Optical and electrical properties of Cu$_6$PS$_5$I-based thin films versus copper content variation

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Abstract. Cu$_6$PS$_5$I-based thin films are deposited onto silicate-glass substrates using magnetron sputtering. Their chemical compositions are determined with the aid of energy-dispersive X-ray spectroscopy. Changes in the Raman spectra of the Cu$_6$PS$_5$I-based thin films with respect to the spectra typical for crystalline Cu$_6$PS$_5$I are discussed. Optical absorption spectra and refractive indices for the films with different Cu contents are studied. Decrease in the energy pseudogap and the Urbach energy is observed with increasing Cu content, accompanied by increase in the refractive index. Electrical conductivity of the Cu$_6$PS$_5$I-based thin films is revealed to increase nonlinearly with increasing copper concentration.

Keywords: thin films, magnetron sputtering, electrical conductivity, Raman scattering, optical absorption, refractive index

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1. Introduction

A superionic conductor Cu$_6$PS$_5$I belongs to the compounds with argyrodite-type structure. Due to the presence of vacancies in copper cation sublattice, it is characterized by intrinsic structural disordering [1, 2]. Owing to its high ionic conductivity, Cu$_6$PS$_5$I represents a promising material for renewable energy sources and electrochemical or optical sensors. Besides, it reveals ferroelastic and nonlinear optical properties. Cu$_6$PS$_5$I belongs to the cubic system (the space group $F\overline{4}3m$) at the room temperature.

Electrical conductivity, Raman scattering and optical absorption spectra of Cu$_6$PS$_5$I have been studied in detail in Refs. [3–7]. In particular, the temperature dependence of the conductivity measured in the region 140–295 K manifests several regions with different activation energies [3].

The most pronounced band in the room-temperature Raman spectrum of Cu$_6$PS$_5$I single crystals is observed at 420 cm^{-1}. It corresponds to the A_1-symmetry vibrations [4]. A broad asymmetric band revealed near 310 cm^{-1} results from superposition of a doubly degenerate E mode and a triply degenerate F_2 mode that corresponds to the internal deformation vibrations of tetrahedral PS$_4^{3-}$ groups [4].

At low temperatures, exciton bands are observed at the optical absorption edge. They become broader with increasing temperature and are then entirely smeared in the course of transition to superionic state [5–7]. The optical absorption edge has an exponential shape in the superionic phase, and its temperature behaviour can be described by the Urbach rule. It has been shown that

the Urbach behaviour of the absorption edge is caused by exciton–phonon interactions, whereas its additional smearing is caused by temperature-related and structural disorderings [5–7].

X-ray diffraction data reveals that the thin Cu_6PS_5I films are amorphous [8]. A typical 'Urbach bundle' is readily observed in their optical absorption spectra, while the temperature dependences of the optical pseudogap and the Urbach energy are described by the Einstein model [9, 10]. Finally, the effects of annealing and ion implantation on the absorption-edge parameters of the Cu_6PS_5I thin films have been investigated in Refs. [11, 12].

Further studies of the Cu_6PS_5I-based thin films are still very interesting because these films can be used for producing miniature solid electrolytes and supercapacitors [13]. Below we report the results for electrical conductivity, Raman scattering and optical absorption of the Cu_6PS_5I-based thin films deposited using a technique of magnetron sputtering. In particular, we focus on the behaviour of the above properties observed with varying copper content in the film composition.

2. Experimental

The Cu_6PS_5I-based thin films were produced using deposition from a single magnetron equipped with a Cu_6PS_5I target (a pressed powder). Another method was based upon co-deposition from two tilted magnetrons, one equipped with a Cu_6PS_5I target and the other with a pure Cu target. The deposition was carried out at the room temperature in Ar atmosphere.

Scanning electron microscopy studies combined with energy-dispersive X-ray spectroscopy (using a Hitachi S-4300 equipment) were performed to examine the thin film surface and determine the chemical composition of the films.

Micro-Raman studies were carried out at the room temperature, using a Horiba LabRAM HR800 spectrometer equipped with a CCD camera. The excitation was provided by a Cobolt Fandango solid-state laser ($\lambda_{exc} = 514.7$ nm). The spectral resolution was better than 2.5 cm^{-1}.

Optical transmission spectra were measured using a LOMO MDR-3 grating monochromator. Spectral dependences of the absorption coefficient and concentration dependences of the refractive index of our thin films were calculated from the interference transmission spectra, using a well known approach developed in Ref. [14].

