Investigation the structures ZnS/HgS, HgS/ZnS

Martyn Sozanskyi[1], Pavlo Shapoval[1], Yosyp Yatchyshyn[1], Vitaliy Stadnik[1], Ruslana Chaykivska[2], Ruslana Guminilovych[1]

[1]Analytical Chemistry Department, Lviv Pol ytechnic National University, UKRAI NE, Lviv, S. Bandera Street 12, E-mail: sozanskyi.m@gmail.com

[2]Department of Technology of Organic Materials, Lviv Polytechnic National University, UKRAI NE, Lviv, St. Yura square 2, E-mail: Ruslana.chaikivska.xt.2013@lpnu.ua

Abstract – The process of synthesis ZnS and HgS thin films by a chemical bath deposition method (CBD) has been investigated. The phase composition, optical transmission, absorption spectra, surface morphology of films and structures based on ZnS and HgS films have been studied.

Key words – semiconductor films, chemical bath deposition, structure and morphology of thin films.

I. Introduction

Zinc sulfide (ZnS) films are important semiconducting materials with a wide-bandgap and n-type conductivity. They are promising for use in optoelectronic devices, such as photovoltaic cells, electroluminescent devices and solar cells [1]. Mercury sulfide (HgS) films have been used in solid-state solar cells, photoelectrochemical 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].

Development of ZnS/HgS heterostructures with different morphologies will provide new possibilities for wave function engineering and in tailoring optical and optoelectronic properties of semiconductor structures.

II. Experimental

The obtaining of ZnS and HgS semiconductor films is carried out by many methods. Technologically convenient way to their obtaining is the method of chemical bath deposition (CBD) [1]. Compared with the other it allows to pursue the deposition at temperatures below 100 °C on the large-sized substrates of different nature and use different combinations of starting substances.

The deposition of thin films of zinc sulfide (ZnS) was conducted with the initial working solution which consisted of zinc chloride ($ZnCl_2$), trisodium citrate ($Na_3C_6H_5O_7$), thiourea $CS(NH_2)_2$ and ammonium hydroxide (NH_4OH). The working solution which consisted of mercury nitrate ($Hg(NO_3)_2$), trisodium citrate and thiourea was used for the deposition of mercury sulphide thin films (HgS). The concentration of the solutions of zinc chloride was equal to 1.0 M; trisodium citrate – 0.5 M; .thiourea – 1.0 M; ammonium hydroxide – 14.28 M. Only freshly prepared reagents entered the working solutions for CBD of ZnS and HgS thin films. The deposition time was 80 min and the temperature 70°C for the ZnS films, 10 min and 80°C for the HgS films. The deposition has carried out on pre-prepared and thermostated glass substrates with an area of 3.24 cm^2. After the end of the reaction 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.

The investigation of surface morphology of the films was carried out using a raster electron microscope REM-106Y equipped with a system for microanalysis. Absorption-transmittance optical spectra of ZnS and HgS films and structures ZnS/HgS, HgS/ZnS on their base were obtained with a spectrophotometer Lambda 25 (Perkin-Elmer). A comparative signal was passed through glass substrates identical to the substrates, used for the investigated films. The phase composition of the ZnS and HgS films and ZnS/HgS and HgS/ZnS structures was investigated by X-ray powder diffraction (diffractometer DRON-3.0, CuKα-radiation). Primary processing of the experimental diffraction data in order to identify the phases was made using the PowderCell program [4]. Optimum exposure for each of the samples was selected.

III. Results and discussion

The structural analysis of ZnS and HgS films on glass substrates has been held. Peaks that corresponded to the cubic phase of ZnS (sphalerite) and hexagonal phase of HgS (Fig. 1 and Fig. 2) on all diffractograms can be identified. The lines of theoretical diffractograms of phases, mentioned above are shown for comparison.

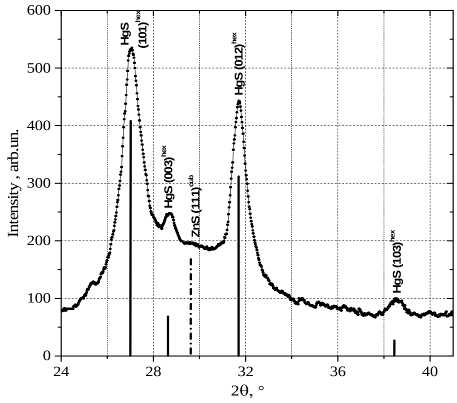

Fig. 1. X-ray diffractogram of ZnS/HgS structure

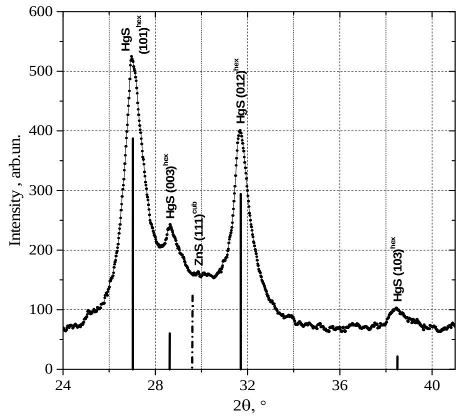

Fig. 2. X-ray diffractogram of HgS/ZnS structure

The optical transmission spectra T(λ) of ZnS/HgS and HgS/ZnS structures were investigated for wavelengths from 200 to 1000 nm (Fig. 3). A rapid increase of the light transmission can be seen at wavelengths 300 nm and. 350 nm, 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/HgS and HgS/ZnS structures in $(\alpha \cdot h\nu)^2$ vs. hν coordinates allow determining the fundamental absorption edges. The optical band gaps of the films are 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 [5-7].

