Structural, electrical and optical investigations of Cu$_6$PS$_5$Br-based thin film deposited by HiTUS technique

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Abstract. Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film was obtained using the high target utilization sputtering onto c-cut sapphire substrates. X-ray diffraction studies show the film to be amorphous with some crystalline inclusions. SEM investigations indicate formation of periodical “forest-like” quasi-two-dimensional pillared structure. Electrical conductivity of Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film was measured in the temperature interval 4.5...300 K, three regions with different activation energy were revealed. Optical constants were obtained using the technique of spectroscopic ellipsometry and used for calculation of optical absorption spectrum. Optical absorption edge has an exponential form, the Urbach energy shows the significant disordering in Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film.

Keywords: thin film, high target utilization sputtering, X-ray diffraction, electrical conductivity, optical constants.

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1. Introduction

Cu$_6$PS$_5$Br crystals belong to the argyrodite family and are well known as superionic conductors [1]. They possess high ionic conductivity and low activation energy, which makes them promising for applications as electrochemical energy sources [2]. The efficient ion transport in Cu$_6$PS$_5$Br crystal is explained by the specific structure that facilitates fast ion transport [3]. At room temperature, Cu$_6$PS$_5$Br crystals belong to the cubic syngony ($F43m$ space group), while at low temperatures two phase transitions (PTs) occur: the ferroelastic one at $T_{II} = (268±2)$ K and superionic one at $T_{I} = (166...180)$ K [4]. Below the ferroelastic PT temperature Cu$_6$PS$_5$Br crystals belong to the monoclinic syngony ($Cc$ space group), and the superionic PT reveals the features of an isostructural transformation [4]. Anomalous behaviour of dielectric, calorimetric and acoustic properties has been revealed in the range of the phase transitions [5-8].

Optical studies in Cu$_6$PS$_5$Br crystal have shown that exciton absorption bands can be observed at $T < T_I$ [9]. In the vicinity of the superionic PT, the bands undergo considerable changes, which are caused by dynamic structural disordering of copper cation sublattice. At $T > T_I$, at the absorption edge the exponential parts appear, being described by the Urbach rule [9]. The optical absorption processes in Cu$_6$PS$_5$Br crystal is well explained in the framework of the known Dow–Redfield model, the nature of electron-phonon interaction remaining unchanged at PT from one
crystalline structure to another. The slope of the exponential Urbach edge of Cu$_6$PS$_5$Br crystal is determined by both temperature and structural disordering.

The investigations of the thin films based on Cu$_6$PS$_5$Br superionic conductors only begin. Thus, in this paper the structural, electrical and optical properties of Cu$_6$PS$_5$Br-based thin film are studied. Besides, the comparative analysis of optical parameters in single crystal and thin film is performed.

2. Experimental

Cu$_6$PS$_5$Br-based thin films were deposited on c-cut sapphire substrates at room temperature by means of high target utilization sputtering (PQL HiTUS S500 sputter coating system) from Cu$_6$PS$_5$Br target (30 mm in Dia.) in radiofrequency Ar discharges. The plasma source power density was fixed at 2000 W yielding the deposition rate of approximately 1.5 nm/min. Target pulsed DC power was fixed at 70 W. Substrates were placed in parallel above the target at the distance 180 mm without additional heating. All depositions were carried out at a floating plasma potential. The base pressure in the chamber was below 7×10$^{-4}$ Pa and the total working gas pressure during deposition was kept at 0.65 Pa.

Structural studies were performed using XRD and SEM techniques (Lyra 3 TESCAN), energy-dispersive X-ray spectroscopy (Bruker XFlash 6) was used to ensure the thin film chemical composition. Electrical resistance of Cu$_6$PS$_5$Br-based thin film was measured using the four-contact method in lab-scale measurement system in the temperature interval $T = 4.5...300$ K. Spectroscopic ellipsometer J.A. Woollam M-2000V was used for measuring the optical constants.

3. Results and discussion

Structural studies were carried out using X-ray diffraction and SEM techniques (Figs. 1 and 2). The diffraction pattern shows the film to be amorphous with some crystalline inclusions, while the diffraction pattern of target was similar to that of Cu$_6$PS$_5$Br single crystal (Fig. 1). SEM studies show that the obtained films represent a periodical quasi-two-dimensional system of nanoscaled pillars 100 nm in diameter 1 µm high with distance 10 to 100 nm between them (Fig. 2). On the whole this system is similar to the “forest” with roots strongly attached to substrate surface, and crowns forming bumpy surface of the film (Fig. 2). EDX measurements were used to determine the thin film chemical composition (chemical formula calculated from EDX measurements is Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$). Thus, films obtained using HiTUS technique appeared to be non-stoichiometric by their chemical composition, enriched with Cu and P atoms and depleted with S and Br atoms, with the sufficiently low Br content.

