

Study of the microstructure of Cu_2SnS_3 films, prepared through sulfurization of metal precursors deposited by magnetron sputtering

S. Petrosyan^{a,*}, A. Musayelyan^a, E. Zaretskaya^b, V. Gremenok^{b,c}, K. Buskis^b,
A. Stanchik^{b,c}

^a*Institute of Radiophysics and Electronics, Alikhanian Brothers str.1, 0203 Ashtarak, Armenia*

^b*Scientific-Practical Materials Research Centre of the National Academy of Sciences of Belarus, 220072, Minsk, Petrus Brovka str. 19, of. 5, Republic of Belarus*

^c*Belarusian State University of Informatics and Radioelectronics, 220013, Minsk, Petrus Brovka str. 6, Republic of Belarus*

We present the results of the study of the microstructure, X-ray diffraction and Raman scattering spectra of Cu_2SnS_3 (CTS) films synthesized at 500 °C by the sulfurization of Sn-Cu stacked metal precursors with different annealing time. The results indicate that sulfurization time has a great influence on both composition and morphology of the film. It is shown that the process of formation of a single-phase CTS compound with a monoclinic structure and composition close to stoichiometry is completed for a synthesis time of 60 - 80 min. With an increase in the time of synthesis to 120 min, the preservation of the monoclinic structural modification of the material is observed, accompanied by a shift in the stoichiometric composition, namely copper enrichment, material delamination and degradation of microstructural characteristics. As a result, it was found that the most optimal conditions for the synthesis of a single-phase Cu_2SnS_3 compound of a monoclinic structure are the temperature 500 °C with the duration of the sulfurization process from 60 to 80 min.

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1. Introduction

Semiconductor compounds of copper-tin-sulfur (Cu-Sn-S) have recently attracted much attention as an alternative to kesterites $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ (CZTSSe), used as an absorbing layer in thin-film solar cells [1]. The Cu-Sn-S material system belongs to group I-IV-VI and contains cheaper elements that are non-toxic and abundant in the Earth's crust. The synthesis and study of these semiconductor compounds began in 1960. Due to their suitable optoelectronic properties three phases of this system such as Cu_2SnS_3 , Cu_3SnS_4 and Cu_4SnS_4 have been investigated as photoactive layers in solar cells. These materials usually exhibit p-type electrical conductivity, have a direct band gap in the range of 0.8–1.7 eV (depending on the structural modification) and high optical absorption coefficient (10^4 – 10^5) cm^{-1} at room temperature [2-7]. In particular, the Cu_2SnS_3 (CTS) material has a wide range of stability in the phase space of the chemical potential of the Cu-Sn-S system [4], which simplifies composition control in comparison with more complex compounds of the CZTSSe class. This compound has a polymorphic structure and crystallizes in various phases, including cubic, tetragonal, triclinic and monoclinic [2-4].

It has been theoretically shown that a single-junction solar cells (SCs) based on Cu_2SnS_3 can have an efficiency of more than 30% [7]. Therefore, Cu_2SnS_3 thin films have been extensively synthesized using various methods, such as magnetron sputtering [8], thermal evaporation [9], electro-deposition [10], sol-gel method [11], chemical bath deposition [12,13] and others [2,3]. To the best of our knowledge the highest efficiency values of SCs based on CTS have been achieved

* Corresponding author: stepan.petrosyan@rau.am
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using vacuum methods [2, 3]. The first solar cell of the Schottky diode has been fabricated from CTS film in 1987 and that had a conversion efficiency of 0.11% [14]. In 1995, a photo-converter of the $\text{Cu}_2\text{SnS}_3/\text{CdS}$ type was reported, having a short-circuit current of $10 \text{ mA}\cdot\text{cm}^{-2}$ and an open-circuit voltage of 520 mV [3]. At present, the efficiencies of 5.2% and 6.7% have been achieved for SCs, based on Na [15] and Ge [16] doped Cu_2SnS_3 absorber layers. Considering these efficiency values achieved in the laboratory, it can be argued that the study of thin film solar cells based on CTS in order to approach the theoretical limit of the efficiency of converting solar radiation energy into electrical energy is still at an early stage.

