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OPTICAL PARAMETERS OF X-RAY IRRADIATED Cu_7GeS_5I THIN FILMS

Cu_7GeS_5I thin films were deposited by non-reactive radio frequency magnetron sputtering onto silicate glass substrates. Optical transmission spectra of X-ray irradiated Cu_7GeS_5I thin films were measured depending on irradiation time. With irradiation time increase the red shift of the short-wavelengt part of transmission spectra and interference maxima were observed. Urbach absorption edge and dispersion of refractive index for X-ray irradiated Cu_7GeS_5I thin films were studied. Under the influence of the X-ray irradiation the decrease of the energy position of absorption edge as well as the increase of the Urbach energy and refractive index were revealed. Influence of X-ray irradiation on the optical parameters and disordering processes in Cu_7GeS_5I thin films was analysed.
Keywords: thin film, magnetron sputtering, X-ray irradiation, optical absorption, refractive index

Introduction

Cu_7GeS_5I crystals belong to the argyrodite family of tetrahedrally close-packed structures and are known as superionic conductors [1]. Some chemical and physical properties of Cu_7GeS_5I crystals are reported in Ref. [2, 3]. They are characterized by high electrical conductivity and low activation energy [4, 5]. Due to the high ionic conductivity, they are the attractive materials for applications in the different functional elements of the solid state ionics. Optical studies have shown that the absorption edge of Cu_7GeS_5I crystals exhibits Urbach behaviour in a wide temperature range [4, 5].

The investigations of the thin films based on Cu_7GeS_5I superionic conductors only begins. In Ref. [6] the temperature behaviour of the optical transmission spectra for as-deposited and annealed Cu_7GeS_5I thin films were investigated 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. It is shown that annealing leads to the energy position of absorption edge and the Urbach energy decrease as well as to the refractive index increase [6].

This paper is devoted to the optical studies of X-ray irradiated Cu_7GeS_5I thin films. Results of similar investigations for the different types of the thin films were presented in Refs. [7, 8]. It is shown in Ref. [7] that soft X-ray irradiation effect on the surface and material properties of highly hydrogenated diamond-like carbon thin films leads to increase of Vickers hardness and to decrease hydrogen content. In the range of 0-200 mA×h, hydrogen content decreased and Vickers hardness increased steeply. Authors in Ref. [8] show that the X-ray irradiation has an effect on the excitonic and impurities levels due to the change in the microstructure of the iron (III) chloride tetraphenyporphyrin thin films. Analysis of refractive index dispersion before and after irradiation is discussed in terms of the single oscillator model and Drude model of free carriers absorption [8].

Thus, in the present paper the influence of X-ray irradiation on optical parameters of Cu_7GeS_5I thin films is studied.

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.

Cu_7GeS_5I thin film was irradiated by wideband energy spectrum radiation of BSV-21 X-ray tube with copper anode. The film was located at 50 mm distance from outer beryllium window of X-ray tube. Anode voltage and current of tube were 33 kV and 15 mA respectively. Thus, the maximum radiation energy was by order of 30 keV and the energy of maximum intensity radiation (Cu Kα line) – 8 keV. The irradiation time was 25, 60 and 120 min. followed by 7-day intervals between irradiation steps. The measurement of thin film transmission spectra was carried out in 24 hours intervals after irradiation for structural changes to become stabilized. Thus, the time intervals that can characterize energy fluence of X-ray radiation are 0, 25, 85 (25+60) and 205 (85+120) min.

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. Spectral dependences of absorption coefficient and dispersion dependences of refractive index of thin films were calculated using the well-known method [9].

Results and discussion

Figure 1 presents the optical transmission spectra at various irradiation time at room temperature for X-ray irradiated Cu_7GeS_5I thin films. With irradiation time increase the red shift of the short-wavelengt part of transmission spectra and interference maxima are observed.

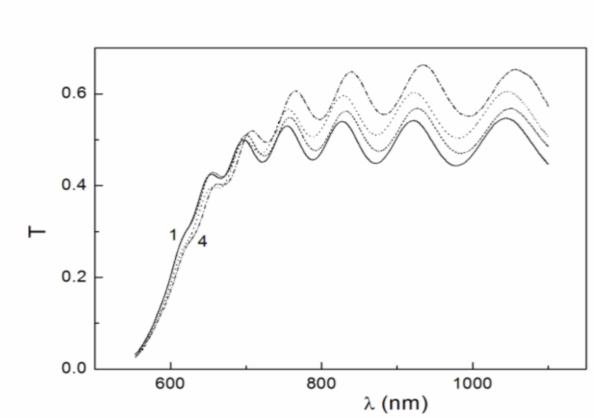

Fig.1. Optical transmission spectra of as-deposited (1) and X-ray irradiated Cu_7GeS_5I thin films at various irradiation time: (2) 25, (3) 85 and (4) 205 min.