The electrical conductivity value for Cu$_6$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film at $T = 300$ K equals 4.0×10$^{-4}$ S/m, while at $T = 4.5$ K it equals 6.6×10$^{-6}$ S/m. It should be noted that the electrical conductivity value for Cu$_6$PS$_5$Br single crystal at $T = 300$ K equals 1.2×10$^{-3}$ S/m. It is shown that the temperature dependence of electrical conductivity for Cu$_6$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film has three regions with different activation energies (Fig. 3).

The dispersion dependences of the refractive index $n$ and extinction coefficient $k$ for the Cu$_6$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film were obtained from the spectral-ellipsometric measurements within the spectral range 0.35 to 1.0 µm (Fig. 4). Thus, the refractive index at $\lambda = 1$ µm for Cu$_6$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film equals 2.362, while for Cu$_6$PS$_5$Br single crystal it equals 2.582. The slight dispersion of the refractive index is observed in the transparency region while it increases when approaching to the optical absorption edge region. The anomalous refractive index dispersion is observed in the region of significant increase of the extinction coefficient.
The spectral dependence of the absorption coefficient $\alpha$ which is obtained as $\alpha = 4\pi k/\lambda$, was analyzed in the exponential region for Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film (Fig. 5). It is shown that the temperature behaviour of absorption spectrum in the exponential region is described by the well-known Urbach rule [10]

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

where $E_U$ is the Urbach energy (the energy width of the exponential absorption edge), $\alpha_0$ and $E_0$ are the convergence point coordinates of the Urbach bundle. In the range of the exponential behaviour of the optical absorption for their spectral characterisation we use such parameter as the energy position of an exponential absorption edge $E_g^a$ at a fixed absorption coefficient $\alpha$.

In our case, we used the $E_g^a$ values taken at $\alpha = 2 \times 10^5$ cm$^{-1}$ for characterization of the absorption edge spectral position in Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film (Table). In Table, we also presents $E_g^a$ at $\alpha = 10^3$ cm$^{-1}$ for Cu$_4$PS$_3$Br single crystal.

It should be noted that the essential characteristic of the absorption edge spectrum of the thin film under investigation is very lengthy Urbach tail, which results in the high value of Urbach energy $E_U$ (Table). Thus, the Urbach energy $E_U$ in Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film is 758 meV, while in the Cu$_4$PS$_3$Br single crystal it equals 28.1 meV. In Ref. [11] it was shown that temperature and structural disordering affects Urbach absorption edge shape, i.e., the Urbach energy $E_U$ is described by the equation

$$E_U = (E_U)_T + (E_U)_X = (E_U)_T + (E_U)_X,\,\text{stat} + (E_U)_X,\,\text{dyn},$$

where $(E_U)_T$ and $(E_U)_X$ are the contributions of temperature-related and structural disordering to $E_U$, respectively; $(E_U)_X,\,\text{stat}$ and $(E_U)_X,\,\text{dyn}$ are the contributions of static structural disordering and dynamic structural disordering to $(E_U)_X$, respectively.

The temperature-related types of disordering consist from the temperature disordering caused by thermal lattice vibrations and dynamic structural disordering related with availability of mobile ions in the superionic
4. Conclusions

Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film was deposited by the high target utilization sputtering onto c-cut sapphire substrates. Temperature behaviour of the electrical conductivity for as-deposited Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film was investigated within the temperature interval 4.5...300 K. At 300 K, the electrical conductivity value equals $4.0 \times 10^{-4}$ S/m, while the temperature dependence of the electrical conductivity has three regions with different activation energies, which is caused by the presence of crystalline inclusions in the amorphous matrix. The spectral dependences of refractive index and extinction coefficient for Cu$_{6.35}$P$_{1.77}$S$_{4.72}$Br$_{0.15}$ thin film may be additionally increased due to the structural imperfection related to the high concentration of disordered copper vacancies and the dynamic structural disordering $(E_U)_{X,\text{dyn}}$ caused by the intense motion of mobile copper ions, participating in ion transport, and which is responsible for the ionic conductivity in crystalline Cu$_6$P(S$_{1-x}$Sex)$_5$Br and Cu$_6$S inclusions as well as due to the their non-uniform distribution in this amorphous matrix.

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