Influence of X-ray irradiation on the optical absorption edge and refractive index dispersion in Cu₆PS₅I-based thin films deposited using magnetron sputtering

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Abstract. Cu₆PS₅I-based thin films were deposited using non-reactive radio-frequency magnetron sputtering. Structural studies of thin films were performed by scanning electron microscopy, their chemical composition were determined using energy-dispersive X-ray spectroscopy. As-deposited thin films were irradiated with wideband radiation of Cu-anode X-ray tube at different exposition times. Optical transmission spectra of X-ray irradiated Cu₅.₅₆P₁.₆₆S₄.₉₃I₀.₈₅ thin films were measured depending on irradiation time. The Urbach absorption edge and dispersion of refractive index for X-ray irradiated Cu₅.₅₆P₁.₆₆S₄.₉₃I₀.₈₅ thin films were studied. It has been revealed the nonlinear decrease of energy pseudogap and nonlinear increase of refractive index with increase of X-ray irradiation time.

Keywords: thin film, magnetron sputtering, X-ray irradiation, optical absorption, refractive index.

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1. Introduction

Cu₆PS₅I compounds belong to an argyrodite family and are known as highly-efficient superionic conductors [1]. They are promising materials for creating new types of solid electrolyte batteries, ionistors, and electrochemical sensors [2]. Optical properties (absorption, luminescence, Raman scattering, refractive index dispersion) for Cu₆PS₅I crystals were extensively studied in Refs. [2-4]. Cu₆PS₅I thin films for the first time were deposited onto silicate glass substrates by non-reactive radiofrequency magnetron sputtering [5]. Structural studies show formation of a homogeneous two-dimensional amorphous structure. No phase transitions are observed in the temperature interval 77…300 K; however, at 470 K the film is partially destructed and detached from the substrate. A typical Urbach bundle is observed, temperature dependences of the energy pseudogap and the Urbach energy are described in the Einstein model.

The influence of annealing on the optical absorption edge parameters of Cu₆PS₅I thin films was investigated in Ref. [6]. It should be noted that the energy pseudogap decreases due to the annealing, but at the same time the Urbach energy increases more than 30%. Optical properties of sulphur and phosphorous implanted Cu₆PS₅I thin films as well as the influence of ionic implantation on energy pseudogap, Urbach energy and refraction indexes were studied in Ref. [7].

Electrical studies have shown that the total electric conductivity of the Cu₆PS₅I-based thin films increases...
with increase of Cu atoms content [8]. Thus, with the Cu content increase in the interval from Cu 5.37P1.88S5.04I0.71 to Cu 7.55P0.89S3.44I1.12, the electric conductivity increases from 0.044 to 0.066 S/m. Besides, with the Cu content increase, a red shift of the optical transmission spectra as well as a typical Urbach bundle, explained by strong electron-phonon interaction, are observed. It is shown that the Urbach tail of the investigated thin films caused by the influence of different type disordering and mainly determined by the contribution of static structural disordering into the film Urbach energy.

In this paper, we report on the influence of X-ray irradiation on the optical transmission spectra, Urbach absorption edge parameters and refractive indexes in Cu6PS5I-based thin films.

2. Experimental

Thin films were deposited from polycrystalline Cu6PS5I target onto a silicate glass substrate at room temperature by using the non-reactive radio-frequency magnetron sputtering. The structure of the deposited films was analyzed by X-ray diffraction and scanning electron microscopy (SEM) technique (Hitachi S-4300). The diffraction pattern shows the films to be amorphous. The thin film chemical composition (Cu 5.56P1.66S4.93I0.85) was determined using the energy-dispersive X-ray spectroscopy (EDX) studies, which enabled us to check the chemical composition in different points of the film surface. The deposited Cu5.56P1.66S4.93I0.85 thin film is observed to be depleted by copper, sulphur, iodine and enriched with phosphorous. SEM-studies of the thin films confirm formation of a uniform two-dimensional structure (Fig. 1).

Fig. 1. SEM image of Cu5.56P1.66S4.93I0.85 thin film.

X-ray irradiation was performed for the different exposition times (30, 60 and 120 min) using wideband radiation of Cu-anode X-ray tube with approximately 400 W of power applied (33 kV, 13 mA). Optical transmission spectra of Cu6PS5I-based thin films were studied at room temperature with MDR-3 grating monochromator. Spectral dependences of absorption coefficient and dispersion dependences of refractive index of thin films were calculated using the well-known method [9].

