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The surface morphology of ZnS–CdS solid solution films

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This paper presents the results of a study of surface morphology of pyrolytic films of solid solutions of ZnS–CdS. We discovered that the change of roughness parameters and microstructure of the surface of the coating film depended on the quantitative composition of the solid solution.

Keywords: scanning atomic force microscopy, roughness parameters, cadmium sulfides, zinc, solid solutions.

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1. Introduction

Modern materials science is constantly stimulating the creation of new technologies from the point of view of the synthesis of compound semiconductors with controlled properties. Much attention is given by scientists to chalcogenide metals for their ability to easily form double and ternary compounds and solid solutions based on them. The desired physical and chemical properties primarily depend on their composition. The considered compounds have many applications, including photodetectors, optical coatings, photovoltaic devices, electro-optic modulators, field effect transistors [1–3]. The methods of obtaining semiconductor compounds allow us to synthesize them in different "types": quantum dots, nanocrystals, thin films, poly- and single crystals.

One of the more common and economical methods for the synthesis of chalcogenide films with a given crystal structure and properties is the method of spraying aqueous solutions of thiourea coordination compounds (TCC) onto a heated substrate [4]. Previous studies [5] have shown that the surface morphology of lead sulfide films obtained from TCC solutions [$Pb(N_2H_4CS)_2Cl_2$] depends on the deposition temperature and composition of the initial solution. In this work, it was shown that increasing the concentration of thiourea in the spray solution, and the deposition temperature during the synthesis of lead sulfide films leads to a more perfect structure and close grain packing [5]. The aim of this work was to study the surface morphology of the ZnS–CdS film system, deposited by the pyrolysis of aqueous solutions of coordination compounds aerosol [$M(N_2H_4CS]$ (M = Cd, Zn).

2. Materials and methods

The synthesis of films of the ZnS–CdS system was carried out by the pyrolysis of an aerosol of thiourea coordination compound solutions [$M(N_2H_4CS)_2Br_2$]. To obtain the TCC we used the salt $CdBr_2 \cdot 4H_2O$, $ZnBr_2$ brand "chemically pure", and thiourea N_2H_4CS brand "ultra pure". Coordination compounds synthesized at room temperature in an aqueous solution containing 0.05 M bromide of the appropriate metal and thiourea (0.2 M). The samples were sprayed at a temperature of 400 °C for 1 minute. As substrates, sital plates were used.

The morphological study of the surface characteristics of the obtained samples was performed using a scanning atomic-force microscope SOLVER P47 (AFM) and determined the average (Ra) and root-mean-square (RMS) (Rq) roughness [6]. For estimation of the surface microrelief of the samples, an analysis of the morphology of the synthesized structures in the following sequence of actions was performed: filtering the phase image of the sample; cross-sectional according to the obtained image; a histogram calculation; determination of roughness parameters.

The film thicknesses were determined by the use of a Jeol JSM-6510LV scanning electron microscope (SEM).

3. Results and discussion

A feature of the aerosol pyrolysis method is that depending on the deposition conditions (temperature, rate of spraying of the aerosol, the type of precursor and the substrate, the concentration of the initial solution), the formation of sulfides of metals with varying structural, optical and electrical properties is possible [7–10]. The chemical nature of the precursor, together with the deposition conditions, can influence the crystalline structure of the formed sulfides. When using solutions of [$M(N_2H_4CS)_2Br_2$] complexes and a deposition temperature of 400 °C, the formation of solid solutions of wurtzite structure $Cd_xZn_{1-x}S$ with unlimited solubility occurs [8].

