Synthesis of a Cu$_2$SnS$_3$ ternary compound by thermal annealing of a metal layer in sulfur vapor

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Abstract. A method for forming thin films of the Cu$_2$SnS$_3$ compound homogeneous in phase composition for use in solar cell devices is proposed. The Cu-Sn alloy layers deposited by thermal spraying in vacuum were annealed in sulfur vapor in a graphite chamber of the quasiclosed volume type. Using X-ray phase analysis, the optimal conditions for the formation of Cu$_2$SnS$_3$ films homogeneous in phase composition were found: annealing temperature 450 °С, sulfur vapor pressure ~ 0.2 torr. The sulfide layers obtained in this way in their elemental composition correspond to the Cu$_2$SnS$_3$ compound stoichiometry. Cu$_2$SnS$_3$ films have an optical band gap of 1 eV, and the absorption coefficient in the visible region of the spectrum is 2·10$^5$ cm$^{-1}$.

1. Introduction

Thin films of p-type direct-gap semiconductor compound Cu$_2$SnS$_3$ (CTS) are promising as a light-absorbing layers in thin-film solar cells (SCs) due to the high absorption coefficient in the visible spectral region ($\sim$ 10$^5$ cm$^{-1}$) [1]. It is possible to achieve power efficiency up to 23% in thin-film technology of SC based on chalcopyrite compounds. However, the cost of such SCs is too high due to the use of rare-earth elements In and Ga. Replacing these elements with more common and cheaper Zn and Sn and using the thin-film technology of kesterites (in the four- and five-component systems of sulfides, selenides, and sulfoselenides) does not allow fabrication of SCs with an efficiency of more than 13% due to the defective structure of the active layer. So it was proposed to study a simpler three-component copper-tin-sulfur system in which stable compounds such as Cu$_2$SnS$_3$, Cu$_3$SnS$_4$, Cu$_4$SnS$_4$, Cu$_2$Sn$_3$S$_7$, and Cu$_2$Sn$_2$S$_7$ crystallize. It was theoretically shown that from the point of view of the band structure and the probability of the formation of intrinsic point defects, the Cu$_2$SnS$_3$ compound should possess the most optimal properties for SC from this series of phases (Zawadzky et al [2]).

In nature, Cu$_2$SnS$_3$ is found in the form of a mineral called Mohite and has a crystalline structure similar to sphalerite [3]. The lattice parameters of Cu$_2$SnS$_3$ and ZnS differ by no more than 0.6 %. The foregoing makes it possible to create a p-Cu$_2$SnS$_3$/n-ZnS heterojunction matched by the lattice parameter with a small number of defects at the interface [4]. At the same time, the Cu$_2$SnS$_3$ compound can crystallize in the form of monoclinic, tetragonal, and cubic modifications, depending on the degree of ordering of copper and tin atoms in the cationic sublattice [5]. The appearance of one or another modification depends on the synthesis conditions and determines the optical band gap of the formed...
film in the range from 0.9 to 1.5 eV. Therefore, the problem of synthesizing Cu₂SnS₃ films uniform in phase composition suitable for use in solar cells is currently relevant.

2. Experimental details
To create a Cu-Sn alloy of various compositions, weighed portions of copper and tin were placed in a quartz vacuum ampoule and melted at a temperature above 800 °C for 1 hour. Glass substrates were washed in a solution of K₂Cr₂O₇ in concentrated sulfuric acid, followed by washing in distilled water. Films of a metal precursor were sprayed onto a glass substrate by thermal evaporation in vacuum. The thickness of the metal layers was controlled using the MII-4 microinterferometer. The process of reactive annealing of metal films in sulfur vapor was carried out in a vacuum graphite chamber [6,7] of the quasi-closed volume type (Figure 1). The vapor pressure of sulfur was set by the temperature of the sulfur source. The processing time varied depending on the thickness of the initial metal film.

