$Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ Thin Films Solid Solutions

Martyn Sozanskyi, Vitalii Stadnik, Ruslana Guminilovych, Pavlo Shapoval, Marta Laruk, Yosyp Yatchyshyn

Department of Physical, Analytical and General Chemistry, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandera Street 12, E-mail: martyn.a.sozanskyi@lpnu.ua

Abstract – The process of synthesis of cadmium-zinc sulfide ($Cd_xZn_{1-x}S$) and cadmium-mercury selenide ($Cd_xHg_{1-x}Se$) thin films solid solutions by a chemical bath deposition method with using complexing agents of tri-sodium citrate and sodium thiosulfate, respectively, has been investigated. The phase composition, transmittion spectra, optical band gaps and surface morphology of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films were studied.

Keywords – zinc sulfide, cadmium sulfide, cadmium selenide, mercury selenide, substitutional solid solution, semiconductor films, chemical bath deposition, optical band gap.

Introduction

Cadmium-zinc sulfide ($Cd_xZn_{1-x}S$) and cadmium-mercury selenide ($Cd_xHg_{1-x}Se$) thin films solid solutions belongs to $A^{II}B^{VI}$ group materials. The reason for using film solid solutions is the ability to adapt its semiconductor properties between values that correspond to pure binary ones. This fact allows to adapt the material properties to the electronic devices. In recent years, several papers have appeared on the synthesis of these compounds [1-5].

Experimental

The obtaining of $A^{II}B^{VI}$ semiconductor films is carried out by many methods. Technologically convenient way to their obtaining is by the method of chemical bath deposition (CBD) [3]. Compared with the other it allows to pursue the deposition at temperatures below 100 °C on large-sized substrates and use different combinations of starting components.

The CBD of solid solution thin films of $Cd_xZn_{1-x}S$ was conducted with the initial working solution, which was based on [6] with addition of cadmium-containing salt. It consisted of zinc cloride ($ZnCl_2$), cadmium cloride ($CdCl_2$), complexing agent, thiourea ($(NH_2)_2CS$) and pH-regulator. As comlexing agent for zinc and cadmium was used a tri-sodium citrate ($Na_3C_6H_5O_7$); the pH-regulator – ammonium hydroxide (NH_4OH). The concentration of the $ZnCl_2$ in the working solution was equal to 0.08 M; $CdCl_2$ – 0.004 M; $Na_3C_6H_5O_7$ – 0.08 M; $(NH_2)_2CS$ – 0.25 M; NH_4OH – 0.10 M.

The CBD of solid solution thin films of $Cd_xHg_{1-x}Se$ was conducted with the initial working solution, which was based on [7] with addition of cadmium-containing salt. It consisted of mercury nitrate ($Hg(NO_3)_2$), cadmium nitrate ($Cd(NO_3)_2$), complexing agent, sodium selenosulphate (Na_2SeSO_3) and pH-regulator. As comlexing agent for cadmium and mercury was used sodium thiosulfate ($Na_2S_2O_3$); the pH-regulator – tri-sodium citrate ($Na_3C_6H_5O_7$). The concentration of the $Hg(NO_3)_2$ in the working solution was equal to 0.005 M; $Cd(NO_3)_2$ – 0.05 M; $Na_2S_2O_3$ – 1.0 M; Na_2SeSO_3 – 0.05 M; $Na_3C_6H_5O_7$ – 1.0 M.

Only freshly prepared reagents entered the working solutions for synthesis of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films. The deposition duration and temperature of $Cd_xZn_{1-x}S$ films, was 80 min and 70°C and for $Cd_xHg_{1-x}Se$ – 180 min and 20°C. The chemical deposition has carried out on pre-prepared glass substrates with an area of 3.24 cm^2. After the end of the reaction the substrates were eliminated; the surface was cleaned with a distilled water to take off the remains of working solution and dried in air.

