Structural disordering studies of Cu_6PS_5I-based thin films deposited by magnetron sputtering

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Abstract. Cu_6PS_5I-based thin films were deposited onto silicate glass substrates by magnetron sputtering. With Cu content increase, a red shift of the optical transmission spectra as well as increase of the total electric conductivity are observed. A typical Urbach bundle are revealed, the temperature behaviour of the Urbach absorption edge in thin films are explained by strong electron-phonon interaction. Temperature dependences of the absorption edge energy position and the Urbach energy for thin film are well described in Einstein model. The influence of different type of disordering on the Urbach tail is studied.

1 Introduction

Cu_6PS_5I superionic conductors belong to the compounds with argyrodite-type structure, characterized by high ionic conductivity and intrinsic structural disordering [1]. Due to the remarkable physical properties Cu_6PS_5I are promising materials for creating renewable energy sources, electrochemical and optical sensors. During the last decades the optical properties of Cu_6PS_5I crystals have been studied in detail [2]. However, the studies of the optical properties of Cu_6PS_5I thin films only begins. For the first time Cu_6PS_5I thin films were deposited and studied in Ref. [3]. It should be noted that the thin films based on superionic conductors can be applied to the production of supercapacitors of new generation [4].

Therefore, investigation of physical properties of Cu_6PS_5I-based thin films is of great interest for argyrodite-type superionic conductors. In the present paper, we study the electrical conductivity and temperature behaviour of optical absorption edge of Cu_6PS_5I-based thin films deposited by magnetron sputtering.

2 Experimental

For Cu_6PS_5I-based thin films **s**puttering we used the co-deposition technique from two tilted magnetrons, one equipped with Cu_6PS_5I target (pressed powder) and second with pure Cu target. The deposition was carried out at room temperature in Ar atmosphere. For target preparing the microcrystalline powder with the average grain size of 50 μm was obtained by grinding of the synthesized material in an agate mortar.

Energy-dispersive X-ray spectroscopy was used to ensure the thin films chemical composition. It is shown that thin films in interval from $Cu_{6.31}P_{1.10}S_{4.68}I_{0.91}$ to $Cu_{7.20}P_{0.83}S_{4.14}I_{0.83}$ are enriched by copper and phophorous (at low concentrations of Cu) atoms, and deficient in phosphorous (at high concentrations of Cu), sulphur and halogen atoms, besides with copper content increase the content of phosphorous, sulphur and halogen decrease.

Electrical conductivity was measured by impedancemeter at frequency 1 MHz. Optical transmission spectra 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 the absorption coefficient and dispersion dependences of refractive index of thin films were calculated from the transmission spectra [5].

3 Results and discussion

Electrical studies have shown that the total electric conductivity of the thin films increase with increase of Cu atoms content. Thus, with Cu content increase in interval from $Cu_{6.31}P_{1.10}S_{4.68}I_{0.91}$ to $Cu_{7.20}P_{0.83}S_{4.14}I_{0.83}$ the electric conductivity increase from 0.053 S/m to 0.060 S/m, respectively. The high value of electrical conductivity in thin films under investigation make them the promising material for creation of solid state batteries and supercapacitors.

Futhermore, with Cu content increase, a red shift of the optical transmission spectra as well as absorption edge spectra is observed. Temperature variations of optical transmission in Cu_6PS_5I-based thin films are similar for all investigated samples (8 samples), but we will illustrate it for $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film. Thus, interferential transmission spectra of $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film at various temperatures within 77–300 K are shown in Fig. 1. With temperature increase, a red shift of both the short-wavelength part of the transmission spectrum and the interferential maxima is observed.

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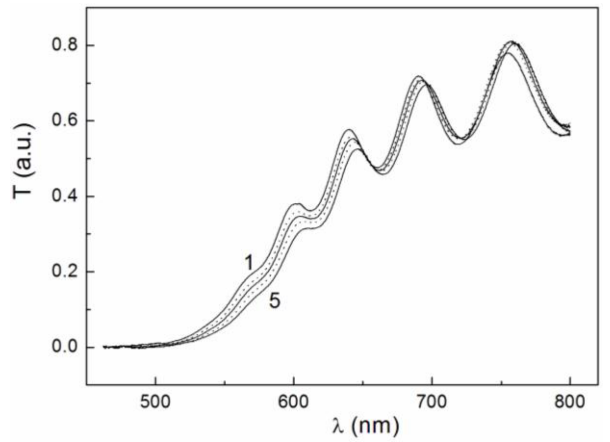

Fig. 1. Optical transmission spectra of $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film at various temperatures: (1) 77, (2) 150, (3) 200, (4) 250 and (5) 300 K.

