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Synthesis and investigation of ZnS and HgS films and ZnS/HgS and HgS/ZnS composites

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ZnS and HgS thin films and ZnS/HgS and HgS/ZnS composites based on these were prepared by the chemical bath deposition method. Optical transmission spectra, absorption spectra, surface morphology, and phase composition were studied.

Semiconductor films / Chemical bath deposition / Structure and morphology of thin films / Optical spectroscopy / Solar cells

Introduction

Zinc sulfide (ZnS) is an important semiconducting material with a large band gap and n-type conductivity. It is promising for use in optoelectronic devices, such as electroluminescent devices and photovoltaic cells [1]. Mercury sulfide (HgS) thin films have been used in solid-state solar cells, photo-electrochemical cells, storage cells, and photoconductors [2]. There is great interest in the physical properties of nanometer size semiconductor films, because their properties are often superior to those of conventional coarse-grained polycrystalline materials [3].

Experimental

Thin films of zinc sulfide and mercury sulfide were synthesized by the chemical bath deposition method with the aim to prepare ZnS/HgS and HgS/ZnS composites.

The films of zinc sulfide were synthesized from a working solution composed of zinc chloride ($ZnCl_2$), trisodium citrate ($Na_3C_6H_5O_7$), ammonium hydroxide (NH_4OH), and thiourea ($CS(NH_2)_2$). The concentration of the zinc-containing salt was equal to 0.04 M, that of trisodium citrate 0.04 M, ammonium hydroxide 0.10 M, thiourea 0.10 M. The working solution for the synthesis of the mercury sulfide films was composed of mercury(II) nitrate ($Hg(NO_3)_2$), trisodium citrate and thiourea. The concentration of the mercury-containing salt was equal to 0.008 M, that of trisodium citrate 0.01 M, thiourea 0.03 M. Only freshly prepared reagents were used in the working solutions for chemical bath deposition. The deposition was carried out on a pre-prepared glass substrate with an area of 3.24 cm^2, which was immersed into the working solutions, where the synthesis of thin films ZnS and HgS had taken place. The pH of the working solutions was equal to 9.6 and 7.3, respectively. The deposition time was 80 min and the temperature 70°C for the ZnS films, 10 min and 80°C for the HgS films. After deposition the substrates were eliminated; the surface was washed with a jet of distilled water to take off the remains of working solution and dried in air. Then the substrates with films on their surface were immersed into similar working solutions to deposit ZnS films on HgS films and HgS films on ZnS films, *i.e.* to produce double layer composites ZnS/HgS and HgS/ZnS.

The phase composition of the ZnS and HgS films and ZnS/HgS and HgS/ZnS composites was investigated by X-ray powder diffraction (diffractometer DRON-3.0, Cu*K*α-radiation). Primary

processing of the experimental diffraction data in order to identify the phases was made using the PowderCell program [4].

Investigation of the optical properties of the ZnS and HgS films and the ZnS/HgS and HgS/ZnS composites was carried out using a spectrophotometer Lambda 25 (Perkin-Elmer). A comparative signal was passed through glass substrates identical to the substrates used to prepare the films.

The surface morphology of the ZnS and HgS films and ZnS/HgS and HgS/ZnS composites was investigated using a raster electron microscope REM-106Y equipped with a system for microanalysis.

Results and discussion

The synthesized ZnS films appeared white on the surface of the glass substrates, and the HgS films were brown – the typical colors of ZnS and HgS, respectively. The composites of ZnS/HgS and HgS/ZnS double layers were brown with a golden hue. Adhesion of the HgS/ZnS composite to the glass substrate, estimated by making mechanical efforts, was high, whereas for the ZnS/HgS composite it was low. This corresponds to the adhesion of the lower layer of the composite, *i.e.* the ZnS and HgS film, respectively, to the glass substrate.

Phase analysis of the ZnS and HgS film samples showed that the ZnS compound is in its cubic modification (sphalerite) and HgS in its trigonal modification (cinnabar) (Fig. 1a,b). X-ray diffraction of the ZnS/HgS and HgS/ZnS composites showed that they contain the two phases, ZnS and HgS, in the modifications described above (Fig. 1c,d). No other phases or solid solutions were found in the composites.

