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Optical studies of as-deposited and annealed Cu_7GeS_5I thin films

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Abstract. Cu_7GeS_5I thin films were obtained by non-reactive radio frequency magnetron sputtering onto silicate glass substrates. Optical transmission spectra of as-deposited and annealed Cu_7GeS_5I thin films were measured in the temperature interval 77–300 K. The temperature behaviour of Urbach absorption edge and dispersion of refractive index for as-deposited and annealed Cu_7GeS_5I thin films was analyzed. Influence of annealing on the optical parameters and disordering processes in Cu_7GeS_5I thin films was studied.

Keywords: thin film, magnetron sputtering, annealing, optical absorption, refractive index, Urbach rule.

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1. Introduction

Cu_7GeS_5I crystals belong to the argyrodite family of tetrahedrally close-packed structures and are known as superionic conductors [1]. Some electrochemical properties of Cu_7GeS_5I crystals are reported in Ref. [2]. They are characterized by high electrical conductivity and low activation energy [3]. Optical studies have shown that the absorption edge of Cu_7GeS_5I crystals exhibits Urbach behaviour in a wide temperature range [3].

The compositional dependence of the lattice parameter of the alloys and single crystals of Cu_7GeS_5I–Cu_7GeSe_5I system was shown to be linear, described by the Vegard law, which is the evidence for formation of a continuous row of substitutive solid solutions [4]. At room temperature $Cu_7GeS(Se)_5I$-based solid solutions crystallize in the cubic symmetry (space group $F\bar{4}3m$). The short-wavelength edge of the diffuse reflection spectra of $Cu_7Ge(S_{1-x}Se_x)_5I$ solid solutions is shown to shift towards longer wavelengths with the substitution of S atoms by Se [4]. The compositional studies of electrical conductivity in $Cu_7Ge(S_{1-x}Se_x)_5I$ solid solutions revealed that S→Se anionic substitution results in a nonlinear increase of the electrical conductivity by more than an order of magnitude [5]. It should be noted that the total electrical conductivity of Cu_7GeSe_5I crystals at room temperature was found to be rather high and typical for the advanced superionic conductors [6]. Due to the high ionic conductivity, they are the attractive materials for applications in the different functional elements of the solid state ionics.

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The investigations of the thin films based on Cu_7GeS_5I superionic conductors only begin. Thus, in this paper the optical properties of Cu_7GeS_5I thin films are studied. Besides, the comparative analysis of optical parameters in single crystals and thin films as well as the comparative analysis of optical parameters in as-deposited and annealed thin films are performed.

2. Experimental

Cu_7GeS_5I compounds were synthesized from extra pure Cu, Ge, S and CuI compounds, additionally purified by distillation in vacuum. Thin films of Cu_7GeS_5I compounds were deposited onto silicate glass substrates by non-reactive radio frequency magnetron sputtering, the film growth rate was 3 nm/min. The deposition was carried out at room temperature in Ar atmosphere. The structure of the deposited films was analyzed by X-ray diffraction; the diffraction patterns show the films to be amorphous. Annealing was performed for 24 h at 100 ºC in vacuum.

Optical transmission spectra of Cu_7GeS_5I thin films were studied in the interval of temperatures 77–300 K by an MDR-3 grating monochromator, UTREX cryostat was used for low-temperature studies. Spectral dependences of absorption coefficient and dispersion dependences of refractive index of thin films were calculated using the well-known method [7].

3. Results and discussion

The optical transmission spectra at different temperatures in the interval of temperatures 77–300 K in as-deposited Cu_7GeS_5I thin film are shown in Fig. 1. A long-wavelength shift of short-wavelength part of absorption spectra and interference maxima with increasing of temperature is observed. The same temperature behaviour of transmission spectra was revealed for annealed Cu_7GeS_5I thin film.

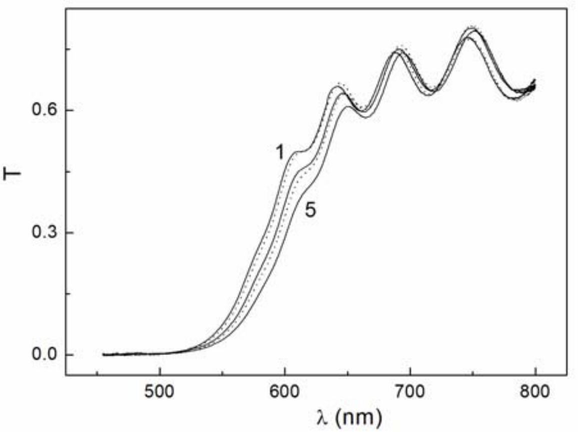

Fig. 1. Optical transmission spectra of Cu_7GeS_5I thin film at various temperatures: (*1*) 77, (*2*) 150, (*3*) 200, (*4*) 250 and (*5*) 300 K.

