy pseudogap and Urbach energy for Cu–As–S thin films.

Film	E_g^{α} (eV)	E_U (meV)
As ₂ S ₃	2.570	109.4
Cu _{0,1} As _{2,1} S _{3,1}	2.450	172.5
Cu _{0,2} As _{2,7} S _{3,3}	2.262	219.8
Cu _{0,4} As _{2,6} S _{4,0}	2.252	230.6
Cu _{0,6} As _{2,9} S _{3,9}	2.242	227.6

Spectrometric studies of the absorption edge in Cu–As–S thin films have shown that its exponential shape and temperature behavior are similar for all the investigated range of composition. However, the absorption edge is shifted to the low energies (by 13%), and the Urbach energy is increased (by more than twice as large) with the copper content increase in Cu–As–S thin films in comparison with that of the As₂S₃ one (Fig. 5, Table 2). The above mentioned Urbach energy increase is the evidence of absorption edge smearing and appearance of Urbach tails caused by the influence of compositional disordering in these Cu–As–S thin films.

4. Conclusions

The Cu–As–S thin films were deposited onto a silica substrate by using the rapid thermal evaporation. Temperature variation of transmission spectra as well as the temperature variation of the absorption edge spectra within the range of its exponential behaviour for Cu_{0,1}As_{2,1}S_{3,1} thin films were studied within the temperature range 77...300 K. Urbach behaviour of the absorption edge determined by the strong electron-phonon interaction has been observed in the Cu_{0,1}As_{2,1}S_{3,1} thin film. Temperature dependences of the energy pseudogap and Urbach energy were obtained and described within the framework of Einstein model. The influence of different types of disordering on the parameters of Urbach absorption edge for the Cu_{0,1}As_{2,1}S_{3,1} thin film has been studied. It is shown that in Cu–As–S thin films at the copper content increase the energy of pseudogap decreases, while the Urbach energy increases. The increase of Urbach energy is related to the increase of disordering processes in thin films under investigation, moreover, the role of contribution of compositional disordering into the Urbach energy is significantly grown. Thus, compositional behaviour of optical properties in Cu–As–S thin films is mainly determined by the influence of compositional disordering caused by the increase of copper content.

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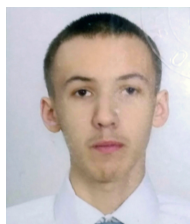
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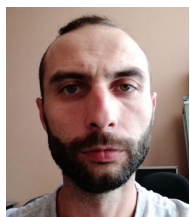
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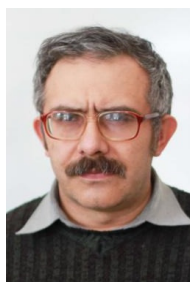
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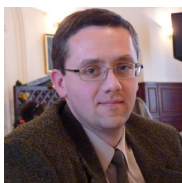
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