3. Results and discussion

Fig. 2 presents optical transmission spectra for various irradiation times at room temperature for X-ray irradiated Cu5.56P1.66S4.93I0.85 thin films. With irradiation time increase, the red shift of the short-wave part of transmission spectra and interference maxima are observed. Spectral dependences of the absorption coefficient at various irradiation times at room temperature for X-ray irradiated Cu5.56P1.66S4.93I0.85 thin films are shown in Fig. 3. In Ref. [8], it was shown that the optical absorption edge for non-irradiated Cu6PS5I-based thin films in the region of its exponential behaviour is described by the Urbach rule [10]

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

where \(E_U(T)\) is the Urbach energy, \(\alpha_0\) and \(E_0\) are the coordinates of the convergence point in the Urbach bundle, \(h\nu\) and \(T\) are the photon energy and temperature, respectively. In the X-ray irradiated Cu5.56P1.66S4.93I0.85 thin films, we also observed the Urbach behaviour of the optical absorption edge. It should be noted that the optical absorption edge for X-ray irradiated Cu5.56P1.66S4.93I0.85 thin films is shifted to the long wave region with the irradiation time increase.

Fig. 2. Optical transmission spectra of non-irradiated (1) and X-ray irradiated Cu5.56P1.66S4.93I0.85 thin films at various irradiation times: (2) 30, (3) 90 and (4) 210 min.
Fig. 3. Spectral dependences of the absorption coefficient of non-irradiated (1) and X-ray irradiated Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films at various irradiation times: (2) 30, (3) 90 and (4) 210 min.

To characterize the absorption edge spectral position, such parameter as the energy pseudogap $E_g^\alpha$ ($E_g$ is the energy position of the exponential absorption edge) at a fixed absorption coefficient value $\alpha$ was determined. We used the $E_g^\alpha$ values taken at $\alpha = 10^4$ cm$^{-1}$ for thin films (Table). The observed variation of the optical absorption edge leads to the $E_g^\alpha$ value decrease and $E_U$ value increase with irradiation time increase (from 2.835 to 2.655 eV and from 249 to 404 meV, respectively). The dependences of $E_g^\alpha$ and $E_U$ for X-ray irradiated Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films on irradiation time are presented in Fig. 4.

It is well-known that Urbach energy $E_U$ characterizes the disordering degree in the investigated system and is described by the equation [11]

$$E_U = (E_U)_{T} + (E_U)_{X},$$

where $(E_U)_T$ and $(E_U)_X$ are the contributions of temperature and structural disordering to $E_U$, respectively. The Urbach energy $E_U$ increase is the evidence of the structural disordering increase caused by X-ray irradiation.

Table. Optical parameters of non-irradiated and X-ray irradiated Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films.

<table>
<thead>
<tr>
<th>Irradiation time (min)</th>
<th>0</th>
<th>30</th>
<th>90</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>2.443</td>
<td>2.450</td>
<td>2.455</td>
<td>2.461</td>
</tr>
<tr>
<td>$E_g^\alpha$ (eV)</td>
<td>2.835</td>
<td>2.792</td>
<td>2.699</td>
<td>2.655</td>
</tr>
<tr>
<td>$E_U$ (meV)</td>
<td>249.3</td>
<td>357.5</td>
<td>382.1</td>
<td>403.6</td>
</tr>
</tbody>
</table>

Fig. 4. Dependences of the energy pseudogap $E_g^\alpha$ ($\alpha = 10^4$ cm$^{-1}$) and Urbach energy $E_U$ on X-ray irradiation time for Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films.

Dispersion dependences of the refractive index for the X-ray irradiated Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films at various irradiation time are presented in Fig. 5. In the transparency region, a slight dispersion of the refractive index for the X-ray irradiated Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films is observed, increasing with approaching to the optical absorption edge. With the irradiation time increase, the nonlinear increase of the refractive index in the X-ray irradiated Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films is revealed (the X-ray irradiation leads to the refractive index increase from 2.443 to 2.461 for $\lambda = 1 \mu$m).

It should be noted that the results of the similar investigations of the optical properties of X-ray irradiated a-Se$_{1-x}$As$_x$ thin films were recently presented in Ref. [12]. It is shown that as a result of X-ray irradiation, there is an increase in the refractive index and a decrease in the film thickness (increase in its density).
4. Conclusions

Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films were deposited onto silicate glass substrates by using the non-reactive radio-frequency magnetron sputtering. The influence of X-ray irradiation on optical properties of Cu$_{5.56}$P$_{1.66}$S$_{4.93}$I$_{0.85}$ thin films has been investigated. With the irradiation time increase, the decrease of the energy pseudogap as well as the increase of the Urbach energy and refractive index have been observed. Thus, the X-ray irradiation leads to the thin films darkening and density increase. Besides, the increase of Urbach energy is the evidence of increase in structural disordering contribution, which is caused by X-ray irradiation.

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References

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