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Chemical composition, morphology and optical properties of zinc sulfide coatings deposited by low-energy electron beam evaporation

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ABSTRACT

The research determines the features of formation, morphology, chemical composition and optical properties of the coatings deposited by the method, proposed for the first time, of the exposure of mechanical mixture of zinc and sulfur powders to low-energy electron beam evaporation. The findings show that the deposited coatings are characterized by high chemical and structural homogeneity in thickness. The study considers the influence of substrate temperature and thickness of the deposited layer on the morphology and the width of the formed ZnS thin layers band gap. Also was shown the possibility to form ZnS coatings with this method using the mixture of zinc and copper sulfide powders.

1. Introduction

Zinc sulfide coatings are widely used as functional elements for different technical application: electroluminescent displays, electro-optical and sensory devices, antireflection coatings, etc. [1–3]. This wide application is directly related to the remarkable optical, electrophysical and chemical properties of zinc sulfide. It has high refractive index and transmittance in the visible range, and it is a wide band gap semiconductor material with band gap energy of 3.72 and 3.77 eV, depending on types of crystal structure cubic zinc blende and hexagonal wurtzite respectively. Last time, ZnS attracts much attention as material on the basis of which it is possible to synthesize unique ZnS nanostructures different in their shapes, including thin films [2].

Their formation can be produced by different methods: thermal evaporation in ultrahigh vacuum [4], close-space sublimation (CSS) [5], chemical vapor deposition [6], RF magnetron sputtering, pulsed laser deposition, electron beam evaporation [7], molecular beam chemical bath deposition [8], pulsed electrochemical deposition [9], sol–gel [10] and spray pyrolysis [11].

Most methods provide current high temperature (>200 °C) of the substrate during deposition, or realization of a high-temperature annealing of the deposited layer [4–11]. It is necessary to equalize the concentrations of the components in the coating and to obtain the desired structure. When using ion sputtering systems, the substrate is situated near the target in the area of intensive exposure to high-energy plasma components [12]. These limitations do not allow applying the coatings on the finished product as well as on the products with low melting point, in particular, on those based on macromolecular compounds. In this context, the particular interest is given to the development of coating deposition methods based on ZnS without these limitations.

2. Experimental

The coatings were deposited from the active gas phase generated by electron-beam dispersion of the powder mixture of sulphur and zinc or sulphur, zinc and copper. The electron-beam generator with filamentary cathode which allows to form beams with current density $j = 0.01–0.03$ A/cm^2, energy $E = 0.8–1.6$ keV is used as the electron source. Such low-energy electron guns are used while obtained polymer-based coatings in vacuum [13,14]. These evaporators cannot be used for forming coatings on the basis of metal, oxides and other chemical compounds of metals, as they are not able to generate high temperature in the beamed area. The deposition process of coatings was produced at initial pressure of residual gases in the vacuum chamber $\approx 4 \times 10^{-3}$ Pa.

The zinc (<150 μm, 99.995% trace metals basis; Aldrich) and sulfur (sulfur, ≥99.5%; Aldrich) powders were used as target material. The formation of the coating on zinc and sulfur was produced with the mixture of the powders in molar correlation 1:1. In some cases the copper powder (copper powder, <425 μm, 99.5% trace metals

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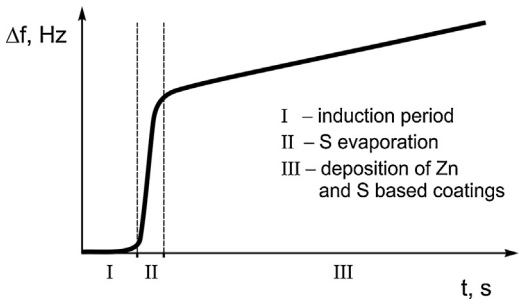

Fig. 1. Evaporation kinetics of sulfur and zinc powders mixture.

basis; Aldrich) (5%, 7%, 10%, 15% in correlation on the initial mixture weight) was introduced into the mixture of zinc and sulfur powders (molar correlation was 1:1) in order to change the stoichiometry of coatings. The targets were made as a result of thorough mixing of powers made with vibrating ball mill.

The thicknesses of deposited layers that were less than 350 nm and the growth speed during the deposition process were controlled by the quartz crystal microbalance (QCM).

The substrates were quartz plates (for spectroscopic measurements in visible area) and silicon (1 0 0) substrates (for microscopic measurements). The deposition of coatings was produced by using as shutter on the substrates with the surface temperature of 25 and 250 °C. It should be mentioned that at high heating temperature of the substrate surface there is no deposition of sulfur coating. The air is added into the chamber only when the temperature of the heated substrate decreases till 50 °C.

