MORPHOLOGY AND CHEMICAL COMPOSITION OF THIN FILMS OF CHALCOPYRITE

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Thin films of chalcopyrite $CuFeS_2$ were deposited on glass substrates by a flash method. The resulting film structure was analyzed by means of scanning electron microscopy combined with energy dispersive X-ray spectroscopy. It was detected that thin films consist of separate grains with the approximately equal areas of about (200–400) μm^2. Thin films of chalcopyrite $CuFeS_2$ have the chemical composition with the atomic content of Cu, Fe, and S of 25.22, 23.38, and 51.40 at. % and the atomic ratios of Cu/Fe and S/(Cu + Fe) equaling to 1.08 and 1.06 respectively that slightly differs from the theoretical values equaling to 1 for both atomic ratios. The small inclusion of the second phase with the chemical composition with the atomic content of Cu, Fe, and S of 29.24, 25.24, and 45.52 at. % was detected and can be attributed to talnakhite $Cu_9Fe_8S_{16}$. The most common occurrence of the inclusion of the second phase along the borders of the grain shows that they are responsible for the cracking of thin films.

Key words: thin films; chalcopyrite; scanning electron microscopy; energy dispersive X-ray spectroscopy; chemical composition.

INTRODUCTION

Multinary semiconducting compounds of the I-III-VI_2 group (I – Cu, Ag; III – Al, Ga, In; VI – S, Se, Te) with crystal structure of chalcopyrite $CuFeS_2$ are at the center of current research as they are used in photovoltaic manufacturing [1]. They are also promising for the production of light-emitting diodes, injection lasers, and optical filters. Other compounds of the Cu-Fe-S system are also promising for use in these fields and in spintronics and thermoelectric conversion. To date, conditions of the existence of the ternary compounds of the Cu-Fe-S system are not yet completely clear. Preparation of thin films of these compounds and determination of the fields of their existence, as well as study of their physical properties, can help to develop the methods of preparation of compounds of the Cu-Fe-S system with properties suitable for optoelectronic applications.

Phase relations in the Cu-Fe-S ternary system have received considerable attention [2-6]. The Cu-Fe-S system contains many phases and solid solutions with a wide solubility range. There are six copper-iron ternary compounds in this system. They are bornite Cu_5FeS_4, chalcopyrite $CuFeS_2$, cubanite $CuFe_2S_3$, haycockite $Cu_4Fe_5S_8$, mooihoekite $Cu_9Fe_9S_{16}$, and talnakhite $Cu_9Fe_8S_{16}$. An isothermal section at 873 K is characterized by the extensively large fields of solutions, one of them is the intermediate solid solution (iss). Chalcopyrite $CuFeS_2$ was found to be a semiconductor with a zero [7] or narrow band gap [8–11]. This compound was extensively studied and it was established that its composition is sulfur deficient and expressed by the formula $CuFeS_{2-\delta}$ [12]. Haycockite $Cu_4Fe_5S_8$ was investigated in papers [5, 13, 14]. The conditions of the existence of other ternary compounds are not completely clear.

Thin films of $CuFeS_2$ were grown by sulphurization of CuFe alloy precursor [11]. Cu/Fe/…/Cu thin layers consequentially were deposited by vacuum evaporation on a substrate heated at temperature $T_s = 723$ K. After deposition of the metal alloy precursor, there is an interdiffusion of the metals all along the thickness. These precursors are sulphured in vacuum chamber using an S source. The sulphurization duration is 20 min. Unfortunately, this method of preparation of thin films is too complicated. Flash method of deposition of thin films is one of the techniques that can be applied for deposition of thin films of multicomponent alloys, which contain different vapor pressures. For example, thin films of $CuInSe_2$ were evaporated onto glass substrates by a flash method [15]. It was found that as-deposited films are amorphous and annealing in selenium atmosphere produces polycrystalline films.

The goal of the present project is to prepare thin films of chalcopyrite by a flash method of deposition of thin films and to study their structural properties using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray spectroscopy (EDX).

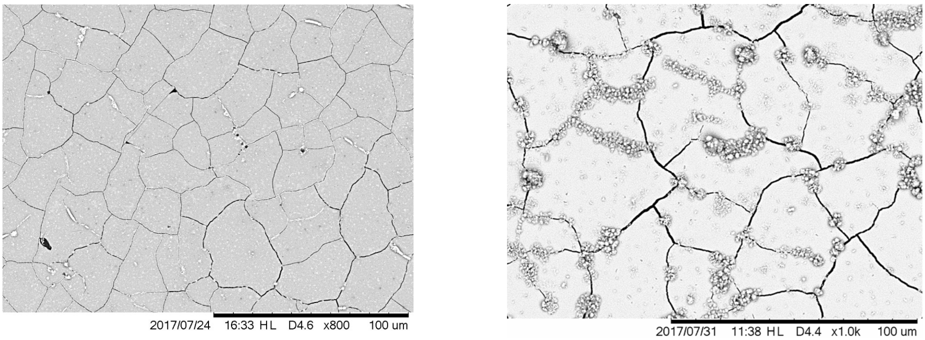
MATERIALS AND METHODS

Thin films on glass substrates were deposited by method of flash from powder of previously prepared ingots of chalcopyrite $CuFeS_2$. Synthesis of the initial ternary compound $CuFeS_2$ was performed in quartz ampules by melting the elements at temperature that exceeds the melting point of the compound by 20 K. The ingots were powdered with the size of grains of 0.1–0.3 mm. The discrete portion of the powder delivered to the tantalum heater with a temperature of 2273 K was no more than 10 mg. Glass substrates were used and their temperature was about 573 K. The distance between heater and substrate was about 10 cm.