Figure 2 presents the spectral dependences of the absorption coefficient at various irradiation time at room temperature for X-ray irradiated Cu_7GeS_5I thin films. In Ref. [6] 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 [10]

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

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. In the X-ray irradiated Cu_7GeS_5I thin films we also observed the Urbach vehaviour of the optical absorption edge. It should be noted that the optical absorption edge for X-ray irradiated Cu_7GeS_5I thin films is shifted to the long-wavelength region with irradiation time increase.

For the characterisation 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 α=10^4 cm^{-1} for thin films (Table 1).

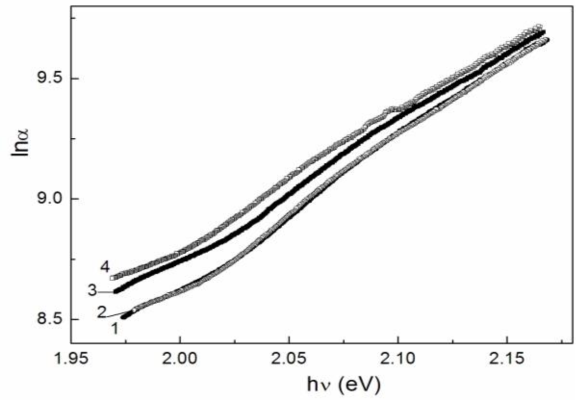

Fig.2. Spectral dependences of the absorption coefficient of as-deposited (1) and X-ray irradiated Cu_7GeS_5I thin films at various irradiation time: (2) 25, (3) 85 and (4) 205 min.

The observed variation of the optical absorption edge leads to the E_g^α value decrease and E_U value increase with irradiation time increase (Table 1). The dependences of E_g^α and E_U for X-ray irradiated Cu_7GeS_5I thin films on irradiation time are presented in Fig. 3. The Urbach energy E_U increasing is the evidence of the increase of the structural disordering due to the X-ray irradiation.

Table 1

Optical parameters of as-deposited and X-ray irradiated Cu_7GeS_5I thin films

Irradiation time (min)	0	25	85	205
n	3.125	3.133	3.143	3.170
E_g^α (eV)	2.086	2.085	2.078	2.068
E_U (meV)	131.9	136.5	153.3	157.6

It is revealed that the optical absorption edge spectra of the thin films under investigation is highly smeared and characterise by the lengthy Urbach tail which results in high values of the Urbach energy E_U (Table 1). Absorption edge smearing and appearance of its Urbach behaviour are explained by the influence of different types of disordering [11], i.e. the Urbach energy E_U is described by the equation

$$E_U = (E_U)_T + (E_U)_X = (E_U)_T + (E_U)_{X,stat} + (E_U)_{X,dyn}, \quad (2)$$

where $(E_U)_T$ and $(E_U)_X$ are the contributions of temperature and structural disordering to E_U, respectively.

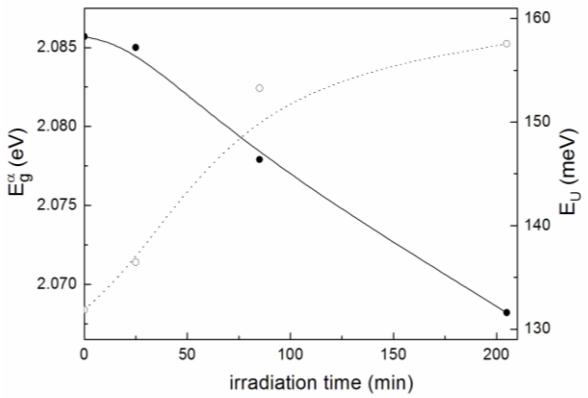

Fig.3. Dependences of the absorption edge energy position E_g^α (α=10^4 cm^{-1}) and Urbach energy E_U on X-ray irradiation time for Cu_7GeS_5I thin films.

In Ref. [12] 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. It should be noted that the increase of the Urbach energy E_U under the influence of the X-ray irradiation is the evidence of the structural disordering in the system “thin film-substrate” due to the increase of the contribution of static structural disordering.