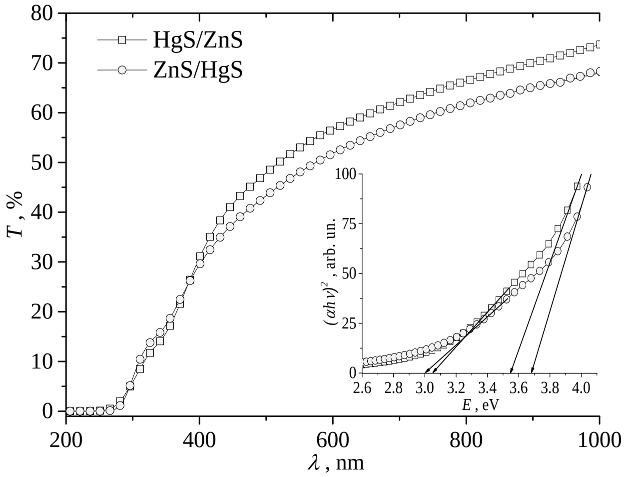

Fig. 3. The spectral dependences of optical transmission of ZnS and HgS films in the ZnS/HgS and HgS/ZnS structures.

Investigation of structures surface morphology (Fig. 4 and Fig. 5) showed that the previous layer of film is completely covered by the top layer, with small amounts of surface defects.

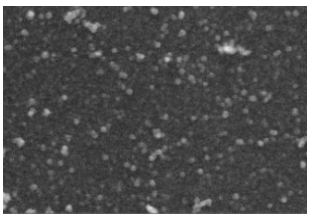

Fig. 4. Surface morphology of the ZnS/HgS structure

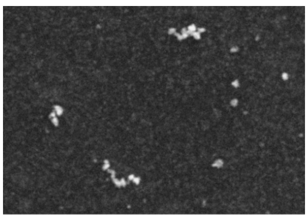

Fig. 5. Surface morphology of the HgS/ZnS structure

On the surface of ZnS/HgS structure there are seen the formation of microcrystals of zinc sulfide. The microanalysis of the surface of the ZnS and HgS films 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 structures shows that they consist of approximately of half of sulfur atoms and of half of a mixture of zinc and mercury atoms. It can be seen that the content of zinc atoms in the HgS/ZnS structure is considerably lower than in the ZnS/HgS structure, despite the fact that each layer of zinc sulfide and mercury sulfide in the structures was synthesized under the same conditions.

Conclusion

The ZnS and HgS thin films were synthesized by the chemical bath deposition method. The possibility of creating a double layer structure 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, surface morphology of ZnS/HgS, HgS/ZnS structures were investigated. According to the results of microanalysis the elemental composition of ZnS, HgS films and of ZnS/HgS, HgS/ZnS structures were studied. The positive research results of obtained ZnS/HgS and HgS/ZnS double layers allows assuming that the chemical bath deposition method can be used to produce not only double structures, but also multilayer coatings and heterocomposites [8].

References

[1] Pawar S. M Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films / S. M. Pawar, B. S. Pawar, J. H. Kim et. all// Curr. Appl. Phys., vol. 11(2), pp.117-161, 2011.

[2] Patil R.S. Successive ionic layer adsorption and reaction (SILAR) trend for nanocrystalline mercury sulfide thin films growth / R.S. Patil, C.D. Lokhande, R.S. Mane et. all // Mater. Sci. Eng., vol. B 129(1), pp. 59-63, 2006.

[3] Meyers M. A. Mechanical properties of nanocrystalline materials / M. A. Meyers, A. Mishra, D. J. Benson // Prog. Mater. Sci., vol. 51(4), pp.427-556, 2006.

[4] W. Kraus, G. Nolze PowderCell for Windows (version 2.4). – Berlin: Federal Institute for Materials Research and Testing, March 2000.

[5] Cheng J. Chemical bath deposition of crystalline ZnS thin films / J. Cheng, D. Fan, H. Wang et. all // Semicond. Sci. Technol., vol 18(7), pp.676-679, 2003.

[6] Shin S.W. Effect of different annealing conditions on the properties of chemically deposited ZnS thin films on ITO coated glass substrates / S.W. Shin, S.R Kang, J.H. Yun et. all // Sol. Energy Mater. Sol. Cells., vol. 95(3), pp.856-863, 2011.

[7] M. Z. Najdoski Chemical bath deposition of mercury(II) sulfide thin layers / M. Z. Najdoski, I. S. Grozdanov, S.K. Deyband // J. Mater. Chem., vol. 8(10), pp.2213-2215, 1998.

[8] G. Decher, J. B. Schlenoff, Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials. – Wiley-VCH Verlag, Weinheim 1088 p., 2012.