The phase composition of the $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films solid solutions was investigated by X-ray powder diffraction (diffractometer DRON-3.0, Cu$K\alpha^-$ radiation). Primary processing of the experimental diffraction data in order to identify the phases was made using the PowderCell program [8]. Optimum exposure for each of the samples was selected.

Absorption optical spectra of the $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films were obtained with a spectrophotometer XION 500 (Dr.Lange). A comparative signal was passed through glass substrates identical to the substrates, used for investigated films.

The investigation of surface morphology of the films samples was carried out using a raster electron microscope REM-106Y. Elemental analysis of films was carried out on an X-ray fluorescence (XRF) spectrometer ElvaX Light SDD (Elvatech).

Results and discussion

The X-ray analysis of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films has been held. It showed that films are substitutional solid solutions. Peaks that corresponded to the cubic phase of zincblende (sphalerite) structure (Fig. 1) can be identified on diffractograms. The lines of theoretical diffractograms of cubic ZnS, CdS, CdSe and HgSe phases are shown for comparison.

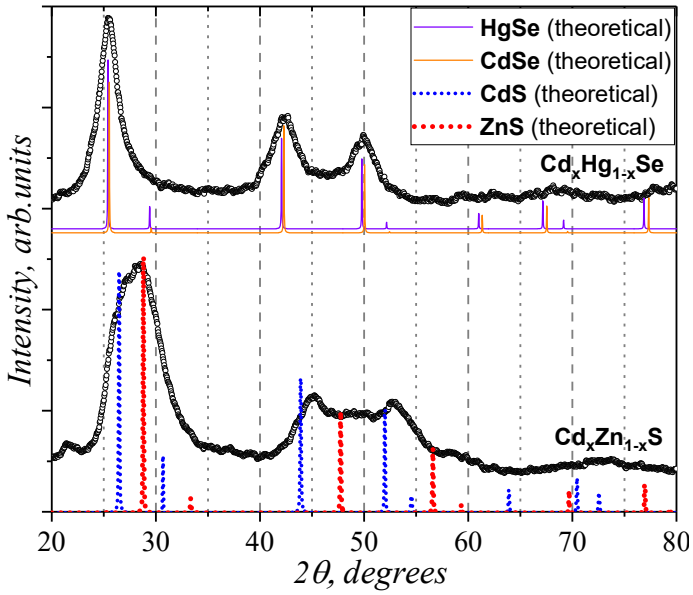

Fig. 1. X-ray diffractograms of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films

The optical absorbtion spectra $A(\lambda)$ of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films solid solutions were investigated for wavelengths from 340 to 900 nm (Fig. 2). The $Cd_xZn_{1-x}S$ film, has the biggest light transmition. It has sharp increasing at ~400-450 nm region. The same of $Cd_xHg_{1-x}Se$ film was observed ~600-700 nm region. The spectral dependences in $(\alpha \cdot h\nu)^2$ vs. $h\nu$ coordinates allow determining the fundamental absorption edges. The optical band gaps of the $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films are localized in the ranges 2.72 eV and 1.86 eV, respectivelly. These values are close to the literary data [9-13].

Investigation of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films surface morphology at x5000 magnification (Fig. 3) showed that the films are homogeneous and solid, with small amounts of surface defects.

The microanalysis of the surface $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films shows nearly stoichiometric atomic ratios of metals to chalcogens with a slight excess of Cd and Zn atoms (in the case of $Cd_xZn_{1-x}S$ films) or a slight excess of Se atoms (in the case of $Cd_xHg_{1-x}Se$ films).