The X-ray studies were carried out using monochromatic Cu K_α-radiation (1.5406 Å, step size 0.01° or 0.04°, counting time 10 s). The Rietveld analysis of the X-ray powder diffraction data was performed using the FullProf software. Morphology and microstructure of thin films and their chemical composition were investigated using the Hitachi Tabletop Microscope TM3000 equipped with Energy Dispersive Spectrometry (EDS) System Quantax 70 (Bruker). The magnification was varied from ×50 to ×10000.

RESULTS AND DISCUSSION

It was discovered that thin films of chalcopyrite $CuFeS_2$ deposited on glass substrates from prepared beforehand ingots of chalcopyrite $CuFeS_2$ consist of separate grains which approximately equal to areas of about (200–400) μm^2 (Fig. 1) with thickness of about 1–2 μm (Fig. 2). It was found that this structure appeared during the cooling process of the thin films because it completely covers the surface of the glass substrates.



a *b*

Figure 1. – Top view of thin films of chalcopyrite $CuFeS_2$ for magnification ×800 (*a*) and ×1000 (*b*)

It was found that thin films have the chemical composition with the atomic content of Cu, Fe, and S of 25.22, 23.38, and 51.40 at. % and the atomic ratios of Cu/Fe and S/(Cu + Fe) equaling to 1.08 for the atomic ration Cu/ Fe and 1.06 for the atomic ratio S/(Cu + Fe) while these theoretical ratios for chalcopyrite $CuFeS_2$ are equal to 1. The small inclusion of the second phase with the chemical composition of atomic content of Cu, Fe, and S varied from 29.24, 25.24, and 45.52 (at. %) (Table). This chemical composition corresponds to talnakhite $Cu_9Fe_8S_{16}$. The most common occurrence of the inclusion of the second phase along the borders of the grain (Fig. 1, *b*) shows that they are responsible for the cracking of thin films.

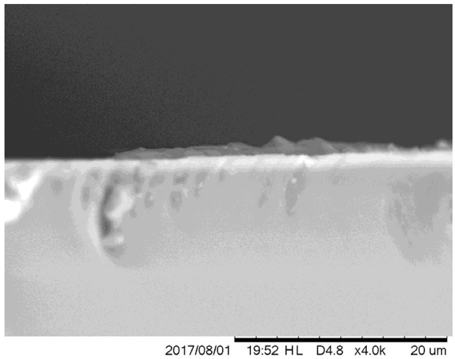


Figure 2. – Cross-sectional view of thin film of chalcopyrite $CuFeS_2$

Table

Chemical composition of the main and additional phase detected in thin films of chalcopyrite

Point	The main phase (at. %) Chalcopyrite					The additional phase (at. %) Talnaknite				
	Cu	Fe	S	Cu/Fe	S/(Cu+Fe)	Cu	Fe	S	Cu/Fe	S/(Cu+Fe)
1	25.18	25.16	49.66	1.00	0.99	29.87	25.80	44.33	1.16	0.80
2	22.84	20.22	56.94	1.13	1.32	29.98	23.71	46.32	1.26	0.86
3	23.94	25.67	50.39	0.93	1.02	28.55	25.86	45.59	1.10	0.84
4	28.40	22.65	49.96	1.26	0.98	28.02	26.51	45.47	1.06	0.83
5	25.99	23.44	50.56	1.11	1.02	29.76	24.33	45.91	1.22	0.85
Aver	25.22	23.38	51.40	1.08	1.06	29.24	25.24	45.52	1.16	0.84

CONCLUSION

Thin films of chalcopyrite $CuFeS_2$ were deposited on glass substrates by a flash method. It was detected that thin films consist of separate grains with the approximately equal areas of about (200 – 400) μm^2. Thin films of chalcopyrite $CuFeS_2$ have the chemical composition with the atomic content of Cu, Fe, and S of 25.22, 23.38, and 51.40 at. % and the atomic ratios of Cu/Fe and S/(Cu + Fe) equaling to 1.08 and 1.06 respectively that slightly differs from the theoretical values equaling to 1 for both atomic ratios. The small inclusion of the second phase with the chemical composition with the atomic content of Cu, Fe, and S of 29.24, 25.24, and 45.52 at. % was detected and can be attributed to talnakhite $Cu_9Fe_8S_{16}$. The most common occurrence of the inclusion of the second phase along the borders of the grain shows that they are responsible for the cracking of thin films.

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