In turn, the properties of the preparing Cu_2SnS_3 films directly depend on the method and conditions of their synthesis. The synthesis parameters affect their phase and chemical compositions, as well as their morphology, the imperfections of the crystal lattice, and the distribution of active centers. Therefore, the modification of the existing methods for fabricating CTS films, which make it possible to achieve stable physical characteristics over time, is a fundamental factor for their application in thin film SCs.

Despite the presence of a fairly large number of publications devoted to the synthesis of Cu_2SnS_3 thin films, the dependence of the crystal structure and phase composition of the synthesized layers on the conditions of preparation remains insufficiently studied. The main problems of forming a photoactive Cu_2SnS_2 layer are associated with the formation of a multiphase mixture of ternary and binary phases, as well as polymorphic crystallization of the material in various lattices. An additional difficulty in preparing a material of the required structural modification is the complexity of phase identification due to insignificant differences in their X-ray patterns and due to the overlap of the reflection angles of a number of crystallographic planes.

In this regard, this work is aimed at studying the effect of the annealing time of Cu-Sn stacked precursors in sulfur vapor on the chemical, phase composition and micro-structural characteristics of the synthesized Cu_2SnS_3 films.

2. Experimental technique

The two-stage fabrication of Cu_2SnS_3 thin films was carried out by sulfurization of stacked Sn/Cu precursors deposited by DC sputtering onto soda lime glass (SLG) glass substrates. The substrates were preliminarily chemically etched in a solution of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) for 2 hours. Then they were subjected to ultrasonic cleaning in deionized water and dried in a nitrogen gas atmosphere.

Precursor's deposition was carried out in a system of co-magnetron sputtering (Nanovak, NVT S500) at direct current, including 2 targets: tin (Sn 99.99%) and copper (Cu 99.9%) two inches in diameter. Layers of metallic precursors in the sequence of Sn and Cu were deposited within 30 min on a substrate at room temperature and a power of 40 W in an argon (Ar) atmosphere at an operating pressure of 19.95×10^{-3} mbar. The content of metal components in the deposited precursors layers was Cu = 61.2 at.% and Sn = 38.8 at.%.

The sulfurization process of Sn/Cu precursors with different durations was carried out under temperature 500 °C by diffusion of elemental sulfur from a solid source in a flowing argon atmosphere. The synthesis system consisted of a specially designed graphite container for substrates and a powdered sulfur source. A container with Sn/Cu/glass samples and 0.8 g of sulfur powder was placed in a two-zone furnace. Before the sulfurization process, the base pressure was 1.8×10^{-3} mbar and the furnace volume was purged with an argon flow. In the process of film synthesis, the working pressure was kept constant, at a level of 4.2 mbar, by filling the tube with gaseous argon. The furnace heating rate was set equal to $0.15 \text{ }^\circ\text{C}\cdot\text{s}^{-1}$. The process was carried out at 500 °C for 20, 40, 60, 80, 100 and 120 min. After completion of the sulfurization process, the furnace was cooled to room temperature at a natural cooling rate.

The study of the phase composition of Cu_2SnS_3 films in relation to sulfurization time was carried out using D8 Advance diffractometer (Bruker AXS) on CuK_α radiation ($\lambda = 0.1542 \text{ nm}$), filtered by multilayer Ni/graphite monochromator. The phases were identified by comparing the experimentally determined inter-planar distances with the JCPDS (Joint Council for Power Diffraction Standards) data. Surface topography and cross section were analyzed using an H-800

scanning electron microscope (SEM) (Hitachi, Japan) with a resolution of 0.2 nm. The elemental composition of the synthesized films was determined using an INCA 350 X-ray microanalyzer (Oxford Instruments, UK) with a resolution of 1.0 μm and a sensitivity of 0.1 at.%. Raman spectra were recorded on an in Via confocal micro-spectrometer (Renishaw, UK). The excitation source was a solid-state laser with a wavelength of 532 nm (0.06 mW, grating 3000 lines/mm). The Raman frequencies were calibrated against a silicon standard along the 520 line. The Raman spectra were taken using a 50x objective and the integration time was 400 s.