Figure 2 shows that the optical absorption edge spectra in the range of their exponential behaviour in $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film are described by the Urbach rule [6]

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

where E_U is the Urbach energy, σ is the absorption edge steepness parameter, α_0 and E_0 are the convergence point coordinates of the Urbach bundle. The coordinates of the Urbach bundle convergence point α_0 and E_0 for the $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film are 1.13×10^6 cm^{-1} and 3.322 eV.

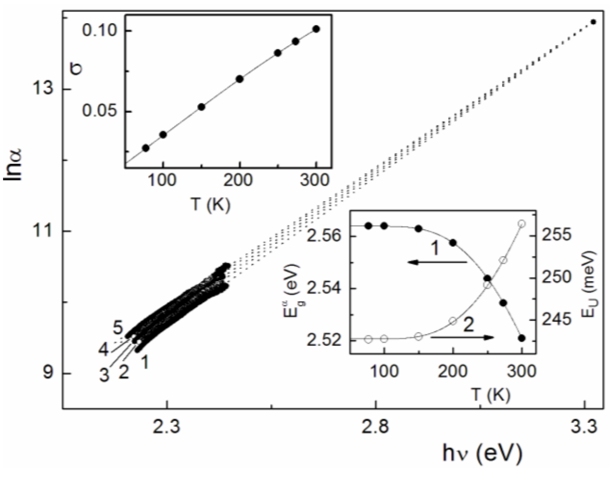

Fig. 2. Spectral dependences of the absorption coefficient of $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film at various temperatures: (1) 77, (2) 150, (3) 200, (4) 250 and (5) 300 K. The insets show (a) the temperature dependence of the steepness parameter σ, (b) the temperature dependences of the absorption edge energy position E_g^α (α=5×10^4 cm^{-1}) (1) and Urbach energy E_U (2).

The temperature behaviour of the Urbach absorption edge in $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film is explained by electron-phonon interaction (EPI) which is strong in the film under investigation. The EPI parameters are obtained from the temperature dependence of absorption edge steepness parameter (Fig.2) using the Mahr formula [7]

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

where $\hbar\omega_p$ is the effective phonon energy in a one-oscillator model, describing the electron-phonon interaction (EPI), and σ_0 is a parameter related to the EPI constant g as $\sigma_0 = (2/3)g^{-1}$ (parameters $\hbar\omega_p$ and σ_0 are given in Table 1). For the $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film $\sigma_0 < 1$ that is the evidence for the strong EPI [8].

It should be noted that in the range of exponential behaviour of optical absorption for their. For spectral characterisation of optical absorption edge we used the energy position of an exponential absorption edge E_g^α values taken at α=5×10^4 cm^{-1} (Table 1). It should be noted that at T=300K E_g^α=2.521 eV, while E_U=256 meV. The temperature dependences of E_g^α and the Urbach energy E_U for $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film (Fig.2) can be described in Einstein model by relations [9, 10]

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

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

where $E_g^\alpha(0)$ and S_g^α are the energy 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 obtained $E_g^\alpha(0)$, S_g^α, θ_E, $(E_U)_0$, and $(E_U)_1$ parameters for the thin film are given in Table 1.

An essential characteristic of the absorption edge spectra of the thin films under investigation is a lengthy Urbach tail which results in the high values of Urbach energy E_U (Table 1). In Ref. [11] it was shown that temperature and structural disordering affect Urbach absorption edge shape, i.e. the Urbach energy E_U is described by the equation

Table 1. Parameters of Urbach absorption edge and EPI for $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film

α_0 (cm^{-1})	E_0 (eV)	σ_0	$\hbar\omega_p$ (meV)	θ_E (K)	$(E_U)_0$ (meV)	$(E_U)_1$ (meV)	$E_g^\alpha(0)$ (eV)	S_g^α
1.13×10^6	3.322	0.2	97.3	1129	243	575	2.564	18.6

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

where $(E_U)_T$ and $(E_U)_X$ are the contributions of temperature-related and structural disordering to E_U, respectively; $(E_U)_{X,stat}$ and $(E_U)_{X,dyn}$ are the contributions of static structural disordering and dynamic structural disordering to $(E_U)_X$, respectively. It is shown that the contribution of static structural disordering into the film Urbach energy equals 95%. Static structural disordering in $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film may be additionally increase due to (1) the absence of long-range order in the atomic arrangement and chemical bond breakdown; (2) lower density of the atomic structure packing due to the presence of pores; (3) the transition from the three-dimensional bulk structure to the two-dimensional planar structure.

