CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 7, No. 3, 2013 Chemical Technology

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THE CONDITIONS EFFECT OF OBTAINING CdS AND CdSe FILMS ON THEIR STRUCTURAL AND OPTICAL PROPERTIES

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Received: January 16, 2013 / Revised: April 06, 2013 / Accepted: May 31, 2013

Abstract. The conditions effect of obtaining CdS and CdSe thin films by a chemical surface deposition method (CSD) on their structural and optical properties has been studied. The optical transmission, absorption spectra and surface morphology of films and degree of phase uniformity were investigated. The content of cadmium ions in the obtained coatings by the method of voltammetry inversion was defined. The thickness of the obtained semiconductor films was calculated according to the mass of cadmium. The optimum conditions for obtaining CSD films of the given thickness with a minimum number of defects on the surface were established.

Keywords: semiconductor films, chemical surface deposition, structure, morphology.

1. Introduction

The films of cadmium chalcogenides Cd(S,Se,Te) as well as their heterostructures combinations are important semiconductor compounds. Due to their semiconducting properties such as a large band gap, photoconductivity, photovoltaic, photochemical and fluorescent properties, the ability to reflect the visible area of the spectrum of radiation and to absorb in the ultraviolet region, as well as small coefficient of linear expansion they are widely used in the production of highly efficient solar cells, semiconductor lasers, photoresists, X-ray detectors, phosphors.

The structure of the films is different from the structure of the surrounding material with similar composition and can vary depending on the obtaining conditions. The obtaining processes of epitaxial films are related with the interaction of atoms of the deposited compound with the substrate surface. The complex processes that take place on the phase boundary have the effect on the mechanism of films deposition, their adhesion to the substrate, the character of nucleation and growth of the film. The structure of the films determines their properties.

The presence of interconnection between the compositional, morphological, optical and electrical properties, structure and microstructure of semiconductor films determines the dependence of their properties on the obtaining method and the deposition process parameters. The establishment of such regularities has created the prerequisites to the managed synthesis of semiconductor epitaxial films with the desired properties.

The chemical surface deposition (CSD) is the technologically convenient method of obtaining films of cadmium chalcogenides [1]. The using of different combinations of source materials and carrying out of deposition on large size substrates with different nature at temperatures below 373 K allows this method to be compared with other methods [2-6].

In order to select the optimal conditions for epitaxial growth of films researches of the effect of CSD parameters on the morphology, structural and optical properties of CdS and CdSe films were conducted. The results of these studies are present in this work.

2. Experimental

The deposition of thin films of cadmium sulfide (CdS) was conducted with the initial working solution which consisted of cadmium chloride $CdCl_2$, thiourea $CS(NH_2)_2$ and 14.28 M solution of the ammonium hydroxide NH_4OH. The working solution which consisted of cadmium chloride $CdCl_2$ and sodium selenosulphate Na_2SeSO_3 was used for the deposition of cadmium selenide thin films (CdSe). Only freshly prepared reagents entered the working solutions for CSD of CdS and CdSe thin films.

Cadmium chloride has been the source of Cd^{2+} ions, thiourea – S^{2-} ions and sodium selenosulphate – Se^{2-} ions. Sodium selenosulphate was prepared by dissolving selenium powder in the aqueous solution of sodium sulfite (Na_2SO_3) at 333 K under constant stirring for 3 h. After the end of the reaction the solution was cooled and filtered. The concentration of the solution cadmium chloride changed between 0.01 and 0.05 M; thiourea 0.15–1.5 M; sodium selenosulphate 0.1–0.4 M. The deposition time was from 3 to 12 min. The temperature varied from 323 to 363 K.

The deposition was carried out on pre-prepared and thermostated glass substrate area of 3.96 cm^2 in accordance with the technique [7, 8]. The dosed coating of the working solution ensured the uniform heating of the surface substrate and, therefore, the uniform deposition of films. The surface was washed with distilled water and dried in the air after heating the substrate film.

The research morphology of the film surface was investigated using the scanning electron microscope EVO-40XVP (Carl Zeiss, Germany) with a system of micro-analysis INCA Energy 350 (Oxford Instruments, England).

Optical absorption and transmission spectra of CdSe and CdS films were obtained using the spectrophotometers AvaSpec-ULS2048 (Avantes, Netherlands) and UV-3600 (Shimandzu, Japan). The comparative signal passed through a substrate which was identical with the substrate for the investigated films.