3. Results and discussions

The elemental composition of CTS thin films, depending on the conditions of formation, was estimated from measurements of the energy dispersive X-ray spectroscopy (EDS) spectra. A typical energy-dispersive spectrum of thin films is shown in Fig. 1. The EDS spectrum of the films exhibits signals from Cu, Sn, S, O, Si, and C. Comparing the intensities of the Cu, Sn, and S peaks, we can conclude that the content of these elements in the films is close to stoichiometry. The presence of Si and O in the spectrum is associated with the use of a glass substrate. In addition, due to the conductive carbon tape that was used to fasten the samples to the sample holder, the C peak corresponding to carbon is also observed in the spectra. A uniform distribution of Cu, Sn, and S atoms on the film surface without local areas with an excess concentration of any element has been established.

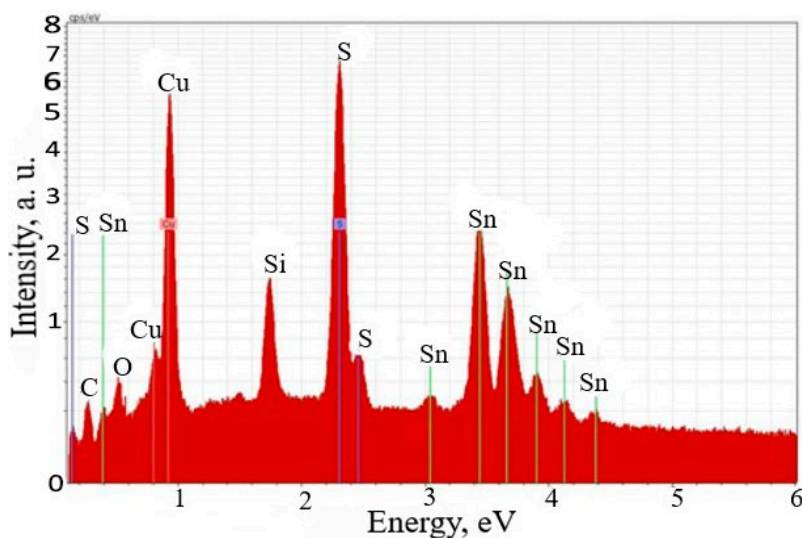


Fig. 1. Typical energy-dispersive spectrum of Cu_2SnS_3 thin films.

The chemical composition of the films was determined by averaging the concentration values from 5 different points on the Cu_2SnS_3 film surface (Table 1).

Table 1. Elemental composition of Cu_2SnS_3 thin films prepared at different durations of the sulfurization process.

| Time, min | Element | Series | Weight % | At. % | Ratio, Cu/Sn | Molar ratio |
|-----------|---------|----------|----------|-------|--------------|-------------------------------------|
| 20 | Cu | K-series | 35.52 | 33.95 | 1.63 | $\text{Cu}_{1.63}\text{SnS}_{2.18}$ |
| | Sn | L-series | 40.55 | 20.74 | | |
| | S | K-series | 23.93 | 45.31 | | |
| 40 | Cu | K-series | 37.31 | 35.53 | 1.78 | $\text{Cu}_{1.78}\text{SnS}_{2.23}$ |
| | Sn | L-series | 39.10 | 19.93 | | |
| | S | K-series | 23.59 | 44.53 | | |
| 60 | Cu | K-series | 38.48 | 36.32 | 1.91 | $\text{Cu}_{1.91}\text{SnS}_{2.34}$ |
| | Sn | L-series | 37.64 | 19.02 | | |
| | S | K-series | 23.88 | 44.66 | | |
| 80 | Cu | K-series | 38.00 | 35.25 | 1.95 | $\text{Cu}_{1.95}\text{SnS}_{2.55}$ |
| | Sn | L-series | 36.69 | 18.22 | | |
| | S | K-series | 25.31 | 46.52 | | |
| 100 | Cu | K-series | 43.48 | 38.92 | 2.68 | $\text{Cu}_{2.68}\text{SnS}_{3.21}$ |
| | Sn | L-series | 30.27 | 14.51 | | |
| | S | K-series | 26.25 | 46.57 | | |
| 120 | Cu | K-series | 42.06 | 37.42 | 2.55 | $\text{Cu}_{2.55}\text{SnS}_{3.27}$ |
| | Sn | L-серия | 30.75 | 14.64 | | |
| | S | K-серия | 27.19 | 47.94 | | |