The optical transmission spectra $T(\lambda)$ of the ZnS and HgS films and ZnS/HgS and HgS/ZnS composites were investigated for wavelengths from 200 to 1000 nm (Fig. 2). A rapid increase of the light transmission can be seen for the ZnS films at wavelengths greater than 300 nm. In the case of the HgS films, a sharp increase of the light transmittance can be seen in the region of wavelengths greater 350 nm. For the ZnS/HgS and HgS/ZnS composites there are two jumps in the light transmission at the same wavelengths, indicating a mixture of zinc sulfide and mercury sulfide, which confirms the results of the phase analysis by X-ray diffraction. The spectral dependences of the absorption of the ZnS and HgS films and of the ZnS/HgS and HgS/ZnS composites in $(\alpha \cdot h\nu)^2$ *vs.* $h\nu$ coordinates allow determining the fundamental absorption edges. Extrapolation of the linear parts of the $(\alpha \cdot h\nu)^2$ curves to the intersection with the energy axis was used to estimate the optical band gaps of the films, which were localized in the ranges 3.54-3.68 eV and 3.00-3.06 eV, which is in good agreement with literature data for films of zinc sulfide and mercury sulfide deposited by chemical methods [5-8].

The investigation of the surface morphology of the ZnS and HgS films (Fig. 3a,b) showed that the films are dense and completely cover the substrates, with small amounts of surface defects. The micrographs of the surface of the ZnS/HgS and HgS/ZnS composites (Fig. 3c,d) show that they are also dense, with small amounts of surface defects, and that the top layer completely covers the previous layer of film. On the surface of the ZnS/HgS composite, formation of microcrystals of zinc sulfide is seen. The microanalysis of the surface of the ZnS and HgS films (Table 1) shows nearly stoichiometric zinc to sulfur and mercury to sulfur atomic ratios, with a slight excess of zinc atoms for the ZnS films and a slight excess of sulfur atoms for the HgS films. The microanalysis of the ZnS/HgS, HgS/ZnS composites shows that they consist of approximately 50 % of sulfur atoms and 50 % of a mixture of zinc and mercury atoms. It can be seen that the content of zinc atoms in the HgS/ZnS composite is considerably lower than in the ZnS/HgS composite, despite the fact that each layer of zinc sulfide and mercury sulfide in the composites was synthesized under the same conditions. This may indicate that, in the case of film deposition of mercury sulfide on top of a zinc sulfide layer, the latter can be partially dissolved in the working solution of the HgS synthesis, because of the low alkaline pH environment.

Conclusions

In this work ZnS and HgS thin films were synthesized by the chemical bath deposition method. The possibility of producing double layer composites in the form of ZnS/HgS and HgS/ZnS combinations was shown. The phase composition of the samples was determined. Optical transmission and absorption spectra and the surface morphology of the ZnS and HgS films and the ZnS/HgS and HgS/ZnS composites were investigated, and the elemental composition was studied by microanalysis. The positive results obtained for the preparation of ZnS/HgS and HgS/ZnS double layers allows assuming that the chemical bath deposition method can be used to produce not only double composites, but also multilayer coatings and heterocomposites [9].