The mechanism of new phase formation can have a significant impact on the subsequent growth of the film and its structure. In previous studies, the discontinuous nature of the film growth of metal chalcogenides by using the method of aerosol pyrolysis was revealed [9, 11]. The particle formation of $Cd_xZn_{1-x}S$ is as follows. The pyrolysis of aerosol on a heated substrate formed nanoparticle phase sulfides and they were fixed on the surface of the glass-ceramic. Further growth of the film occurs due to the stretching possibilities of the fragments M–S released in the process of thermal decomposition of the complexes and interacts with the sulfide, which is formed on the active center of the substrate. The impact of continuous flow aerosol leads to the enlargement of nanoparticles in the islets, which create a mesh-like structure permeated with pores and channels. The surface roughness on the substrate reduces the nucleation barrier and allow the film structure to crystallize in different directions before the final stage at which the growth rate decreases and usually eventually stops ("the effect of growth saturation") and that can be associated with aerosolized sulfide [9, 11].

Fig. 1 shows the surface scans, obtained by mapping the phase and density histograms of the distribution of surface heights within the scanned area obtained during the topographical measurement by AFM, showing the surface morphology of the films CdS, $Cd_{0.5}Zn_{0.5}S$ and ZnS. The scanning area was 1×1 μm^2.

An analysis of AFM images showed that the growth of the investigated films is accompanied by the development of surface topography in the form of densely packed grains with distinct boundaries. In the studied areas, recorded elements (units) are rounded, formed by sulfide nanoparticles, which spread in different directions to completely cover the surface of the substrate. As can be seen from Fig. 1(a,c,e), the surface of the films formed by the components have average sizes of 40–80 nm.

With the transition from cadmium sulfide to zinc sulfide there is a change of the surface topography and the average size of nanoparticle aggregates. Thus, the average size of the elements on the surface of the CdS films is 35–60 nm, $Cd_{0.5}Zn_{0.5}S$ 60–80 nm, and for samples of ZnS they are observed in larger aggregates with an average size of 70–90 nm. Thus, there is a gradual enlargement of cells on the surface of the films with increasing content of zinc sulfide. This may be due to the following reasons. In the formation of solid solutions of $Cd_xZn_{1-x}S$ the substitution of cadmium atoms in smaller atoms of zinc (rZn = 0.125 nm; rCd = 0.141 nm [12]) leads to a deformation distortion and compression of the crystal lattice of the resulting sulfide. Perhaps this, in turn, contributes to the merging of closely spaced crystallites and generally leads to the enlargement of the cells on the surface of the films, similar in composition to ZnS. It is also possible the influence of the amorphous crystal structure of zinc sulfide [13].

Density histograms for the distribution of surface elevation values (Fig. 1(b,d,f)) show that the height of the largest number of particles within the scanned area is increased from 18–25 to 35–50 nm for films of CdS and ZnS, respectively. For these samples, the average roughness values change from 2.43 (ZnS) to 8.61 (CdS) nm and RMS roughness from 4.12 (ZnS) to 8.26 (CdS) nm. The graphic dependence is shown in Fig. 2. An analysis of the roughness parameters for all the membranes of the ZnS–CdS system showed that equimolar composition can be observed for the minimum values of Ra and Rq, which are 2.30 and 3.02 nm respectively. The obtained results allow us to conclude that film compositions close to zinc sulfide have less deviation of the roughness profile relative to the mean plane (Ra). A similar dependence is characteristic for the standard deviation of the surface profile relative to the baseline. For the composition $Cd_{0.5}Zn_{0.5}S$, the minimum values of the main parameters were noted. This can be explained by the formation of a uniform crystal lattice during the formation of solid solutions of substitution by cadmium and zinc ions as the film coating is formed. Because of this, the effect of a smooth surface is created.

Electron microscopic study of the surface morphology of the synthesized $Cd_xZn_{1-x}S$ films showed that they are uniform and continuous, and their thickness is 500–1000 nm. As an example, Fig. 3 shows electron microscopic image obtained by the SEM in the study of the cleavage of cadmium sulfide films.