![Figure 1. A schematic representation of a quasi-closed volume type reaction chamber.](image)

1, 4, 7 – heaters from W-Mo wire in a ceramic insulator for areas of the substrate (1), the walls of the chamber (4) and the source of sulfur (7);
2, 6 – graphite;
3 – sample;
5 – quartz cylinder;
8, 10 – thermocouples to control the temperature of the sulfur source (8) and the substrate (10);
9 – sulfur source.

The elemental composition of the films was determined by X-ray microanalysis using a JSM-6380-LV JEOL electron microscope with an INCA 250 energy dispersive microanalysis system. X-ray phase analysis of the sulfide films was carried out on a DRON 4-07 instrument with an X-ray source CoKα. IR transmission spectra were measured on a Bruker Vertex 70 spectrometer. The surface morphology of sulfide films was studied using a scanning electron microscope JSM-6380-LV JEOL.

3. Results and discussion
The quality of the synthesized sulfide film strongly depends on the formation conditions – substrate temperature and sulfur vapor pressure above the surface of the treated metal layer of the precursor [8]. For a detailed analysis in this paper, three were selected from a large number of samples (Table 1).

| Sample No. | Alloy compositionCu:Sn ratio | Metal precursor thickness, μm | Sulfurization temperature, °C | Sulfur source temperature, °C | Sulfurization duration, min |
|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| No. 3      | 2.0                         | 0.40                        | 400                         | 130                         | 35                          |
| No. 14     | 2.0                         | 0.50                        | 450                         | 160                         | 140                         |
| No. 27     | 1.9                         | 0.28                        | 450                         | 150                         | 80                          |

Sample No. 3, formed at an annealing temperature of 400 °C for 35 minutes, is characterized by phase composition heterogeneity. Figure 2a shows an X-ray diffraction pattern of sample No. 3, which contains diffraction peaks corresponding to both the CTS ternary compound (PDF No. 01-089-4714) and the phases of copper and tin double sulfides (PDF No. 01-075-2235 and PDF No. 00-039-0354). An X-ray diffraction pattern of the tetragonal modification of this compound was chosen as the reference...
diffraction pattern for the CTS film. It should be noted that monoclinic, tetragonal, and cubic modifications of CTS have such similar diffraction patterns that it is practically impossible to distinguish them only by the results of X-ray diffraction.

**Figure 2.** X-ray diffraction patterns of samples No. 3 (a), No. 14 (b) and No. 27 (c).

Table 2 presents the results of the study of the elemental composition of the synthesized sulfide films. The shift of the stoichiometric Cu:Sn ratio in the sulfide film for sample No. 3 toward copper enrichment compared to the composition of the initial metal precursor as a result of annealing in sulfur vapor is explained by the known phenomenon of evaporation of volatile tin sulfides during annealing [1,9].

| Sample | Atomic % | Atomic ratio | Cu:Sn | S/(Cu+Sn) |
|--------|----------|--------------|-------|----------|
| No. 3  | 32.02    | 14.80        | 53.18 | 2.16     | 1.15     |
| No. 14 | 32.20    | 16.81        | 50.99 | 1.92     | 1.04     |
| No. 27 | 30.08    | 17.93        | 51.99 | 1.68     | 1.08     |

At first glance, an increase in the annealing temperature and processing time should contribute to this phenomenon, however, this effect is not detected in the sample No. 14. In our opinion, an increase in the pressure of sulfur vapor over a layer of growing sulfide prevents the evaporation of volatile tin sulfides. An increase in the temperature of the sulfur source from 130 to 160 °C corresponds to an increase in the pressure of sulfur vapor by about 4 times to 0.2 torr. In addition, there is a change in the kinetics of chemical sulfurization processes with a simultaneous increase in the annealing temperature and sulfur vapor pressure.