The samples were dissolved in a fixed volume of 0.2 M hydrochloric acid (HCl) and the content of Cd^{2+} ions was determined by inversion voltammetry (AKV-07 analyzer MK, Akvilon, Russia) for determining the amount of CdS and CdSe in the obtained films and calculating their thickness. The method based on the property of the analyzed element to accumulate electrochemically on the surface of the working electrode and to dissolve in the anodic or cathodic polarization characteristic for each element potential. The height or peak area of the element which was fixed on the voltamperohrama is proportional to its mass part in the solution. The film thickness was calculated without taking into account the roughness, using the mass part of the element, the area of the substrate and tabular data density of CdS and CdSe, in accordance with the technique [9].

3. Results and Discussion

The working substrate surface was coated with a continuous film with characteristic for CdS green-yellow and for CdSe red-orange color after completion of CSD. The spectral dependence of the optical transmission in the visible and close infrared region evidences the existence of CdS and CdSe compounds in all films.

The research results obtained by the methods of inversion voltammetry (determination content of cadmium in coatings), scanning electron microscopy (the surface morphology, the microanalysis of films) and spectrophotometry in the visible and close infrared region (optical transmission and absorption characteristics) were compared to investigate the interconnection between CSD parameters (concentration cadmium chloride, thiourea, sodium selenosulphate, temperature and time of deposition) and the properties of CdS and CdSe films.

Satisfactory reproducibility of the epitaxial layer thickness is possible only at a constant deposition rate, and for this it is necessary to maintain a constant concentration of initial materials and process temperature.

Changing of concentration initial salt which contains cadmium has different effect on the amount of deposited CdS and CdSe. When using the working solutions with low concentrations of $CdCl_2$ (0.01–0.02 M) the cadmium content in the produced films CdS and CdSe is practically the same (Fig. 1). Subsequent increasing of $CdCl_2$ concentration to 0.05 M leads to a linear increase in the cadmium content in the films of cadmium sulfide. For cadmium selenide films the increase of the salt concentration reduces cadmium content.

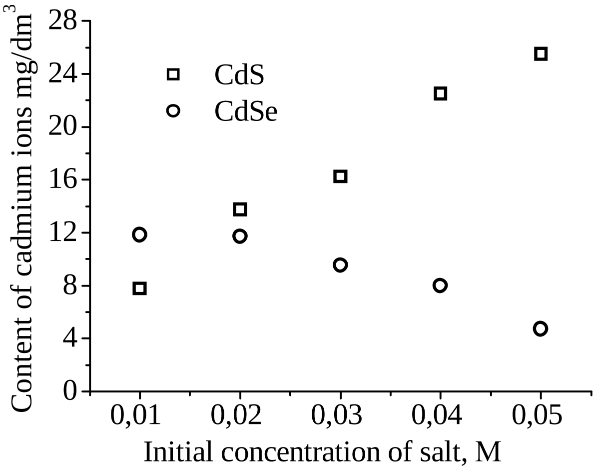
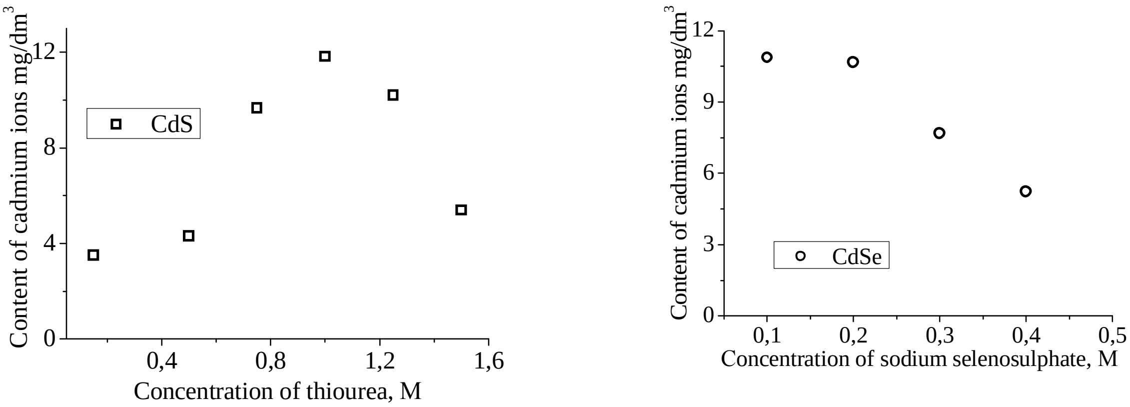


