Cd_{2}Zn_{1-x}S and Cd_{2}Hg_{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_{x}Zn_{1-x}S) and cadmium-mercury selenide (Cd_{x}Hg_{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, transmission spectra, optical band gaps and surface morphology of Cd_{x}Zn_{1-x}S and Cd_{x}Hg_{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_{x}Zn_{1-x}S) and cadmium-mercury selenide (Cd_{x}Hg_{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_{x}Zn_{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 chloride (ZnCl_{2}), cadmium chloride (CdCl_{2}), complexing agent, thiourea ((NH_{2})_{2}CS) and pH-regulator. As complexing agent for zinc and cadmium was used a tri-sodium citrate (Na_{3}C_{6}H_{5}O_{7}); the pH-regulator – ammonium hydroxide (NH_{4}OH). The concentration of the ZnCl_{2} in the working solution was equal to 0.08 M; CdCl_{2} – 0.004 M; Na_{3}C_{6}H_{5}O_{7} – 0.08 M; (NH_{2})_{2}CS – 0.25 M; NH_{4}OH – 0.10 M.

The CBD of solid solution thin films of Cd_{x}Hg_{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_{2}SeSO_{3}) and pH-regulator. As complexing agent for cadmium and mercury was used sodium thiosulfate (Na_{2}S_{2}O_{3}); the pH-regulator – tri-sodium citrate (Na_{3}C_{6}H_{5}O_{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_{2}S_{2}O_{3} – 1.0 M; Na_{2}SeSO_{3} – 0.05 M; Na_{3}C_{6}H_{5}O_{7} – 1.0 M.

Only freshly prepared reagents entered the working solutions for synthesis of Cd_{x}Zn_{1-x}S and Cd_{x}Hg_{1-x}Se films. The deposition duration and temperature of Cd_{x}Zn_{1-x}S films, was 80 min and 70°C and for Cd_{x}Hg_{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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$Se films solid solutions was investigated by X-ray powder diffraction (diffractometer DRON-3.0, CuK$\alpha$ 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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$Se films](image)

The optical absorption spectra $A(\lambda)$ of Cd$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$Se films solid solutions were investigated for wavelengths from 340 to 900 nm (Fig. 2). The Cd$_x$Zn$_{1-x}$S film, has the biggest light transmission. It has sharp increasing at $\sim$400-450 nm region. The same of Cd$_x$Hg$_{1-x}$Se film was observed $\sim$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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$Se films are localized in the ranges 2.72 eV and 1.86 eV, respectively. These values are close to the literary data [9-13].

Investigation of Cd$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$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$_x$Zn$_{1-x}$S films) or a slight excess of Se atoms (in the case of Cd$_x$Hg$_{1-x}$Se films).
Fig. 2. The spectral dependences of optical absorption of Cd$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$Se films (inset – $(\alpha \cdot h\nu)^2$ vs. $h\nu$ dependensе)

Fig. 3. Surface morphology of Cd$_x$Zn$_{1-x}$S (left) and Cd$_x$Hg$_{1-x}$Se (right) films

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<td><strong>Results of microanalysis of thin films solid solutions</strong></td>
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**Conclusion**

The Cd$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$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$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$Se samples was determined. The optical absorption spectra, surface morphology of Cd$_x$Zn$_{1-x}$S and Cd$_x$Hg$_{1-x}$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.

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References

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