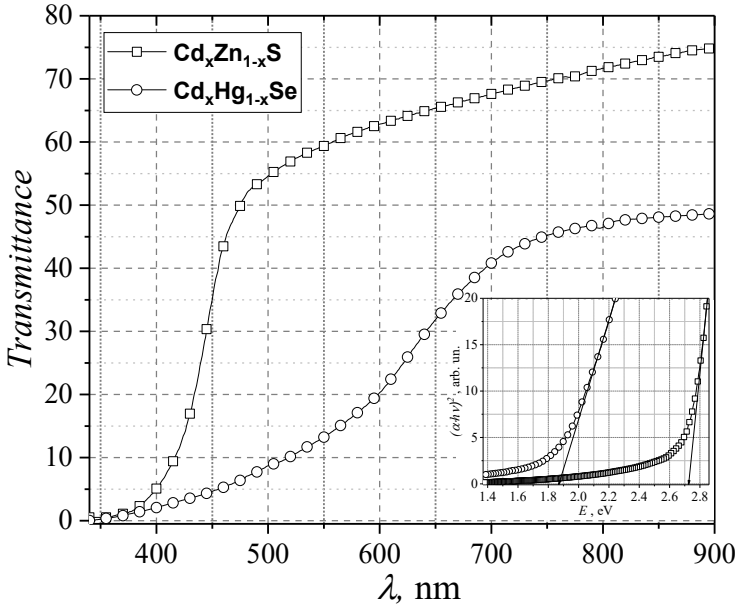

Fig. 2. The spectral dependences of optical absorbtion of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films (inset – $(\alpha \cdot h\nu)^2$ vs. $h\nu$ dependense)

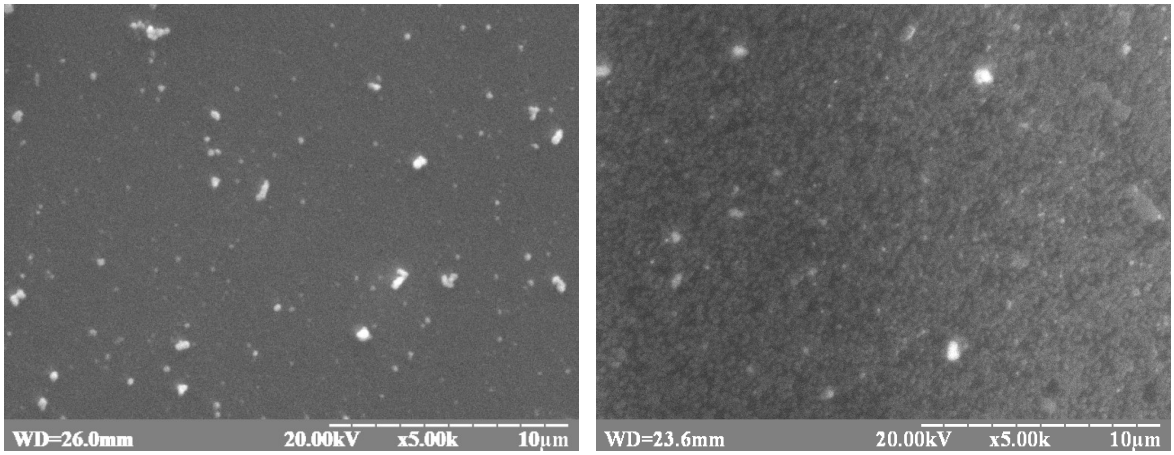

Fig. 3. Surface morphology of $Cd_xZn_{1-x}S$ (left) and $Cd_xHg_{1-x}Se$ (right) films

Table 1

Results of microanalysis of thin films solid solutions

Film	Component	Weight %	Atomic %
$Cd_xZn_{1-x}S$	Cd	60.62	35.35
	Zn	15.20	15.24
	S	24.18	49.43
$Cd_xHg_{1-x}Se$	Cd	25.96	25.01
	Hg	31.95	17.25
	Se	42.09	57.74

Conclusion

The $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ thin films solid solutions were synthesized by the CBD method. For this, the tri-sodium citrate or sodium thiosulfate, have been used for complexation of cadmium and zinc or cadmium and mercury at the same time, respectively. The phase composition of obtained $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ samples was determined. The optical absorption spectra, surface morphology of $Cd_xZn_{1-x}S$ and $Cd_xHg_{1-x}Se$ films were investigated. According to the results of microanalysis the elemental composition of coatings were studied.