Fig. 1. Dependence of Cd^{2+} ions content on $CdCl_2$concentration at CSD of CdS and CdSe films. *C* ($CS(NH_2)_2$) = 1 M; *C* (Na_2SeSO_3) = 0.1 M; *T* = 343 K; the deposition time is 4x3 min.

Differences in Cd^{2+} content in the deposited films are observed at the concentration change of substances that generated S^{2-}ions and Se^{2-} ions in the working solution. At CSD of CdS films the minimum concentration of thiourea, in which during synthesis the coating being formed, was 0.15 M. At lower concentrations the coating was not formed. Maximum content of cadmium is achieved while using 1 M thiourea solution (Fig. 2a).

The maximum cadmium content is achieved by using the minimum (0.1–0.2 M) concentrations of sodium selenosulphate during deposition of CdSe films. Subsequent increasing of Na_2SeSO_3 concentration leads to a linear decrease of Cd^{2+} content in the deposited films (Fig. 2b).



a) b)

Fig. 2. Dependence of cadmium ions content on thiourea (a) and sodium selenosulphate (b) concentrations at CSD of CdS and CdSe films. *C* ($CdCl_2$) = 0.01–0.02 M; *T* = 343 K; the deposition time is 3 min.

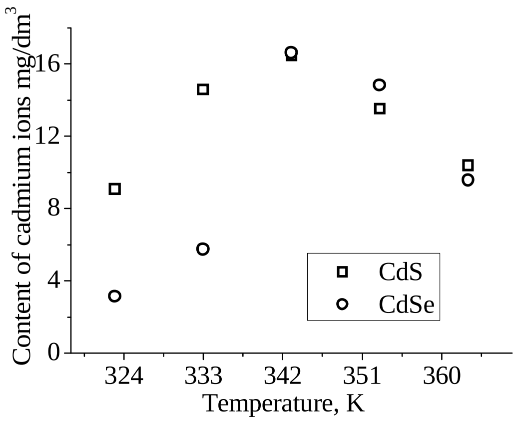
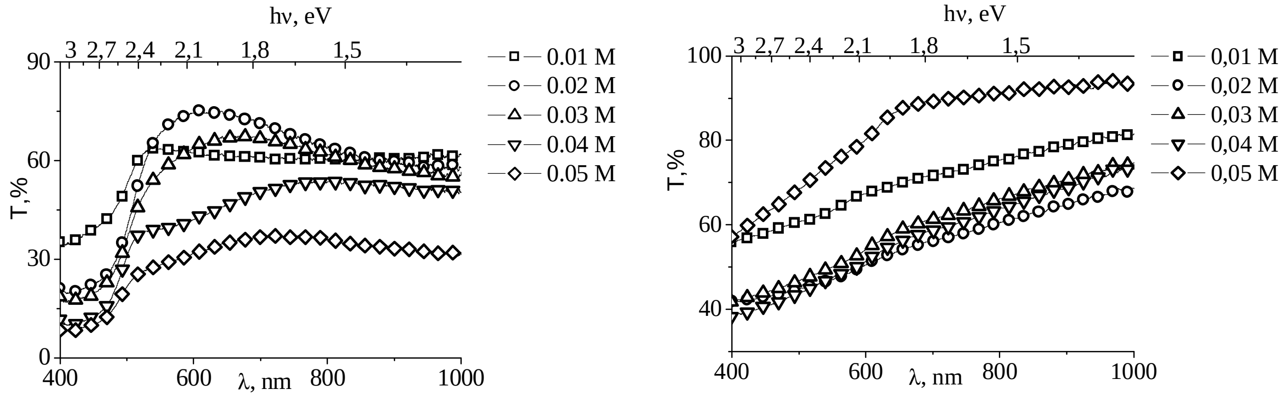