4. Conclusion

The study of the surface morphology of films of $Cd_xZn_{1-x}S$ using atomic force microscopy revealed a highly developed surface of deposited layers of the terrain which has a height difference of 50 nm. The average size of aggregates formed by nanoparticles of the corresponding sulfide is 35–60 nm and 70–90 nm for films of CdS and ZnS, respectively. Visually, the sample has a surface which contains terrain drops: the pronounced depression and localized point of the hill. The microheterogeneity of the surface topography of films of $Cd_xZn_{1-x}S$ ($0.5\leq x\leq1$) is smooth, and the layers are smoother. With increased zinc sulfide content in the studied samples there is a change of the microrelief of their surface by consolidation of the particles. The thickness of the layers that was determined by SEM to be 500–1000 nm.

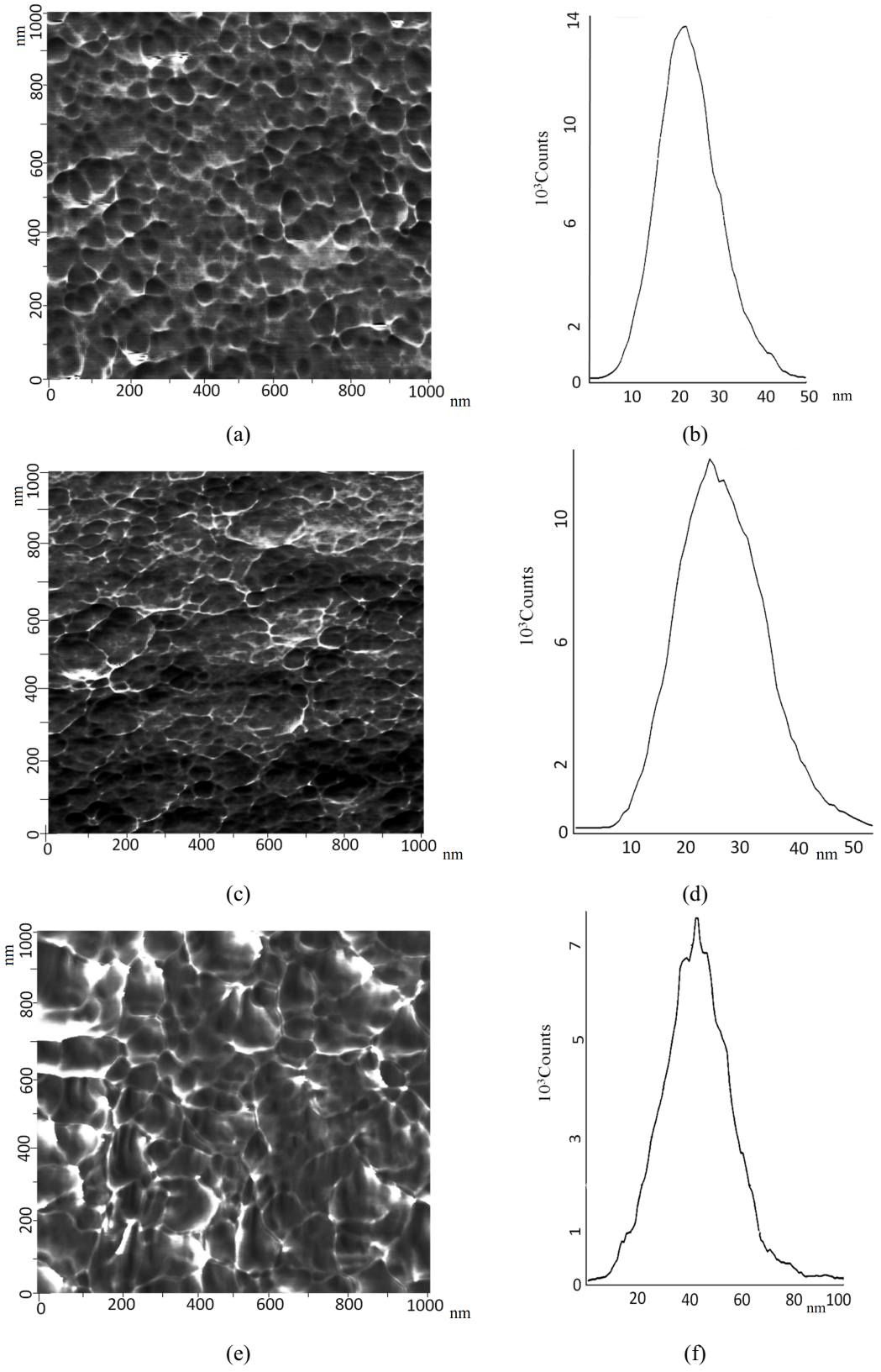

FIG. 1. AFM scans of the surface mode of phase contrast (a,c,e) and density histograms of distribution of values of surface elevation (b,d,f) films of CdS (a,b), $Cd_{0.5}Zn_{0.5}S$ (c,d) and ZnS (e,f)

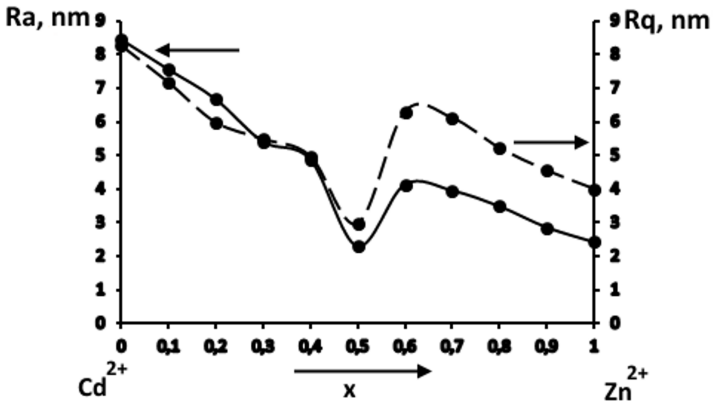

FIG. 2. The average and quadratic mean roughness, depending on the quantitative composition of the $Cd_xZn_{1-x}S$ films

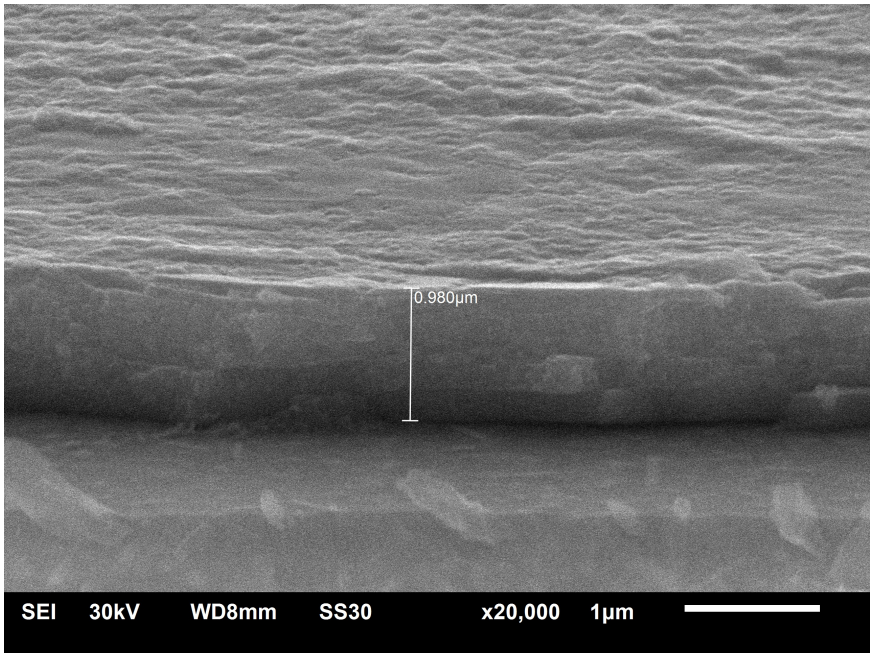

FIG. 3. Micrograph of the surface of the films of CdS

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