It follows from the analysis of the elemental composition of sulfurized films that, at an annealing time of less than 60 min, the formed material is significantly depleted in copper, and an increase in the annealing time from 20 to 60 min is accompanied by an increase in the ratio of the Cu/Sn components from 1.63 to a value close to the stoichiometric value of 1.91. A significant deviation of the composition of the CTS material from the stoichiometric one ($\text{Cu/Sn} = 2.55$) is due to the re-evaporation of highly volatile tin sulfides (Sn_xS_y), which increases significantly with an increase in the annealing time up to 120 min. Note that such effect was observed when using a similar process for the synthesis of Cu_2SnS_3 thin films at a crystallization temperature $T = 520\text{--}550\text{ }^\circ\text{C}$ [17].

It is well known that, from the point of view of increasing the efficiency of thin film SCs, the use of Cu-poor CTS films as an absorbing layer is more preferable, since vacancies of copper atoms play the role of acceptors and lead to an increase in the *p*-type conductivity of this hetero-layer [18]. Therefore, in our experiments, the most optimal time for the synthesis of CTS films at $500\text{ }^\circ\text{C}$ with an elemental composition close to stoichiometry was the annealing time interval from 60 to 80 min. However, it should be kept in mind that in these cases the atomic ratio $\text{S}/(\text{Sn}+\text{Cu})$ in the film is less than unity, which indicates a certain deficiency of sulfur atoms in the Cu_2SnS_3 crystal lattice.

When studying the microstructure of the synthesized CTS films, it was found that the topography of their surface, morphological characteristics, such as the type, size, and density of grain conjugations, are also largely determined by the annealing time. Surface morphologies and cross-sectional SEM images of the layer of Sn/Cu precursors subjected to thermal annealing in sulfur vapor for different durations demonstrate clear differences in the shape, average size,

packing density, and orientation of crystallite growth in the film (Fig. 2). During annealing in a sulfur-containing atmosphere for 20 min, 496 nm thick polycrystalline layer is formed by crystallites 100-150 nm in size, with a pronounced growth direction perpendicular to the substrate. On the surface of the synthesized layer, a separate fraction appears in the form of grains 50×120 nm in size (most likely, of sulfur), which indicates an incompleteness of the crystallization process. With an increase in the annealing time from 40 to 60 min, the synthesized layer becomes a two-layer structure with an intermediate layer 298-311 nm thick adjacent to the substrate, consisting of fine, unafaced grains 20-40 nm in size, and an upper layer formed by 200×400 nm grains with random growth direction. A further increase in the sulfurization duration up to 80 min is accompanied by the transformation of the two-layer system into a continuous layer of CTS semiconductor material with a segregation of the Cu_xS phase in the form of individual large hexagonal crystals 400-500 nm in size. It is important to note that the surface of the CTS layers prepared by sufficiently long sulfurization is more homogeneous and is characterized by the presence of a small amount of uninfected pores. A characteristic feature of CTS layers prepared at a sulfurization time of 100 to 120 min is the degradation of a single layer and its subsequent transformation into a two-layer structure. The lower layer of the synthesized material with a thickness of 410-437 nm is formed from small crystallites with a large number of pores and with packing density that decreases as the synthesis duration increases (Fig. 2). The thickness of the upper layer, which consists of densely intergrown grains, increases from 185 to 437 nm as the annealing time increases. Segregation of the Cu_xS phase is also observed on the surface of such copper-rich layers ($\text{Cu}/\text{Sn} = 2.55 \div 2.68$).