Fig. 3. Dependence of cadmium ions content on CSD temperature of CdS and CdSe films. *C* ($CdCl_2$) = 0.01 M; *C* ($CS(NH_2)_2$) = 1 M; *C* (Na_2SeSO_3) = 0.1 M; the deposition time is (4x3) min



a) b)

Fig. 4. The spectral dependence of CdS (a) and CdSe (b) films transmission on $CdCl_2$ concentration

Temperature dependences of CSD on the content of cadmium ions in the films of cadmium sulfide and cadmium selenide have the same character (Fig. 3). The minimum temperature of CdS and CdSe films formation in selected time intervals constituted 323 K. In the range of 323–333 K the cadmium content in the films of CdSe is twice less than in the films of CdS. The maximum content of cadmium ions is achieved at the CSD temperature of 343 K.

The spectral dependences of the absorption cadmium sulfide and cadmium selenide films in $(\alpha \cdot h\nu)^2/h\nu$ coordinates indicate the presence of the edge of fundamental absorption, which is localized in the region of 2.4 eV for CdS films, while for films CdSe – 1.8 eV that is in agreement with literature data [10, 11], respectively. Linear character of the dependence $(\alpha \cdot h\nu)^2 = f(h\nu)$ in the region of the absorption edge for all samples implies that this edge is formed by the direct optical interband transitions.

The influence of kinetic parameters of CSD on maximum transmission bandwidth and the nature of changes in the transition from short to longer wavelengths regions are different for CdS and CdSe films. These differences can be explained by different nature of the initial materials, by the composition and structures of the obtained films.

For CdS films (Fig. 4a) the increase in the initial salt concentration leads to a shift of the maximum transmission from short to longer wavelengths regions and the maximum 76 % was achieved using 0.02 M $CdCl_2$. The large absolute values of transmission (70–94 %) are characteristic for CdSe films (Fig. 4b). The maximum of the transmission is situated in the longer wavelength region, and applies only to the initial salt with a maximum concentration of 0.05 M; there has been an abrupt bandwidth increase in the transition from short to longer wavelength region.

Similar patterns were observed for the films obtained at different concentrations of thiourea and sodium selenosulphate (not shown here) and at different CSD temperatures. The maximum value of CdS and CdSe films transmission were obtained with 1 M $CS(NH_2)_2$ and 0.1 M Na_2SeSO_3, respectively, and CSD temperature of 343 K.

During the deposition of CdS all absorption curves are extrapolated completely straight, which indicates the absence of impurity and defect energy levels in the band gap and high quality semiconductor CdS films. For CdSe films the nature of the absorption change with no pronounced maximum in the transition from short to longer wavelength region can be explained by the presence of defects in the volume, the same as on the surface of the film which arise due to contamination of film impurities. Quantity of impurity depends on the nature of raw materials and deposition mechanism.

During heat transfer to the working solution the deposition is performed by heterogeneous nucleation compound on the substrate surface when using CSD. For the purpose of binding ions Cd^{2+} [12] while using the method of chemical bath deposition (CBD) CdS and CdSe films the complexing agent was added to the working solution. Both the reaction rate and the amount of deposited CdS and CdSe decrease, and the final film thickness increases as a result.

The deposition of CdS thin films from aqueous solutions occurs by heterogeneous mechanism through the stage of forming a complex ion cadmium tetraamine $[Cd(NH_3)_4]^{2+}$ [13], which reduces the overall rate of the reaction and prevents the formation of $Cd(OH)_2$. Ion formed reacts with tetraamine cadmium sulfide ions that are formed *via* thiourea hydrolysis:

$$Cd^{2+} + 4NH_4OH \rightarrow [Cd(NH_3)_4]^{2+} + 4H_2O$$

$$[Cd(NH_3)_4]^{2+} + S^{2-} \rightarrow CdS \downarrow + 4NH_3$$

In the general form:

$$[Cd(NH_3)_4]^{2+} + (NH_2)_2CS + OH^- \rightarrow$$
$$\rightarrow CdS \downarrow + 4NH_3 + H^+ + (NH_2)_2CO$$

The attempts of obtaining CdSe films by the CSD method according to the technique of obtaining CdS were not successful. Introduction of ammonium hydroxide to the working solution increased the minimum deposition time to 7 min at 363 K. Reduction of CSD temperature and accordingly the increase of the deposition time led to the formation of non-continuous surfaces and a large number of CdSe in the volume of the working solution So we abandoned the use of ammonia as a complexing agent and the working solution which consisted of $CdCl_2$ and Na_2SeSO_3 was used for the deposition of CdSe films. The working solution pH varied between 9.2–9.6 at changing the ratio of reagents.