The dispersion dependences of the refractive index for the $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film was obtained from the interference transmission spectra (Fig. 3). With temperature increase the nonlinear increase of refractive index in $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film is revealed.

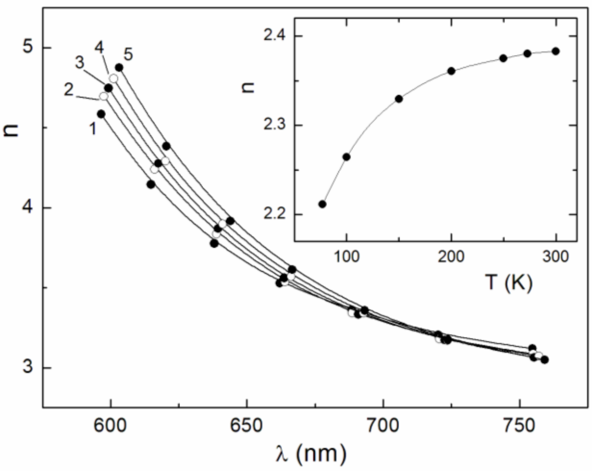

Fig. 3. Refractive index dispersions of $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film at various temperatures: (1) 77, (2) 150, (3) 200, (4) 250 and (5) 300 K. The inset shows the temperature dependence of refractive index.

4 Conclusions

Cu_6PS_5I-based thin films were deposited onto silicate glass substrates by magnetron sputtering. Electrical conductivity of Cu_6PS_5I-based thin films was studied depends on chemical composition, with Cu content increase of the total electric conductivity was increased. Optical transmission spectra of $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film was investigated in the temperature interval 77–300 K. With Cu content increase as well as with temperature increase, a red shift of the optical transmission spectra was revealed. Temperature variations of optical transmission in Cu_6PS_5I-based thin films are similar for all investigated samples, however it illustrated for $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film. It is shown that the optical absorption edge spectra in the range of their exponential behaviour in $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film are well described by the Urbach rule. Temperature dependences of the energy position of absorption edge, Urbach energy and refractive index of $Cu_{6.35}P_{1.12}S_{4.57}I_{0.95}$ thin film were analysed. The origin of lengthy Urbach tail and role of the different type of disordering were discussed.

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References

1. W.F. Kuhs, R. Nitsche, K. Scheunemann, Mat. Res. Bull. **11**, 1115-1124 (1976)
2. I.P. Studenyak, M. Kranjčec, M.V. Kurik, J. Phys. Chem. Solids **67**, 807-817 (2006)
3. I.P. Studenyak, M. Kranjčec, V.Yu. Izai, A.A. Chomolyak, M. Vorohta, V. Matolin, C. Cserhati, S. Kökényesi, Thin Solid Films **520**, 1729-1733 (2012)
4. A.L. Despotuli, A.V. Andreeva, B. Rambabu, Ionics **11**, 306-314 (2005)
5. R. Swanepoel, J. Phys. E: Sci. Instrum. **16**, 1214-1222 (1983)
6. F. Urbach, Phys. Rev. **92**, 1324-1326 (1953)
7. H. Sumi, A. Sumi, J. Phys. Soc. Japan **56**, 2211-2220 (1987)
8. M.V. Kurik, Phys. Stat. Sol. (a) **8**, 9-30 (1971)
9. M. Beaudoin, A.J.G. DeVries, S.R. Johnson, H. Laman, T. Tiedje, Appl. Phys. Lett. **70**, 3540-3542 (1997)
10. Z. Yang, K.P. Homewood, M.S. Finney, M.A. Harry, K.J. Reeson, J. Appl. Phys. **78**, 1958-1963 (1995)
11. G.D. Cody, T. Tiedje, B. Abeles, B. Brooks, Y. Goldstein, Phys. Rev. Lett. **47**, 1480-1483 (1981)