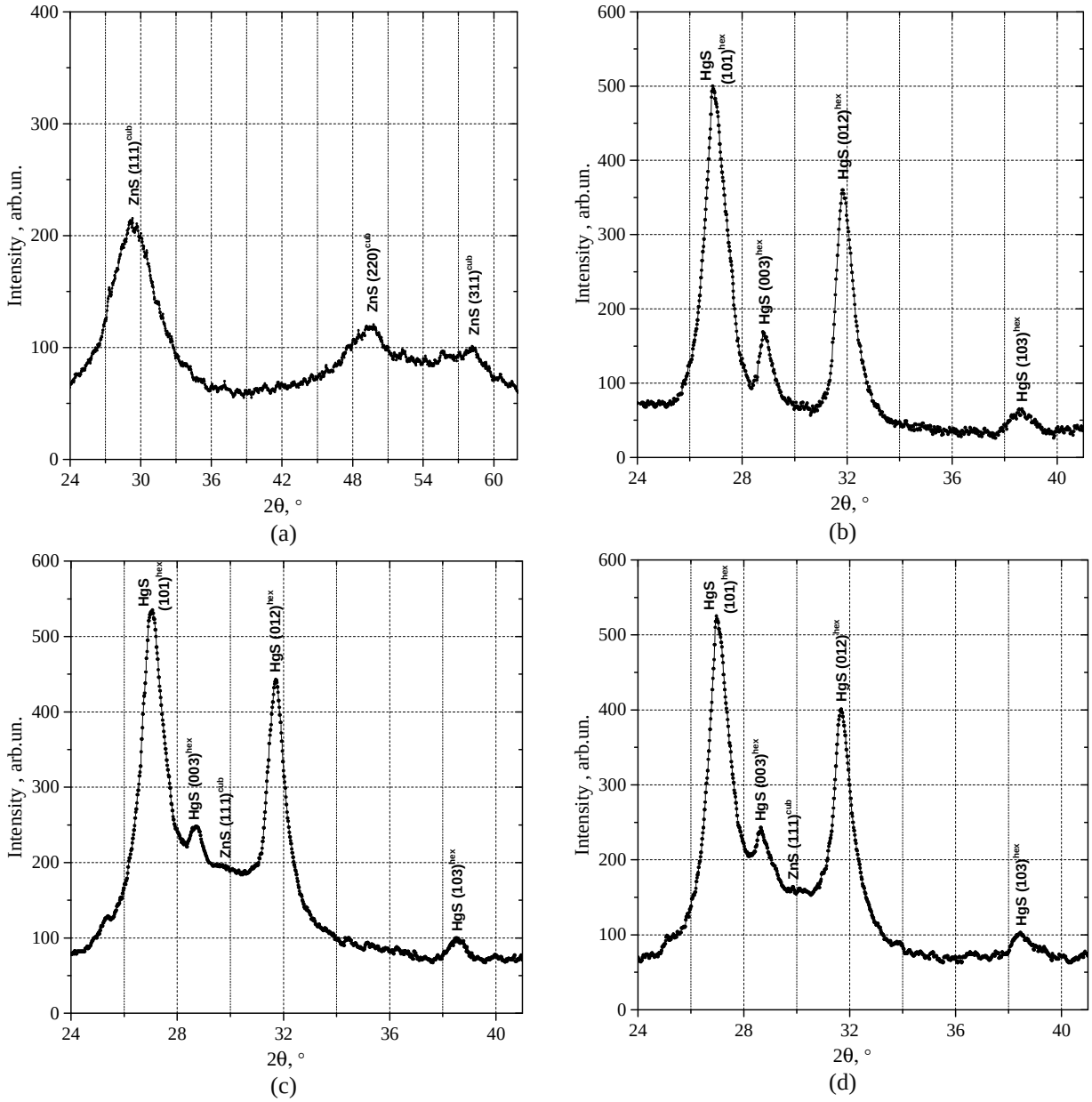

Fig. 1 Experimental diffractograms of ZnS (a) and HgS (b) films, and of ZnS/HgS (c) and HgS/ZnS (d) composites.

Table 1 Results of the microanalysis of the surface of ZnS and HgS films and ZnS/HgS and HgS/ZnS composites.

Sample	Component	wt.%	at.%
ZnS	Zn	68.53	51.57
	S	31.57	48.43
HgS	Hg	85.18	47.89
	S	14.82	52.11
ZnS/HgS	Hg	73.22	35.66
	Zn	11.07	16.52
	S	15.71	47.82
HgS/ZnS	Hg	80.06	42.36
	Zn	5.08	8.30
	S	14.86	49.34

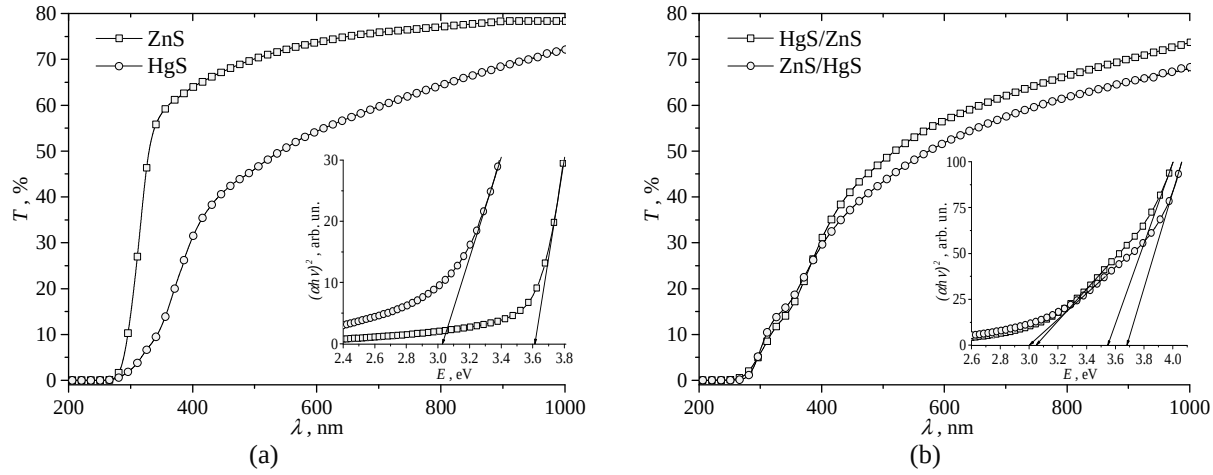

Fig. 2 Optical transmittance and absorbance spectra of ZnS and HgS films (a), and ZnS/HgS and HgS/ZnS composites (b).