The reaction between selenide (Se^{2-}) or hydroselenid (HSe^-) anions and cations Cd^{2+} occurs very fast due to the low solubility of CdSe. The decomposition of complex anion selenosulphates of Cd^{2+} in alkaline medium is the limiting stage of the CdSe deposition from the solution [12, 14].

$$2SeSO_3^{2-} + Cd^{2+} \rightarrow \left[Cd(SeSO_3)_2\right]^{2-}$$

$$\left[Cd(SeSO_3)_2\right]^{2-} + 2OH^- \rightarrow$$

$$\rightarrow CdSe \downarrow + SeSO_3^{2-} + SO_4^{2-} + H_2O$$

In the general form:

$$Cd^{2+} + SeSO_3^{2-} + 2OH^- \rightarrow CdSe \downarrow + SO_4^{2-} + H_2O$$

The processes deposition of sulphides and selenides films, which pass through the stage of forming coordination compounds, may have certain features that can be seen from the following reaction mechanisms. A variety of anions depending on the composition of the working solution can enter the inner sphere of the complex. The closest entourage of cadmium atoms can be sulfur, halogens and oxygen atoms. At the same time at thermal destruction the part of the Cd-Hal or Cd-O bonds are preserved and $Hal_S^{\bullet}$, $Hal_{Se}^{\bullet}$ and $O_S^{\bullet}$, $O_{Se}^{\bullet}$ defects are formed in sulfide or selenide grid.

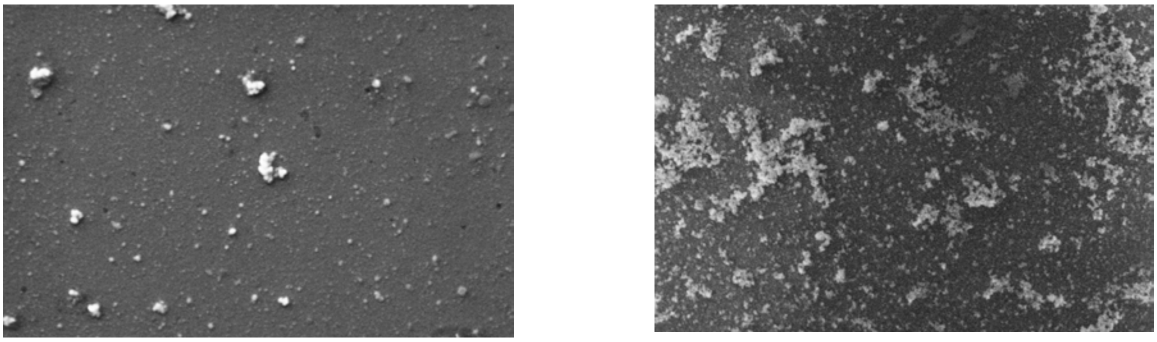
The investigation of films surface morphology by scanning electron microscopy and microanalysis system in the reflected-electron mode (qualitatively represents the surface composition) and the secondary-electron mode (represents the surface topography) confirm the presence of impurities and surface defects of the films. As seen from micrographs (Fig. 5) the CdS and CdSe films completely cover the substrate. The whole area is uniform and continuous. Comparison of figures in the reflected and secondary- electron modes (not shown here) has given the opportunity to make sure that the build-up of the heavy phase is on the surface of the film.

The quantity particles on the surface at deposited CdS films are less than at the deposition of CdSe films. The quantity of particles number grows with increasing concentration of thiourea and sodium selenosulphate, temperature and deposition time. Investigation results of the morphology and X-ray microanalysis of the films show that the formations on the surface are the particles of CdS and CdSe with stoichiometry other than in the film. In both cases the difference of stoichiometry of the particle and the film is due to the presence of sulfur (2.7 mas %). Such aggregates of colloidal particles are formed in the final stage of the deposition when the film formation is terminated as a result of the depletion of the boundary layer and becomes the dominant self-willed form of the deposit, which adsorbs onto the surface. The lower value by several orders of the CdSe product solubility, compared with CdS, leading to a rapid formation of the precipitate in the bulk was due to larger number of particles on selenide films.