Finally, electrical conductivity of our films was studied at the room temperature with a two-electrode technique under application of 1 kHz AC voltage.

3. Results and discussion

Our scanning electron microscopy studies have demonstrated that, in the case of samples prepared with increased amounts of Cu provided by the second magnetron, extended inhomogeneities are observed on the film surfaces. As seen from Fig. 1, they can possibly be related to the formation of copper metal dendrites. As follows from our energy-dispersive X-ray spectroscopy data, the composition of the thin films varies from $Cu_{5.4}P_{1.9}S_{5.0}I_{0.7}$ to $Cu_{9.3}P_{0.5}S_{2.6}I_{0.6}$, depending on the preparation conditions.

The Raman spectrum of the Cu_6PS_5I single crystals is dominated by a narrow (7 cm^{-1}) peak located at 420 cm^{-1} that corresponds to a symmetric vibration of PS_4 tetrahedra. A less intense and broader (27 cm^{-1}) peak observed at 309 cm^{-1} results from unresolved degenerate E and F_2 bands (see Fig. 2). For the
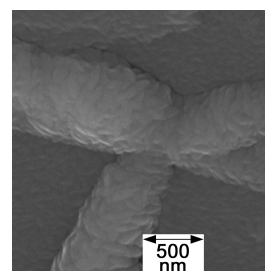

Fig. 1. Scanning electron microscopy image of our $Cu_{8.6}P_{0.6}S_{3.1}I_{0.7}$ thin film.

Cu_6PS_5I-based films, the corresponding bands are much broader (30–40 and 80–90 cm^{-1}, respectively), which can evidence a strongly amorphized structure (see Fig. 2). The most intense peak in the spectra detected for the films is shifted down to 392–396 cm^{-1}. The latter can be explained by the appearance of tensile strains in the films. Evidently, the structural PS_4 groups are to a large extent preserved in the short-range order, even though the structure of these groups is noticeably distorted. An additional band in the spectra of the films positioned near 425 cm^{-1} is probably related to the vibrations of PS_3 groups formed in sulphur-deficient films.
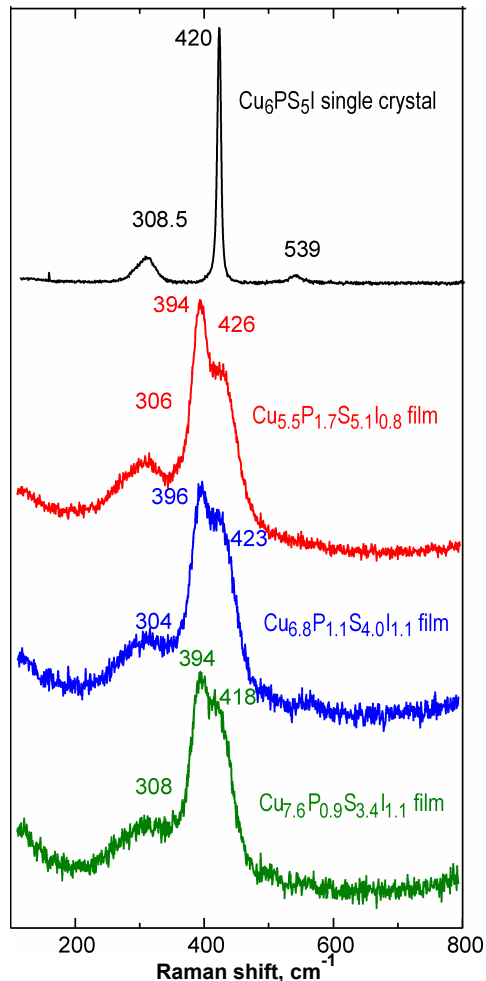

Fig. 2. Raman spectra of Cu_6PS_5I single crystals and Cu_6PS_5I-based thin films with various copper contents.