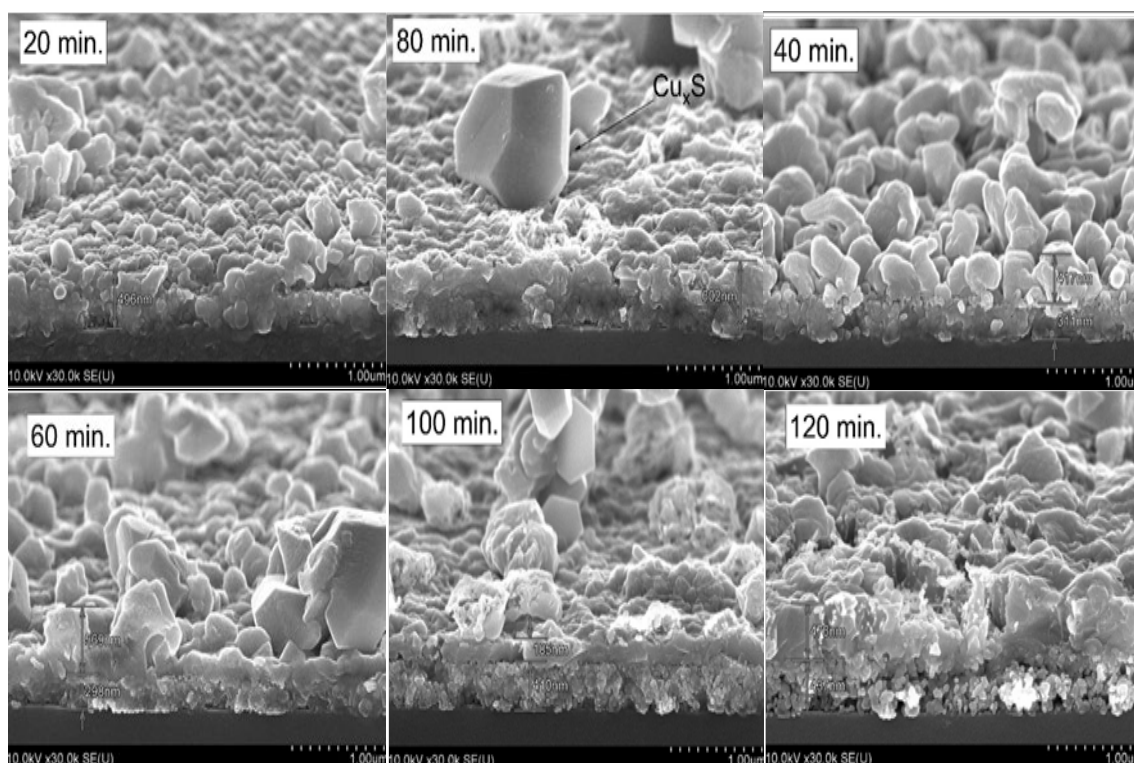


Fig.2. Cross-sectional SEM images of CTS films prepared at 500 °C with different duration of the sulfurization process.

Note that the segregation of the Cu_xS phase with grain sizes comparable to the thickness of the synthesized layer can lead to the appearance of a shunt resistance in the absorbing layer of the SC and is an undesirable factor. To eliminate this effect during the formation of SCs, it becomes necessary to perform an additional operation of selective etching of the highly conductive Cu_xS phase, which complicates and increases the cost of SC fabrication technology.

Figure 3 shows typical X-ray diffraction patterns of CTS films obtained by sulfurization at 500 °C depending on the duration of annealing from 20 to 120 min. The reflection peaks of the synthesized material can be attributed to the monoclinic structure of the Cu_2SnS_3 compound (JCPDS 01-070-6338) and the Cu_xS phase (JCPDS 6-464).

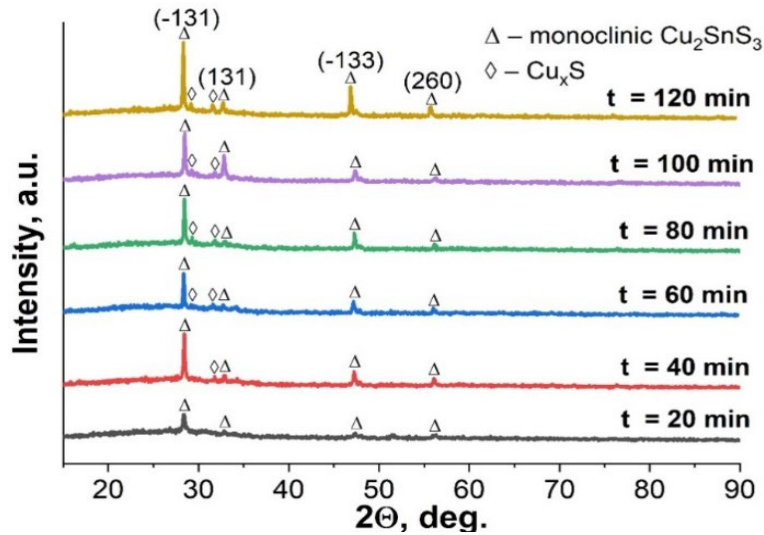


Fig. 3. XRD patterns of CTS films synthesized at a temperature of 500 °C with different duration of the sulfurization process.