The cross-section morphology and the depth profile of ZnS layers were observed by scanning electron microscopy (SEM, Quanta 200F) with EDAX Microanalysis and Auger electron spectroscopy (AES, Perkin Elmer PHI-660) with Ar-ion energy of 3 keV. The surface morphology of films was studied by AFM using the multimode scanning microscope Solver-PRO (NT-MDT) that was operated in the tapping mode. The NSG 10 series silicon cantilever with rigidity of 11.5 N/m and tip radius of less than 10 nm was applied. The morphology of the products was characterized using the transmission electron microscope (TEM) JEM 2100 (Jeol). During TEM investigation were used substrates with a special carbon-coated Cu grid.

The crystal structure of the products was examined with Bruker D8 Advanced X-ray powder diffractometer (XRD) using Cu Kα as characteristic radiation (λ = 1.54056 Å), 40 kV, 40 mA). XPS was performed with PHI Quantera II Scanning XPS Microprobe spectrometer with the base pressure of 1×10^{-10} Torr using monochromatized Al(Kα) X-rays, at $h\nu$ = 1486.6 eV.

The spectroscopic research was done with UV–vis spectrophotometer Cary-50 (Varian). The value of the band gap (E_g) was calculated on the basis of the optical absorption spectra using linear part extrapolation of the spectral dependence of the absorption coefficient square $\alpha^2 \sim f(h\nu)$ on the axis of the photon energy [15,16].

3. Results and discussion

3.1. The coatings deposited by electron-beam evaporation of sulfur and zinc

It is found that electron-beam evaporation of sulfur and zinc powder mixture has a number of kinetic features. The melting of sulfur is observed at the first step of electron beam influence on the mixture of the powders in the crucible after some breakdown time and it is accompanied by its intense transition into the gas phase (Fig. 1, stage I). The intense growth of deposition speed is stated at this stage (Fig. 1, stage II). Further (Fig. 1, stage III), when boiling is finished in the area adjacent to the crucible, we observe intense pink glow. At this stage, according to the results of the X-ray structure analysis of the crucible material, there is no unbound sulfur. The deposition of the coating on the substrate is made with persistent glow. At stage III, the deposition speed considerably decreases, stabilizes and on the average it is around 0.12 nm/s.

The electron heating of powders mixture with subsequent melting of sulfur can initiate the formation of ZnS chemical compound. The energy released in chemical interaction of zinc and sulfur, is sufficient to convert generating ZnS compound into the gas phase with subsequent formation of the coating. Thus, in our opinion, the formation of zinc sulfide does not happen on the substrate, as for the majority of vacuum deposition methods [5,17], but during the formation of the gas phase.

It is established that the introduced method allows forming quite continuous, densely packed and pinhole-free coatings which have the grain texture in the boundary layers near the substrate (Fig. 2).

The analysis of absorption spectra of the formed coatings shows that the substrate temperature does not have any considerable influence on the value of the band gap (Fig. 3), the value of which is determined by the chemical composition, grains size that form the coating [5,11,18]. For the coatings with 330 and 230 nm thickness, the value of E_g is 3.58 and 3.54 eV, respectively. It should be mentioned that when the coatings are formed by thermal evaporation of zinc sulfide in vacuum, or by chemical bath deposition technique using an aqueous solution and other methods, we observe, as a rule, the high influence of thermal treatment on the width of the forbidden area. It can be explained by the formation of the defect structure

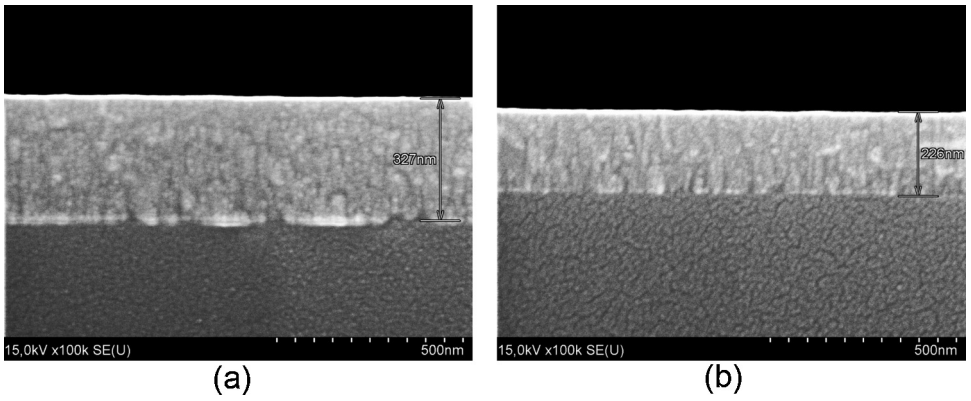

Fig. 2. Cross-section SEM images of ZnS coatings, thickness of 330 nm (a) and 230 nm (b).