The optical absorption-edge spectra of the Cu_6PS_5I-based thin films in the region of their exponential behaviour are described by the Urbach rule [15]. In this region we use the energy pseudogap E_g^α for characterization of the films. Note that the pseudogap is usually defined as the energy position of the exponential absorption edge at a fixed value of absorption coefficient α. To be specific, we have used the E_g^α values taken at $\alpha = 5 \times 10^4$ cm^{-1} when characterizing the spectral position of the absorption edge. As seen from Fig. 3, the E_g^α parameter for the Cu_6PS_5I-based thin films decreases nonlinearly with increasing copper content. The refractive index increases nonlinearly under the same condition.
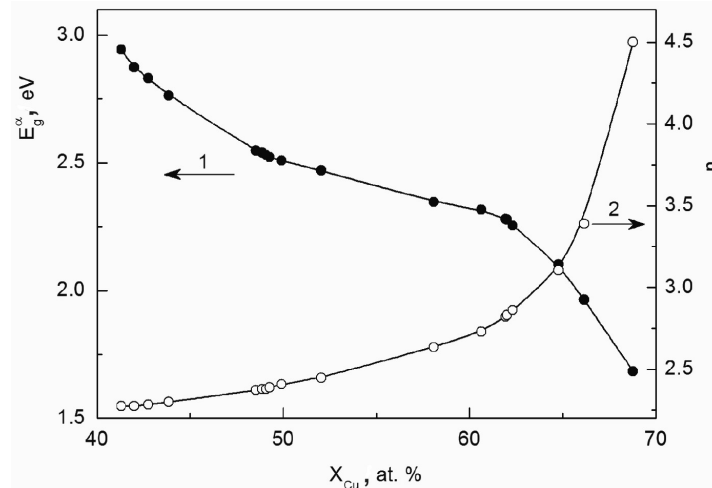
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Fig. 3. Dependences of energy pseudogap E_g^{α} taken at $\alpha = 5 \times 10^4$ cm^{-1} (curve 1) and refractive index n at $\lambda = 1$ µm (curve 2) on copper content in the Cu_6PS_5I-based thin films.

Formation of the Urbach-like absorption edge is usually explained in terms of electron–phonon interaction (EPI). The EPI characteristics, such as the σ_0 parameter related to the EPI constant and the effective phonon energy $\hbar\omega_{ph}$, can be obtained from the temperature dependence of the absorption-edge slope, using the Mahr formula [16]. In case of the Cu_6PS_5I-based thin films, we obtain the inequality $\sigma_0 < 1$, thus evidencing a strong EPI [17]. It is seen from Fig. 4 that the σ_0 parameter and the effective phonon energy $\hbar\omega_{ph}$ behave non-monotonously with increasing Cu content. The both EPI parameters reach their maxima approximately at the copper concentration 52 at. % and decrease when the copper content increases further on (see Fig. 4).
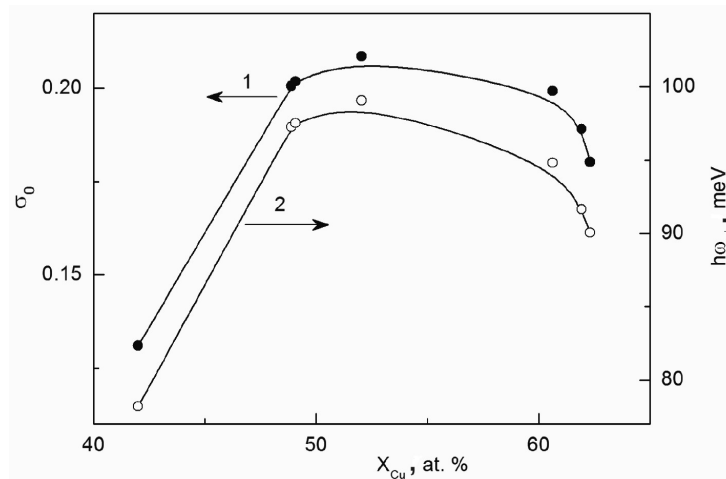

Fig. 4. Dependences of σ_0 parameter related to the EPI constant (curve 1) and effective phonon energy $\hbar\omega_{ph}$ (curve 2) on copper content in the Cu_6PS_5I-based thin films.