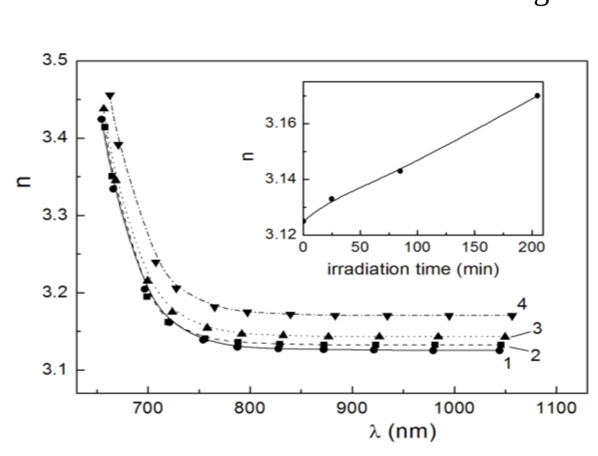

Fig.6. Refractive index dispersions of as-deposited (1) and X-ray irradiated Cu_7GeS_5I thin films at various irradiation time: (2) 25, (3) 85 and (4) 205 min. The inset shows the dependence of refractive index on X-ray irradiation time.

Dispersion dependences of the refractive index for the X-ray irradiated Cu_7GeS_5I thin films at various irradiation time are presented in Fig.4. In the transparency region a slight dispersion of the refractive index for the X-ray irradiated Cu_7GeS_5I thin films is observed, increasing with approaching the optical absorption edge. With irradiation time increase the nonlinear increase of the refractive index in the X-ray irradiated Cu_7GeS_5I thin films is revealed (the X-ray irradiation leads to the refractive index increase from 3.125 to 3.170 at λ=1 μm).

Conclusions

Cu_7GeS_5I thin films are deposited onto silicate glass substrates by non-reactive radio frequency magnetron sputtering. The influence of X-ray irradiation on optical properties of Cu_7GeS_5I thin films was investigated. It is shown that under the influence of the X-ray irradiation the red shift of the short-wavelengt part of transmission spectra and interference maxima were observed. Exponential absorption edge which characterize by Urbach behaviour for X-ray irradiated Cu_7GeS_5I thin films is shifted to the long-wavelength region with irradiation time increase. With irradiation time increase the decrease of the energy position of absorption edge as well as the increase of the Urbach energy and refractive index were revealed. Increase of the Urbach energy under the influence of the X-ray irradiation is the evidence of the structural disordering in the system “thin film-substrate” due to the increase of the contribution of static structural disordering.

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ОПТИЧНІ ПАРАМЕТРИ ОПРОМІНЕНИХ РЕНТГЕНІВСЬКИМ ВИПРОМІНЮВАННЯМ ТОНКИХ ПЛІВОК Cu_7GeS_5I

Тонкі плівки на основі Cu_6PS_5I були нанесені на підкладинки з силікатного скла методом нереактивного радіочастотного магнетронного розпилення. Спектри оптичного пропускання опромінених рентгенівським випромінюванням тонких плівок Cu_7GeS_5I вивчалися в залежності від часу опромінювання. Зі збільшенням часу опромінювання спостерігається червоне зміщення коротнохвильової частини спектру пропускання та максимумів інтерференції. Досліджено урбахівський край оптичного поглинання та дисперсію показника заломлення опромінених рентгенівським випромінюванням тонких плівок Cu_7GeS_5I. Показано, що під впливом рентгенівського випромінювання енергетичне положення краю поглинання зменшується, тоді як енергія Урбаха та показник заломлення збільшуються. Проаналізовано вплив рентгенівського випромінювання на оптичні параметри та процеси розупорядкування в тонких плівках Cu_7GeS_5I.
Ключові слова: тонкі плівки, магнетронне напилення, рентгенівське випромінювання, оптичне поглинання, показник заломлення

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ОПТИЧЕСКИЕ ПАРАМЕТРЫ ОБЛУЧЕННЫХ РЕНТГЕНОВСКИМ ИЗЛУЧЕНИЕМ ТОНКИХ ПЛЕНОК Cu_7GeS_5I

Тонкие пленки на основе Cu_6PS_5I были нанесены на подложки из силикатного стекла методом нереактивного радиочастотного магнетронного распыления. Спектры оптического пропускания облученных рентгеновским излучением тонких пленок Cu_7GeS_5I изучались в зависимости от времени облучения. С увеличением времени излучения наблюдается красное смещение кратковолновой части спектра поглощения, а максимумов интерференции. Исследованы урбаховский край оптического поглощения и дисперсия показателя преломления облученных рентгеновским излучением тонких пленок Cu_7GeS_5I. Под воздействием рентгеновского излучения энергетическое положение края поглощения уменьшается, тогда как энергия Урбаха и показатель преломления возрастает. Проанализировано влияние рентгеновского излучения на оптические параметры и процессы разупорядочения в тонких пленках Cu_7GeS_5I.

Ключевые слова: тонкие пленки, магнетронное распыление, рентгеновское излучение, оптическое поглощение, показатель преломления