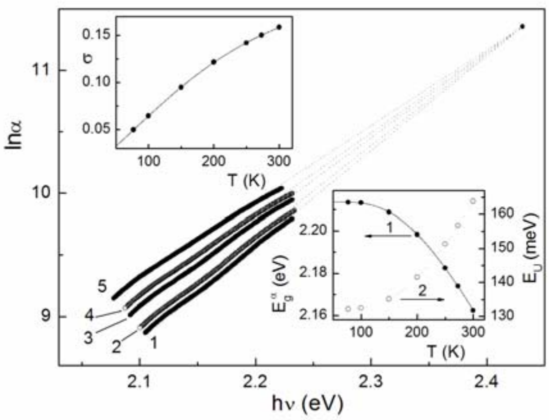

Fig. 2. Spectral dependences of the absorption coefficient of Cu_7GeS_5I thin film at various temperatures: 77 (*1*), 150 (*2*), 200 (*3*), 250 (*4*), and 300 K (*5*). The insets show the temperature dependence of the steepness parameter σ as well as the temperature dependences of the absorption edge energy position E_g^{α} ($\alpha = 10^4$ cm^{-1}) (*1*) and Urbach energy E_U (*2*).

Table. The parameters of Urbach absorption edge and EPI for Cu_7GeS_5I crystal and thin films.

Material	As-deposited film	Annealed film	Crystal
E_g^{α} (300 K), eV	2.162	2.090	2.125
E_U (300 K), meV	163.8	131.9	35.0
α_0, cm^{-1}	5.18×10^4	5.31×10^4	1.1×10^6
E_0, eV	2.431	2.310	2.371
σ_0	0.223	0.265	0.81
$\hbar\omega_p$, meV	59.3	54.6	28.7
θ_E, K	688	634	333
$(E_U)_0$, meV	132.2	103.1	17.8
$(E_U)_1$, meV	281.4	210.0	35.1
$E_g^{\alpha}(0)$, eV	2.213	2.138	2.247
S_g^{α}	7.67	6.36	8.5

Fig. 2 presents the spectral dependences of the absorption coefficient at different temperatures in interval 77–300 K for as-deposited Cu_7GeS_5I thin film. It is shown that the optical absorption edge for both as-deposited and annealed Cu_7GeS_5I thin films in the region of its exponential behaviour are described by Urbach rule [8]

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

where $E_U(T)$ is the Urbach energy, α_0 and E_0 are the coordinates of the convergence point of the Urbach bundle, $h\nu$ and T are the photon energy and temperature, respectively. Constants α_0 and E_0 for as-deposited and annealed Cu_7GeS_5I thin films are given in Table. For comparison the Table contains the corresponding parameters for Cu_7GeS_5I crystal. The exponential form of the long-wavelength side of the absorption edge is usually associated with exciton (electron)-phonon interaction (EPI) [9]. The Urbach energy $E_U(T)$ is related to another parameter, the slope of the Urbach edge $\sigma(T)$ as $E_U(T)=kT/\sigma(T)$, k being the Boltzmann constant. The inset in Fig. 2 shows that for Cu_7GeS_5I thin film in whole investigated temperature interval the $\sigma(T)$ dependence described by the Mahr relation [9]:

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

where σ_0 is a constant independent of temperature and related to the EPI constant g as $\sigma_0 = 2/3g$; $\hbar\omega_p$ is the effective average phonon energy in a single-oscillator model, describing the EPI. For as-deposited and annealed Cu_7GeS_5I thin films $\sigma_0 < 1$, which is an evidence for the strong EPI [10]. The values of effective phonon energy $\hbar\omega_p$ taking part in formation of the absorption edge and σ_0 parameter are given in Table. It is revealed that annealing leads to the insignificant weakening of EPI (increase of σ_0 parameter) and decrease of $\hbar\omega_p$ value.

For the characterization of the absorption edge spectral position, such parameter as E_g^α (E_g^α is the energy position of the exponential absorption edge) at a fixed absorption coefficient value α was determined. We used the E_g^α values taken at $\alpha = 10^4$ cm^{-1} for thin films as well as $\alpha = 10^3$ cm^{-1} for single crystal (Table). The temperature dependences of the E_g^α and Urbach energy E_U for Cu_7GeS_5I thin film are presented in the inset in Fig. 2. It is shown that for as-deposited and annealed Cu_7GeS_5I thin films it can be described in the Einstein model by relations [11, 12]

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

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

where $E_g^\alpha(0)$ and S_g^α are the energy position of absorption edge at 0 K and a dimensionless constant, 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 $E_g^\alpha(0)$, S_g^α, θ_E, $(E_U)_0$ and $(E_U)_1$ parameters obtained for the as-deposited and annealed Cu_7GeS_5I thin films are listed in Table. The temperature dependences of the E_g^α and Urbach energy E_U for as-deposited Cu_7GeS_5I thin film calculated from Eqs. (3) and (4) are shown in the inset in Fig. 2 by solid and dashed lines, respectively. It should be noted that the E_g^α and E_U values are seen to decrease with annealing. The Urbach energy E_U decrease being an evidence for the ordering processes in the annealed film. Besides, Table contains the above mentioned parameters for Cu_7GeS_5I single crystal.