It is worth noticing that the thin films under test are characterized by high Urbach energies E_U. Moreover, Fig. 5 testifies that the Urbach energy decreases nonlinearly with increasing copper content.
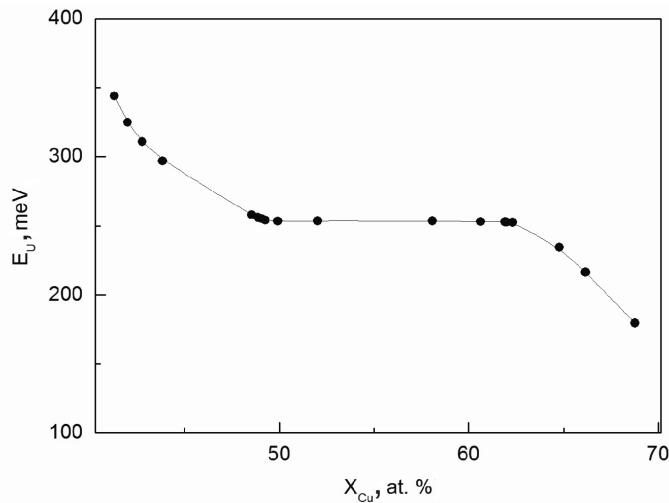
Fig. 5. Dependence of Urbach energy E_U on copper content in the Cu_6PS_5I-based thin films.
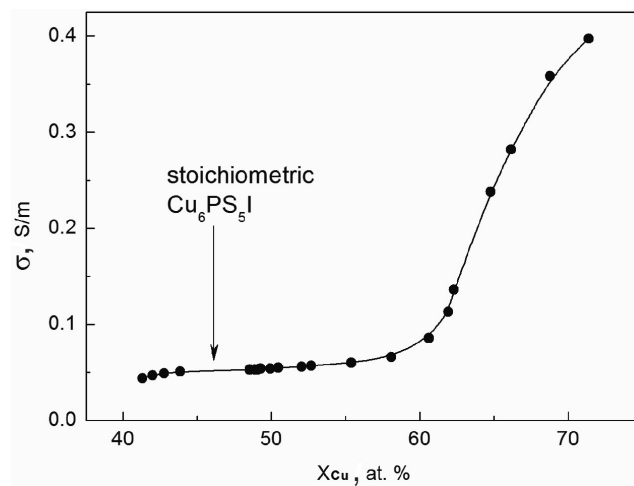

Fig. 6. Dependence of electrical conductivity on copper content in the Cu_6PS_5I-based thin films.

Our electrical studies have shown that the conductivity of the Cu_6PS_5I-based thin films increases monotonously with increasing copper content. Two different regions can be revealed in the compositional dependence, as seen from Fig. 6. Namely, a slight increase in the electrical conductivity occurring in the copper-content region 41–58 at. % gives way to a more rapid increase at the concentrations higher than 60 at. %. This phenomenon can be explained by a large amount of vacancies in the copper cationic sublattice, which are filled whenever the copper content increases up to 60 at %. The Cu atoms occupy interstitial positions at higher copper contents, thus leading to a rapid increase of the conductivity.

4. Conclusions

The Cu_6PS_5I-based thin films have been deposited onto the silicate-glass substrates, using the magnetron sputtering technique. The scanning electron microscopy images of the films obtained by us have shown that the surface remains homogeneous for the film compositions closer to stoichiometric one. On the other hand, we have given evidence for some extra dendrite-like (evidently copper-enriched) structures on the surface of the films sputtered under condition of ex-

cessive copper content. The film-composition data determined from the energy-dispersive X-ray spectroscopy spectra has revealed that the exact copper content depends on the sputtering conditions.

The bands observed in the Raman spectra of our Cu_6PS_5I-based thin films are much broader than those peculiar for the Cu_6PS_5I single crystals. This fact can be evidence for a strongly amorphized film structure. The downward shift to about 400 cm^{-1} of the most intense band is, most likely, explained by tensile strains available in the films. An additional band observed in the Raman spectra of our thin films near 425 cm^{-1} is probably related to the vibrations of PS_3 groups formed in the sulphur-deficient films.

Basing on the spectral dependences of the absorption coefficient and the refractive index, we have obtained the concentration dependences of the energy pseudogap and the refractive index. In particular, we have demonstrated that the energy pseudogap decreases and the refractive index increases with increasing Cu content. The formation of the Urbach-like absorption edge in the Cu_6PS_5I-based thin films is explained by the strong electron–phonon interactions.

The electrical conductivity of our thin films is shown to increase slowly with increasing copper content up to about 60 at. %, with a much more rapid increase occurring at higher Cu contents. This phenomenon can be due to increasing concentration of copper interstitials.

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Анотація. *Тонкі плівки на основі Cu_6PS_5I висаджено на силікатні скляні підкладки із застосуванням магнетронного розпилення. Їхній хімічний склад визначено за допомогою енергетично-дисперсійної рентгенівської спектроскопії. Обговорено зміни раманівських спектрів тонких плівок на основі Cu_6PS_5I, знайдені відносно спектрів кристалічного Cu_6PS_5I. Вивчено спектри оптичного поглинання та показники заломлення для плівок з різним вмістом Cu. Зі зростанням вмісту Cu спостерігається зменшення енергетичної псевдощілини та енергії Урбаха, а також зростання показника заломлення тонких плівок на основі Cu_6PS_5I. Показано також, що з підвищенням концентрації міді їхня електрична провідність зростає нелінійно.*