MICROSTRUCTURE OF $ZnIn_2S_4$ THIN FILMS

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Abstract

$ZnIn_2S_4$ films on MgO and CaF_2 oriented substrates were prepared by precipitation from aqueous suspensions. The films were annealed in various regimes. Their stoichiometry was confirmed by the diffraction method. The microstructure of the films was studied via optical microscopy.

1. Introduction

Recently, semiconductor materials of ternary chalcogenide compounds have gained much attention because they exhibit tunable electronic and optical properties. $ZnIn_2S_4$ is also of interest because it can be used for charge storage, electrochemical recording, in solar cells, etc. The synthesis and deposition of $ZnIn_2S_4$ in the form of thin films and preparation of nano- and microstructures of this material was reported [1]. This allows one to prepare materials with new properties in comparison with bulk crystals.

The technology of preparation of $ZnIn_2S_4$ films has been developed for a long time, since this material exhibits a high photosensitivity, intensive photoluminescence, and the anisotropy of properties. However, the previously developed technology required complicated vacuum installations VUP, and the method of preparation of films in quasi-closed volumes was used. The efforts were made to ensure the reproducibility of the properties identical to those of $ZnIn_2S_4$ bulk crystals [2, 3]. Nowadays it remains an urgent problem to develop simple and inexpensive methods of preparation of thin semiconductor films. In particular, in [4] the method of chemical deposition of PbS–ZnS thin films is described. The replacement of lead by zink in PbS shifts and widens the range of photosensitivity of the material, which can be used in solar cells and sensors. $ZnIn_2S_4$ perpendicular nanosheet films were directly deposited on FTO substrates by a facile hydrothermal method and investigated as the electrode materials for solar cells in [5]. The method of preparation of $ZnIn_2S_4$ nano- and microstructures via a facile solution route was described in [1]. These works confirm that the development of the technology of preparation of $ZnIn_2S_4$ in the form of films and structures with various morphologies is of interest and important for their further possible applications.

2. Experimental

A promising method of preparation of $ZnIn_2S_4$ films was developed and described in detail in [6, 7]. The main feature of this method is that $ZnIn_2S_4$ powder is deposited from saturated $ZnCl_2$ solutions. In the present communication, we report a method of preparation of $ZnIn_2S_4$ films by deposition of $ZnIn_2S_4$ from water suspensions on oriented substrates: MgO (001) face and CaF_2 (111) face. The films with the specified thickness can be obtained, since we know the density of the material, the surface of the substrate, and can calculate the necessary quantity of the powder. The films with a thickness of about 2 μm were prepared and studied. With the aim to increase the adhesion between the films and the substrate and orientation of the crystallites, the films were annealed in a muffle furnace at a temperature of T = 650°C for 14 h.

However, the annealing in this regime did not change markedly the microstructure of the films, and the annealing under the same conditions was repeated.

The microstructure of the films was studied using Amplival and XJL-101 optical microscopes with digital image registration. The stoichiometry of the films was controlled using a DRON-UM1 diffractometer (Fe K_{α} radiation, Mn filter, θ/2θ method).

3. Results and discussion

The resulting $ZnIn_2S_4$ films have the form of continuous yellow deposits. The diffractogram exhibits the spectrum of lines that completely corresponds to the stoichiometry of the initial bulk samples of the material. This can be seen in Fig. 1, where the diffractogram of the $ZnIn_2S_4$ thin film on a CaF_2 substrate is shown.