Approximation of the dominant peak at $2\theta = 28.40^\circ$ reveals the formation of a two-phase Cu_2SnS_3 material consisting in the initial stage of crystallization (annealing time $t = 20$ min) of a mixture of tetragonal and monoclinic crystal structures (Fig. 4), which is confirmed by its splitting to the reflection peak at $2\theta = 28.29^\circ$ from the (112) plane of the Cu_2SnS_3 tetragonal structure (JCPDS No.89-4714) and the reflection peak from the (-131) plane of the Cu_2SnS_3 monoclinic structure. With an increase in the annealing time to 40min the material crystallizes in a monoclinic structure, which follows from the disappearance of the peak at $2\theta = 28.29^\circ$ and the appearance of highly symmetrical reflection peak (-131) with increased intensity.

Table 2 gives the structural parameters of the films synthesized under the above conditions, calculated using the WinPLOTR module of the FullProf program. The crystallite size L of the films can be estimated according to the Scherrer's equation [19] as follows:

$$L = \frac{0.94 \cdot \lambda}{\beta \cdot \cos\theta}, \quad (1)$$

where β - is the full width at half maximum of the peak in radians, $\lambda = 0.1542$ nm is the X-ray wavelength and θ is the Bragg diffraction angle. The density of dislocations (δ) present in the films was estimated using the Williamson-Smallman relation [20]:

$$\delta = 1/L^2 \quad (2)$$

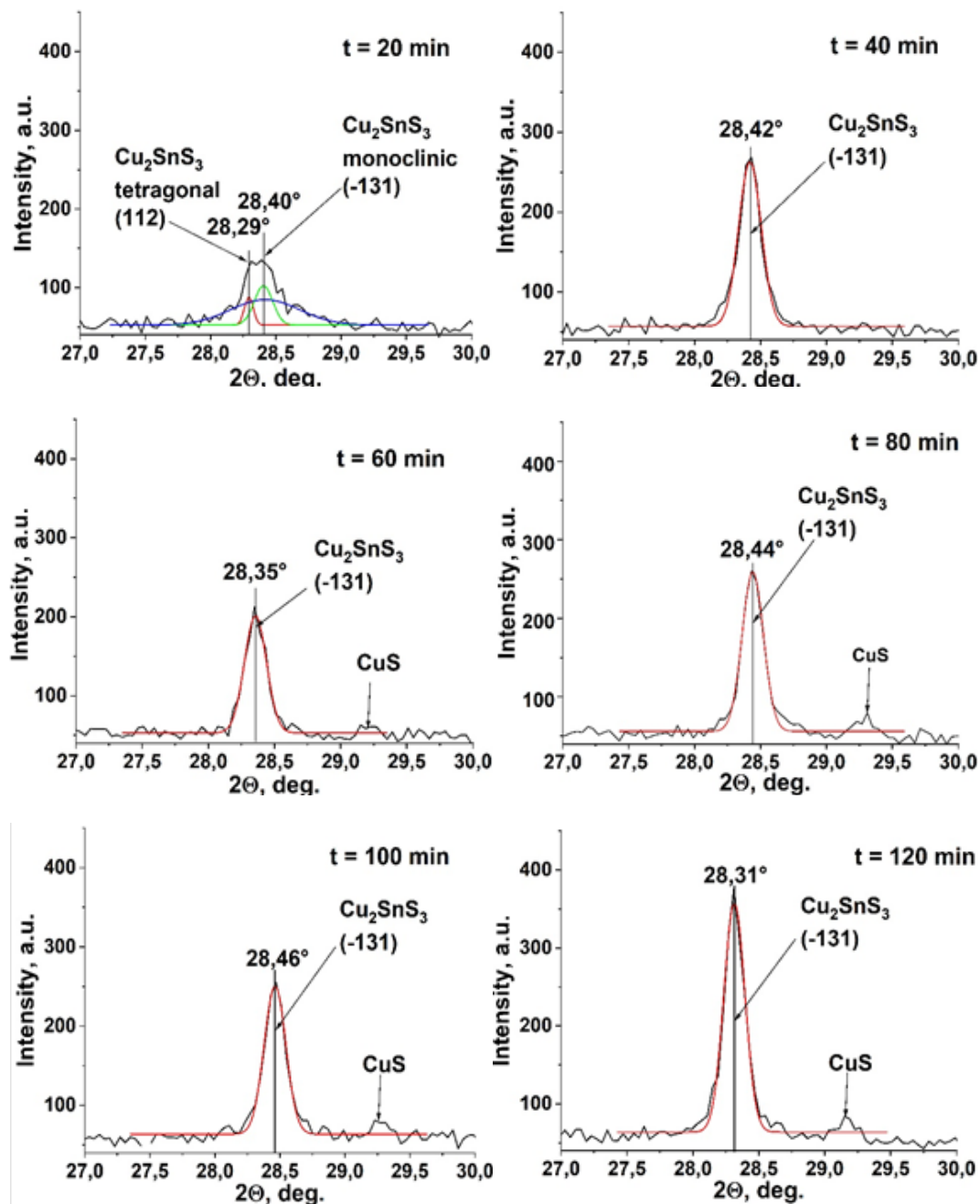


Fig. 4. Detailed XRD spectra of CTS films at diffraction angles around 28.40° , synthesized during the annealing time from 20 to 120 min.

A comparison of data given in Table 2 shows that the lattice parameters of the CTS films, synthesized under all tested conditions, have insignificant differences. However, the microstructural characteristics of the films show a clear dependence on the annealing time. An increase in the sulfurization time from 20 to 40 min leads to a gradual increase in the crystallite size from 37.44 nm to 48.12 nm and a decrease in the dislocation density.

Table 2. Structural parameters of CTS films prepared at different annealing times.

| Time,min | 2 θ (grad) | (hkl) | a (Å) | b (Å) | c (Å) | B (deg) | L (nm) | $\delta \times 10^{14}$ (lines/m ²) |
|----------|----------------------|--------|----------|----------|----------|------------|-----------|--|
| 20 | 28.39 | (-131) | 6.59 | 11.60 | 6.72 | 109.40 | 37.44 | 7.0 |
| 40 | 28.43 | (-131) | 6,66 | 11.52 | 6.72 | 109.54 | 48.12 | 4.3 |
| 60 | 28.35 | (-131) | 6,65 | 11.54 | 6.74 | 109.56 | 122.9 | 0.7 |
| 80 | 28.43 | (-131) | 6,66 | 11.53 | 6.72 | 109.53 | 59.74 | 2.8 |
| 100 | 28.47 | (-131) | 6,65 | 11.53 | 6.72 | 109.52 | 51.57 | 3.8 |
| 120 | 28.31 | (-131) | 6,64 | 11.51 | 6.64 | 109.29 | 74.12 | 1.8 |

At an annealing time of 60 min, a sharp transformation of the microstructure occurs. CTS films prepared under these conditions are characterized by a significant increase in the size of crystallites up to 123nm and a decrease in the dislocation density down to 0.7×10^{14} lines·m⁻². The opposite picture is observed with a further increase in the synthesis time from 80 to 100 min: the crystallite size decreases to 51.57 nm, and the dislocation density increases, which is fully consistent with the data of SEM.

It should be noted that the stable monoclinic structure is also retained with an increase in the annealing time up to 120 min, but is accompanied by the formation of a higher content of the Cu_xS binary compound, which is in good agreement with the data of SEM, revealing the segregation of this phase in the form of separate crystallites on the surface of the Cu₂SnS₃ layer.