The self-willed precipitate formation is undesirable for realization of controlled deposition. Based on pre-selected data of reactant ratio and temperature we have found that in order to reduce its effect on the properties of the films, the best time of one cycle of the deposition is 3 min. The multiple depositions to provide the necessary thickness of the films were used. The film thickness increases linearly with the number of deposition cycles (Fig. 6).

The continuous durable films with a smooth surface and good adhesion to the substrate were obtained (Fig. 7).

Almost the same deposition rate at the chosen CSD conditions is attained already after the first cycle when the function of the substrate performs the formed film. Consequently the growth rates following successively deposited layers are the same and the total film thickness is increased by the same amount. This circumstance makes it possible to control the thickness of the films accurately.



a) b)

Fig. 5. Surface morphology of CdS (a) and CdSe (b) films

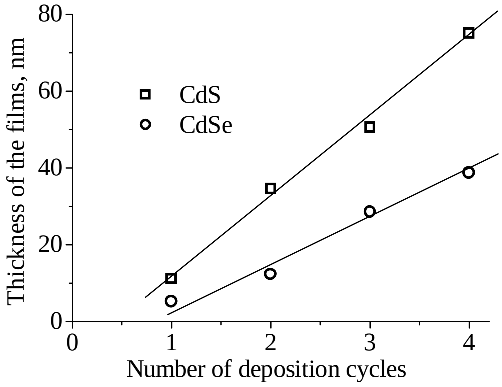


Fig. 6. Dependence of CdS and CdSe film thickness changes on the number of deposition cycles

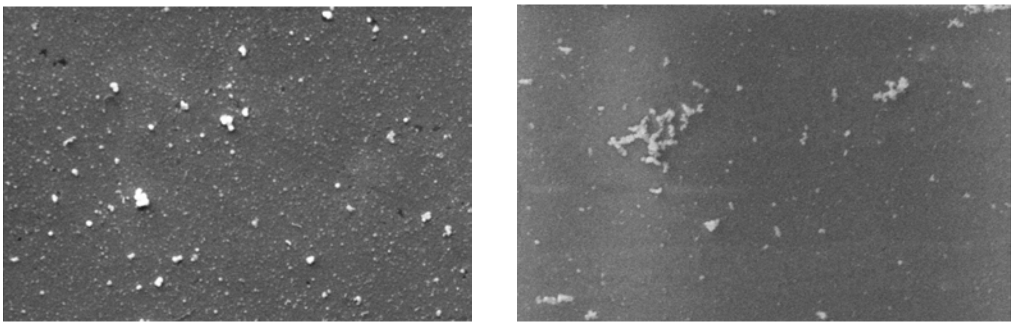


Fig. 7. Surface morphology of CdS(a) and CdSe (b) films. $C(CdCl_2) = 0.01$ M; $C(CS(NH_2)_2) = 1$ M; $C(Na_2SeSO_3) = 0.1$ M; $T = 343$ K; the deposition time is (4x3) min

4. Conclusions

The interconnection between the CSD process parameters on the structure, microstructure, composition, morphology and optical properties of semiconductor CdS and CdSe films was established. The continuous durable films with a small number of defects on the surface, suitable for the creation of photosensitive semiconductor structures were obtained under the chosen optimum conditions.

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ВПЛИВ УМОВ ОТРИМАННЯ ПЛІВОК CdS І CdSe НА ЇХ СТРУКТУРНІ ТА ОПТИЧНІ ВЛАСТИВОСТІ

Анотація. *Досліджено вплив умов одержання тонких плівок* CdS *і* CdSe *методом хімічного поверхневого осадження (ХПО) на їх структурні та оптичні властивості. Досліджено оптичні спектри пропускання та поглинання, морфологію поверхні плівок та ступінь їх фазової однорідності. Методом інверсійної вольтамперометрії визначено вміст йонів кадмію в одержаних покриттях. За отриманими даними маси кадмію розраховано товщини отриманих напівпровідникових плівок. Встановлено оптимальні умови ХПО для одержання плівок заданої товщини з мінімальною кількістю дефектів на поверхні.*

Ключові слова: *напівпровідникові плівки, хімічне поверхневе осадження, структура, морфологія.*