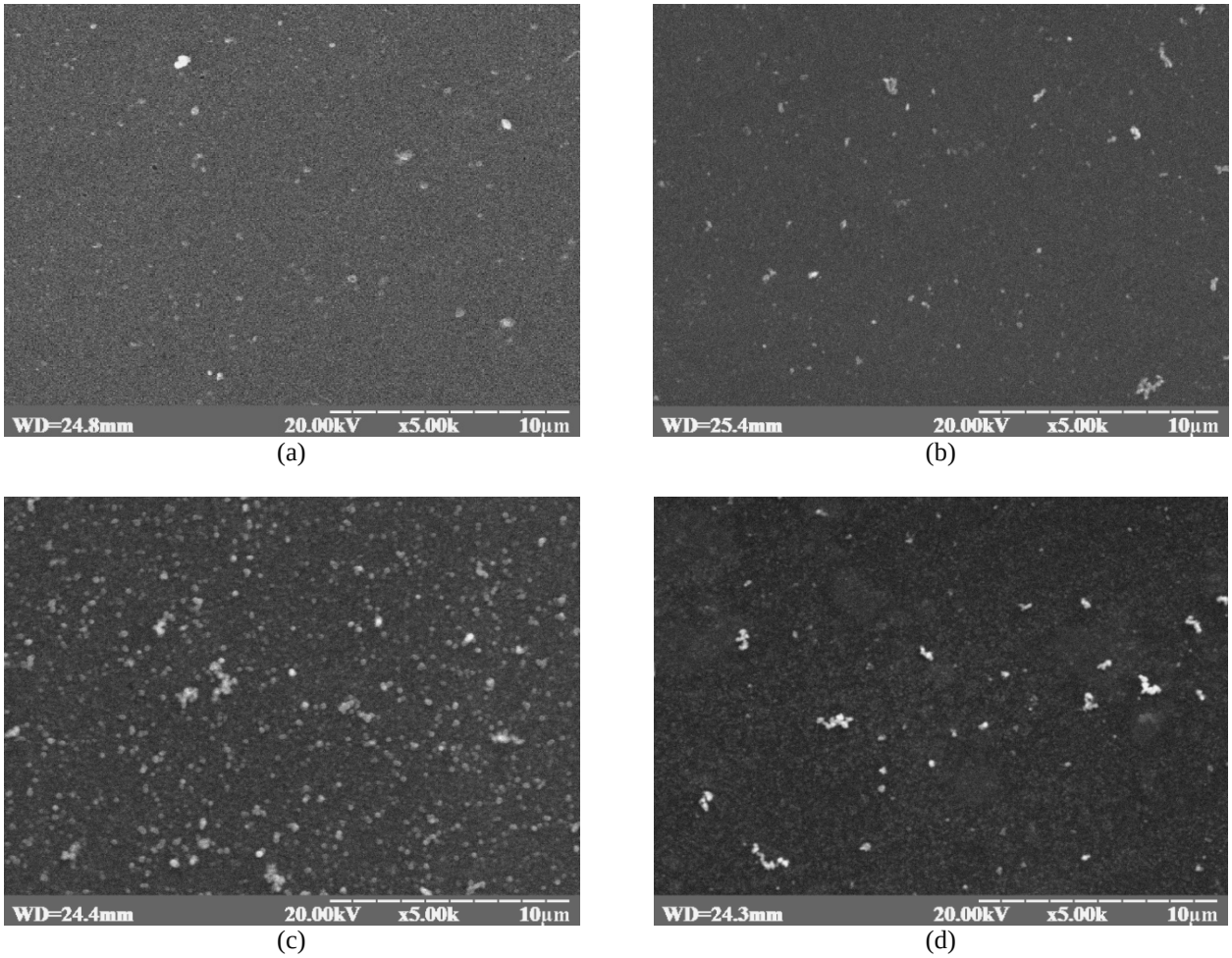

Fig. 3 Surface morphology of ZnS (a) and HgS (b) films and ZnS/HgS (c) and HgS/ZnS (d) composites.

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