According to theoretical data [10], to obtain a CTS film homogeneous in phase composition, the most optimal conditions are: annealing temperature from 400 to 570 °C and atmospheric pressure over the growing sulfide film from 0.01 to 1 torr. Indeed, samples No. 14 and 27 synthesized at a substrate temperature of 450 °C and a sulfur vapor pressure of ~ 0.2 torr according to X-ray diffraction data are characterized by the absence of secondary phases of copper sulfides (Figure 2,b and 2,c). At the same time, low-intensity peaks corresponding to tin disulfide SnS₂ are found (PDF No. 01-089-3198). The elemental composition of these samples is slightly biased toward copper depletion, but generally corresponds to the ternary compound Cu₂SnS₃ stoichiometry (Table 2).
From the point of view of X-ray diffraction, samples No. 14 and 27 differ only in the sequence of intensities of the diffraction peaks. The closest reference sequence corresponds to the diffraction pattern on sample No. 27, when the peak intensity near $2\theta = 33^\circ$ is maximum, and the peak intensity near $2\theta = 64^\circ$ is ~ 70% of the maximum. The difference in the intensity sequence from the reference one for sample No. 14 can be explained by the appearance of the preferred direction of crystallite growth in the polycrystalline film, which is unlikely due to the absence of the directing action of the amorphous glass substrate.

The transmission spectra of sulfide films are shown in Figure 3. The optical absorption coefficient $\alpha$ was estimated from the transmittance data. It in the presented spectral region for samples No. 3 and 27 is of the order of ~ $10^5$ cm$^{-1}$. The spectra rearranged in the $(\alpha h\nu)^2$ from $h\nu$ axes allow one to estimate the activation energies of absorption processes in films for direct-gap transitions.

![Figure 3. Transmittance spectra of the CTS films. Sample 3 (line 1) and sample 27 (line 2).](image)

The activation energy $E_a$ near 1 eV corresponds to the optical band gap of the CTS ternary compound [11]. The somewhat different values of $E_a = 0.96$ eV for sample No. 3 and $E_a = 1.05$ eV for sample No. 27 would seem to be the same within the error of the method. However, from the analysis of the spectrum of the external quantum yield of the SC device based on the CTS film during the absorption of light, electronic transitions are found with both an activation energy of 0.96 eV and an activation energy of 1.05 eV [12]. According to our data, under conditions of excess copper in the sulfide film, the optical band gap of 0.96 eV is more often observed. Under conditions of copper deficiency, an activation energy of 1.05 eV is observed. Differences in the band gap for different samples can be explained by the predominant content of a particular CTS crystalline modification in the sulfide film.

The results of the surface morphology studying of samples No. 14 and No. 27 using scanning electron microscopy (SEM) are shown in Figure 6. Due to weak adhesion to the glass surface, aggregation of crystallites of the polycrystalline CTS film occurs in formations with a lateral roughness size of several microns. The roughness height according to atomic force microscopy (the corresponding images are not given in this paper) is in the range from 0.5 to 0.7 $\mu$m. At present, our group is starting work with the use of glass with a layer of metal molybdenum for better adhesion, which in the future may allow the formation of a film that completely covers the substrate.
4. Conclusion

In this paper, we propose a method for forming a film of a ternary compound Cu$_2$SnS$_3$ uniform in phase composition for use in solar cells. A Cu-Sn alloy of a given composition is proposed as a metal precursor, which is a technologically more advantageous solution than, for example, multilayer precursor films deposited by magnetron sputtering of copper and tin layers described in [1,5,9]. On the one hand, this approach is cheaper to implement, on the other hand, it allows you to get more homogeneous layers of sulfide. In the process of annealing in sulfur vapor, the use of multilayer precursors inevitably leads to the appearance of inhomogeneities in the composition over the volume of the growing film and, consequently, to inhomogeneities in the phase composition of the grown sulfide. At the same time, a homogeneous layer of a metal precursor makes it possible to obtain a uniform sulfide film. It is only necessary to create a sufficient pressure of sulfur vapor during the annealing process to ensure the supply of sulfur during the chemical reaction at the entire depth of the film. The quasi-closed volume graphite chamber shown in Figure 1 allowed us to achieve the required sulfur vapor pressure inside the reaction volume and to accurately control the temperature of the substrate during annealing.

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