For more reliable identification of the monoclinic structure of the CTS material, we also studied the Raman spectra of films synthesized at T = 500 °C for various sulfurization time. The monoclinic structure with the space group Cc (N^o1) is characterized by the irreducible representation $\Gamma=3A^I \oplus 3A^{II}$ with six Raman and IR active modes [21]. Similar to CIS compounds with the chalcopyrite structure [22], in the monoclinic Cu₂SnS₃ structure, the dominant vibration is the A^I, which includes the vibration of anions observed in the range of 178–180 cm⁻¹. In addition, allowed vibrations of the A^I symmetry are vibrations at 83 and 244 cm⁻¹. Symmetry modes A^{II} are observed at 204, 231 and 291 cm⁻¹. Fig.5 shows the Raman spectra of the synthesized films recorded in the range of 200-500 cm⁻¹. As can be seen the Raman spectra of the synthesized films are characterized by two main vibrations in the region of 290 cm⁻¹ and 351 cm⁻¹. The frequency positions of the observed oscillations are in good agreement with the data of the authors [21-24]. The peak at 209 cm⁻¹ can be attributed to the Raman active mode A^{II} and the high-frequency peak at 351 cm⁻¹ to the second-order mode of the dominant A^I mode of the CTS anionic sublattice [21]. A weak Raman peak at 471 cm⁻¹ may attributed to the Cu_xS compound, which is confirmed by studies of the elemental composition of the prepared films, showing the presence of an excess of copper and sulfur atoms in the synthesized material (Cu_{2.68}SnS_{3.21} and Cu_{2.55}SnS_{3.27}) (see Table 1). Some deviation in the positions of these peaks from the results of [23] is apparently due to the difference in the composition and micro-structure of the films, as well as the possible existence of secondary phases that cannot be identified. It should be noted that the intensity of mentioned lattice vibrations increases with an increase in the annealing time to 80 min, which indicates a stronger ordering in the crystal structure. A further increase in the duration of annealing (up to 120 min) is accompanied by a decrease in the intensity of the dominant vibrations and is an indicator of the degradation of the crystal structure of the material. The observed changes in the Raman spectra are in a good agreement with the results of studies of the phase composition and micro-structural characteristics of the CTS films.

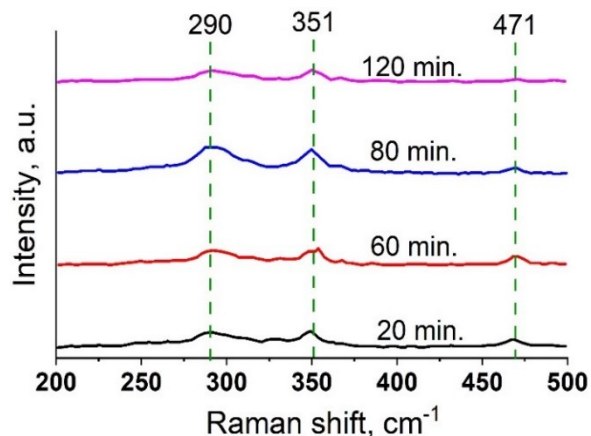


Fig.5. Raman scattering spectra of Cu_2SnS_3 films depending on the annealing time at a temperature of $500\text{ }^\circ\text{C}$.

It should be noted that in addition to Raman spectroscopy, a number of other methods such as the transmission electron microscopy, secondary ion mass spectrometry depth profiling, and photoluminescence spectroscopy can be also used to identify the defect and secondary phases.

4. Conclusions

The physical properties of Cu_2SnS_3 thin films fabricated on glass substrates by annealing of stacked metallic (Sn-Cu) precursor in sulfur vapor at $500\text{ }^\circ\text{C}$ during the time of 20-120 min were investigated. Changes occurred in the micro-structural properties of CTS film were examined using EDX, SEM, XRD, and Raman spectroscopy techniques. The EDX analyses of the films showed that depending on sulfurization time the films may have Cu-poor and Cu-rich composition. The SEM images of the samples demonstrated a denser and smoother microstructure with an increase in the annealing time up to 80 min. XRD spectra of the films are dominated by strong peaks of monoclinic phase of CTS regardless of the annealing time. In addition to the main CTS phase, Cu_xS as secondary phase was detected in some films. The formation of single-phase CTS compound of a monoclinic structure, with a composition close to stoichiometry, is completely ended during the sulfurization time of 60-80 min. The structural parameters such as lattice parameters, coherent scattering region, and dislocation density of monoclinic CTS phase were calculated on XRD data. Raman spectra of the films confirmed formation of Cu_2SnS_3 monoclinic structure. Overall, it was found that the annealing at $500\text{ }^\circ\text{C}$ with the duration of the process from 60 to 80 min yield more promising results for CTS-based thin film solar cell application.

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