It is revealed that the optical absorption edge spectra of the thin films under investigation is highly smeared and characterize by the lengthy Urbach tail which results in high values of the Urbach energy E_U (Table). Absorption edge smearing and appearance of its Urbach behaviour are explained by the influence of different types of disordering [13], i.e. the Urbach energy E_U is described by the equation

$$E_U=(E_U)_T+(E_U)_X=(E_U)_T+(E_U)_{X,stat}+(E_U)_{X,dyn}\qquad(5)$$

where $(E_U)_T$ and $(E_U)_X$ are the contributions of temperature and structural disordering to E_U, respectively. In Ref. [14] it is shown that structural disordering $(E_U)_X$ consists from the contributions of static structural disordering $(E_U)_{X,stat}$ and dynamic structural disordering $(E_U)_{X,dyn}$. The static structural disordering $(E_U)_{X,stat}$ in Cu_7GeS_5I thin film is primarily caused by structural imperfections due to the high concentration of disordered copper vacancies and the dynamic structural disordering $(E_U)_{X,dyn}$ is related to the intense motion of mobile copper ions, participating in the ion transport, and is responsible for the ionic conductivity. The first term in the right-hand side of Eq. (4) represents the static structural disordering, and the second one represents temperature-related types of disordering: temperature disordering due to thermal lattice vibrations and dynamic structural disordering due to the presence of mobile ions in the superionic conductor. Preliminary electrical studies have shown the total electrical conductivity of the thin film at $T = 300$ K to be $\sigma_t = 0.07$ S/m at the frequency of 1 MHz. Thus, the thin film prepared on the base of Cu_7GeS_5I compound was shown to be characterized by a high value of the electrical conductivity which can be used for the creation of miniature solid electrolyte batteries and supercapacitors of new generation.

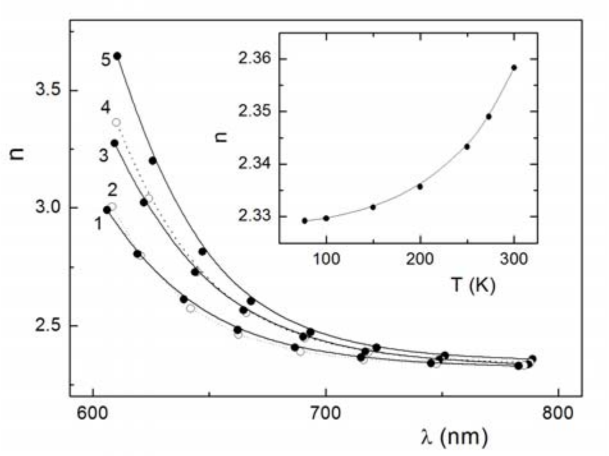

Fig. 3. Refractive index dispersions of Cu_7GeS_5I thin film at various temperatures: 77 (*1*), 150 (*2*), 200 (*3*), 250 (*4*) and 300 K (*5*). The inset shows the temperature dependence of refractive index.

For the estimation of the contribution of the different types of disordering into the Urbach energy E_U we used the procedure described in Ref. [15]. Thus, the contribution of static structural disordering into the as-deposited Cu_7GeS_5I film Urbach energy is shown to be 80.7%. The high value of above mentioned contribution for Cu_7GeS_5I thin film caused by the (1) the absence of long-range order in the atomic arrangement and chemical bond breakdown, (2) a lower density of the atomic structure packing due to the presence of pores, (3) transition from the three-dimensional bulk structure to the two-dimensional planar structure. It is revealed that annealing leads to the decrease of absolute and relative contributions of static structural disordering into E_U what is the evidence of structural ordering.

Dispersion dependences of the refractive index for the as-deposited Cu_7GeS_5I thin film (Fig. 3) were obtained from the interference transmission spectra. In the transparency region a slight dispersion of the refractive index is observed, increasing with approaching the optical absorption edge. With increasing temperature, a nonlinear increase of the refractive index in the as-deposited and annealed Cu_7GeS_5I thin films is revealed. Besides, the annealing leads to the refractive index increase from 2.360 to 3.120 at $\lambda = 1$ µm.

Finally, it should be noted that the transition from crystal to thin film caused the substantial increase of Urbach energy E_U, enhance the EPI (decrease of σ_0 parameter) and increase of the effective phonon energy $\hbar\omega_p$ as well as the increase of the relative contribution of static structural disordering into E_U from 50.9 to 80.7%.

4. Conclusions

Cu_7GeS_5I thin films are deposited onto silicate glass substrates by non-reactive radio frequency magnetron sputtering. Temperature behaviour of the optical transmission spectra for as-deposited and annealed Cu_7GeS_5I thin films is similar in the interval 77–300 K. With increasing temperature, a red shift of the optical absorption edge was revealed, in the range of its exponential behaviour is well described by the Urbach rule. The temperature dependences of the energy position of absorption edge, the Urbach energy, and the refractive index of as-deposited and annealed Cu_7GeS_5I thin films were analyzed. The temperature and structural disorder affect the shape of the Urbach absorption edge, the contribution of static structural disordering into the Urbach energy for the as-deposited and annealed Cu_7GeS_5I thin films was estimated.

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