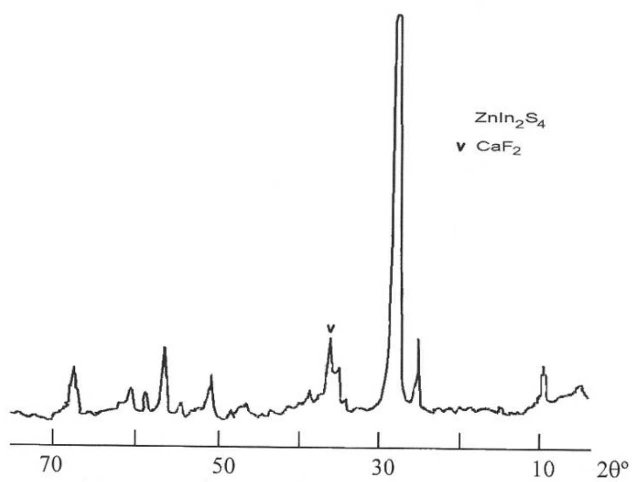


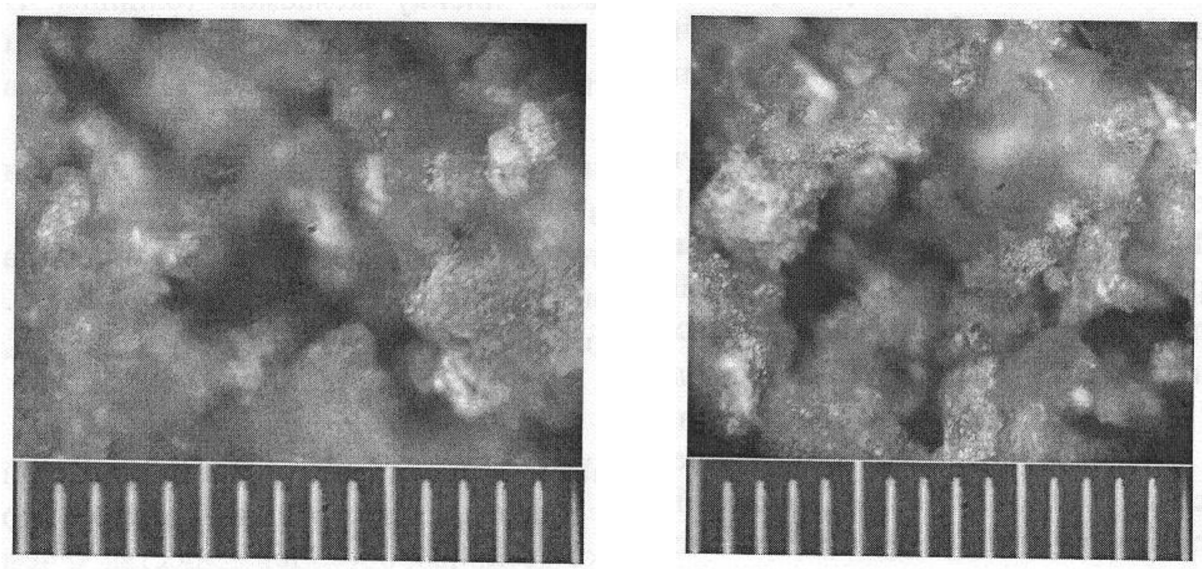
Fig. 1. Diffractogram of the $ZnIn_2S_4$ thin film on the (111) face of the CaF_2 substrate.

Porous spots were observed on the surface of as-grown films. Then we additionally ground the initial powder and then used the finer powder for preparation of films. The optical microscopy showed that this improved the homogeneity of the films. The subsequent annealing of the films also improved their characteristic structure. The surface of the films after the first annealing is shown in Figs. 2a and 2b.

However, the further experiments showed that a repeated annealing has markedly improved the microstructure of the films (Figs. 3a, 3b).

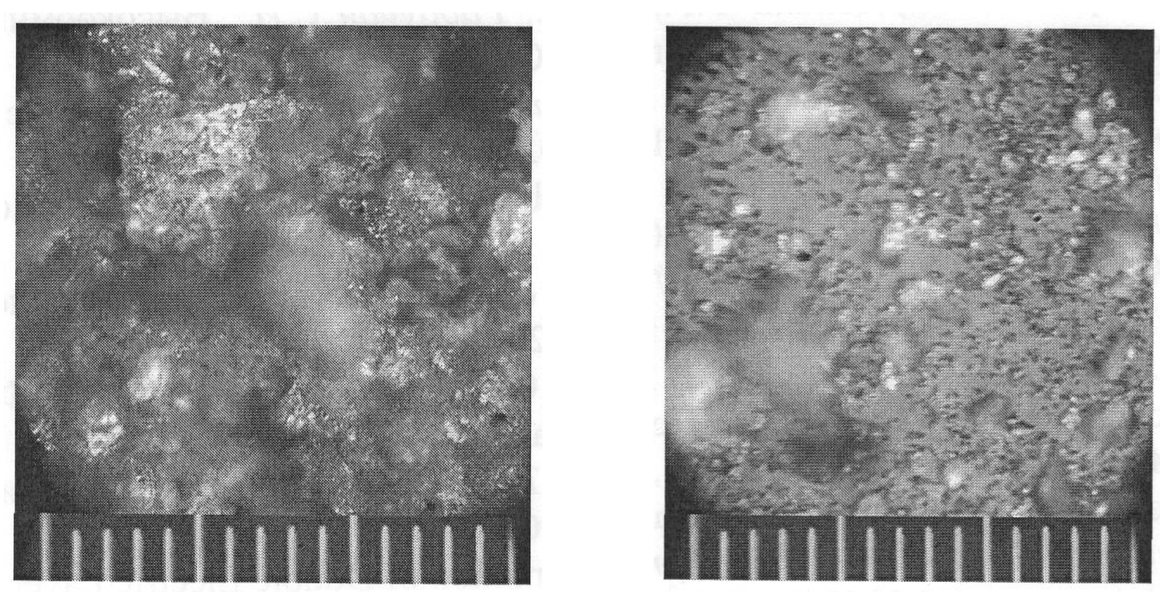
A similar picture was observed in the case when MgO substrates were used. The films were also deposited on mica and glass substrates at 560 and 600°C, and similar results were obtained. In comparison with the results described in [3, 6], this method is the simplest. The variation of the method allows one to prepare multilayer structures with alternation of ultrathin ZnO and In_2O_3 layers as described in [8]. The number of layers can be varied. As was shown in [4], the replacement of lead by zink in PbS can improve the photosensitivity of the material.

A similar phenomenon is observed also in $ZnIn_2S_4$. In particular, the variation of the Ni dopant [9] decreases the forbidden gap width by 0.6 eV, shifts the spectra of optical absorption, photoconductivity, and luminescence.



a b

Fig. 2. Microstructure of the $ZnIn_2S_4$ thin film on the CaF_2 substrate after the first annealing at a temperature of 650°C in various regions of the film (1 division = 10 μm).



a b

Fig. 3. Microstructure of the $ZnIn_2S_4$ thin film on the CaF_2 substrate after the second annealing at a temperature of 650°C in various regions of the film (1 division = 10 μm).

This can be used for the development of various radiation sensors [10] and electrochemical cells [11]. This is promising for various practical applications, especially taking into account the observed anisotropy of the material [12].

3. Conclusions

A simple method of preparation of $ZnIn_2S_4$ thin films was developed. The regimes of their annealing were found. The stoichiometry of the films was confirmed by the diffraction method. The surface microstructure was studied via optical microscopy.

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