From the obtained data, the most suitable complexing reagent can be selected. The positive research results of obtained HgSe films allows to assuming that the chemical bath deposition method can be used to produce optical materials based on this coatings.

Acknowledgments

This research is under the project “Thin Film Semiconductor Materials for Photo Sensitive Solar Cells” (State Registration № 0117U004455).

References

[1] H. Yao, H. Shen, X. Zhu, J. Jiao, J. Li, W. Wang “Influence of Cd source concentration on photo-current response property of $Cd_xZn_{1-x}S$ film prepared by chemical bath deposition”, Ceram. Int., 2016, vol. 42, iss. 2A, pp. 2466-2471.

[2] R. Shrivastava, R.S. Singh, A.K. Singh “Optical Characterization of the (Cd-Zn)S:$CdCl_2$ Thin Film Deposited by CBD Method”, International Journal of Advancements in Research & Technology, 2013, vol. 2, iss. 9, pp. 152-158.

[3] I. Carreón-Moncada, L.A. González, M.I. Pech-Canul, R. Ramírez-Bon “$Cd_{1-x}Zn_xS$ thin films with low Zn content obtained by an ammonia-free chemical bath deposition process”, Thin Solid films, 2013, vol. 548, iss. 1, pp. 270-274.

[4] V.B. Pujari, L.P. Deshmukh “Photoelectrochemical Investigations on $Hg_xCd_{1-x}Se$ Thin Film Electrode/Electrolyte System”, Turkish Journal of Physics, 2008, vol. 32, pp. 105-114.

[5] V.M. Bhuse “Photo-electrochemical properties of $Cd_{1-x}Hg_xSe$ thin films”, Mater. Chem. Phys., 2007, vol. 106, iss. 2-3, pp. 250-255.

[6] M.A. Sozanskyi, P.I. Shapoval, I.I. Yatchyshyn, V.E. Stadnik, R.E. Gladyshevskii “Synthesis of ZnS thin films from aqueous caustic of trisodium citrate and their properties”, Odes’kyi Politechnichnyi Universytet. Pratsi, 2015, iss. 3, pp. 119-125.

[7] M.A. Sozanskyi, V.E. Stadnik, R.T. Chaykivska, P.Yo. Shapoval, Yo.Yo. Yatchyshyn, L.O. Vasylechko “The effect of different complexing agents on the properties of mercury selenide films deposited from aqueous solutions”, Voprosy khimii i khimicheskoi tekhnologii, 2018, vol. 119, iss 4, pp. 69-76.

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

[9] V.B. Pujari, D.J. Dhage, L.P. Deshmukh “n-$Hg_xCd_{1-x}Se$ thin film electrodes for photoelectrochemical applications”, Indian J. Eng. Mater. Sci., 2008, vol. 15, pp. 275-280.

[10] V.B. Pujari, S.H. Mane, V.S. Karande, J.S. Dargad, L.P. Deshmukh “Mercury–cadmium–selenide thin film layers: structural, microscopic and spectral response studies”, Mater. Chem. Phys., 2004, vol. 83, iss. 1, pp. 10-15.

[11] S. Azizi, H. Rezagholipour Dizaji, M.H. Ehsani “Structural and optical properties of $Cd_{1-x}Zn_xS$ (x = 0, 0.4, 0.8 and 1) thin films prepared using the precursor obtained from microwave irradiation processes”, Optik, 2016, vol. 127, iss. 18, pp. 7104-7114.

[12] C.O. Mosiori, W.N. Njoroge, J. Okumu “Electrical and optical characterization of $Cd_xZn_{1-x}S$ thin films deposited by chemical bath deposition in alkaline conditions”, Direct Res. J. Chem. Mater. Sci., 2014, vol. 2, iss. 1, pp. 13-20.

[13] X.J. Wang, Y.X. Chen “Preparation and characterisation of $Cd_xZn_{1-x}S$ thin films grown in chemical bath deposition”, Mater. Res. Innovations, 2015, vol. 19, iss. sup5, pp. S5-208-S5-211.