

## Synthesis of ZnSe Films by Hydrochemical Sedimentation Method

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Zinc selenide films were obtained by hydrochemical sedimentation method by interplay of zinc ions with selenium in the presence of hydrazine. It is found that during the deposition from ammonia solutions the zinc oxide phase is present in the films. This phase is formed by coalescence between spherical particles with sizes of 1-1.5  $\mu\text{m}$ . During the deposition from sodium hydroxide solutions with concentration of 0.5-3 M formation of sphalerite phase of zinc selenide was observed; and films were formed by spherical particles with sizes of 0.15-0.20  $\mu\text{m}$ . Increase in the concentration of alkali from 0.5 to 3 M does not change the particle size in the condensates.

**Keywords:** Films, Hydrochemical sedimentation, Zinc selenide, Phase composition, Band gap.

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### 1. INTRODUCTION

$\text{A}_2\text{B}_6$  compounds, to which ZnSe belongs, find wide application in different fields of science and engineering [1-2]. Recently, zinc selenide is considered as the material alternative to CdS for windows of thin-film solar cells (SC) on basis of absorbing layers  $\text{CuInSe}_2$  (CIS),  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS),  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) and  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) [2-3]. Band gap of zinc selenide is larger ( $E_g = 2.67$  eV) than of CdS ( $E_g = 2.42$  eV) that allows to extend the range of photosensitivity of transducers in the ultraviolet spectral region and, correspondingly, to increase their short-circuit currents [4]. It is important from the ecological point of view that ZnSe is nontoxic ("Cd-free") material due to the absence in its composition of heavy metals.

Further decrease in the cost of thin layer deposition is necessary for a large-scale utilization of SC with ZnSe window. In connection with this, attention of scientists is attracted by non-aerated production methods of zinc selenide films, such as chemical material synthesis from solution, electrochemical deposition, spray-pyrolysis, etc. (see [5-8]).

Hydrochemical deposition from aqueous solutions is one of the promising methods of ZnSe film production. It allows to obtain thin layers of metal chalcogenides and solid substitutional solutions based on them of acceptable quality [9]. This method differs by simplicity of implementation, does not require special technological conditions of layer deposition (vacuum, high pressure and temperature) [10-12]. However, information about the production of zinc selenide films by hydrochemical method is almost absent in literature.

It is known that formation of zinc selenide occurs in an alkaline medium at the interaction of zinc ions with selenium in the presence of hydrazine hydrate during heating [13-15]. The method allows to obtain ZnSe of high purity with good practical yield (more than 90% of the theoretical one). The aim of the present work was the production of zinc selenide films by hydrochemical

deposition from solutions during interaction of zinc ions with selenium in the presence of hydrazine and investigation of their phase composition and morphological characteristics.

### 2. EXPERIMENTAL TECHNIQUE

The following precursors were used for the synthesis of ZnSe films: ZnO, Se, aqueous solution of ammonia, NaOH and hydrazine hydrate by "Reachim". Additional cleaning of the initial substances was not performed.

Film deposition was realized from ammonia solution and solutions of sodium hydroxide. Ammonia solution was prepared as follows: a glass substrate was placed into the reaction volume (100 ml); then 50 ml of aqueous ammonia solution, 0.04 g of zinc oxide, 0.035 g of selenium, 0.1 ml of hydrazine hydrate were added. For the preparation of sodium hydroxide solution the following procedure was performed: a glass substrate was placed into the reaction volume (100 ml); then 50 ml of distillate water, sodium hydroxide, 0.04 g of zinc oxide, 0.035 g of selenium, 0.1 ml of hydrazine hydrate were added. Concentration of NaOH in the solution was varied from 0.5 to 3 M. The prepared solutions were heated to boiling and boiled during 30 minutes. Then they were cooled to room temperature. Substrate with deposited film was taken out from the solution and washed some times by distillate water and then by ethanol. After that the obtained samples were dried at room temperature during 2 hours.

Crystal structure of the deposited films was determined by the X-ray diffractometry method in the Bragg-Brentano geometry with graphite monochromator on the primary beam in K $\alpha$ -Cu radiation. Phase analysis of the film structure was performed by the comparison of interplanar spacings and relative intensities of X-ray peaks from the studied samples and standard by the JCPDS data [16]. Film morphology was investigated by using scanning microscope JSM-6390LV.

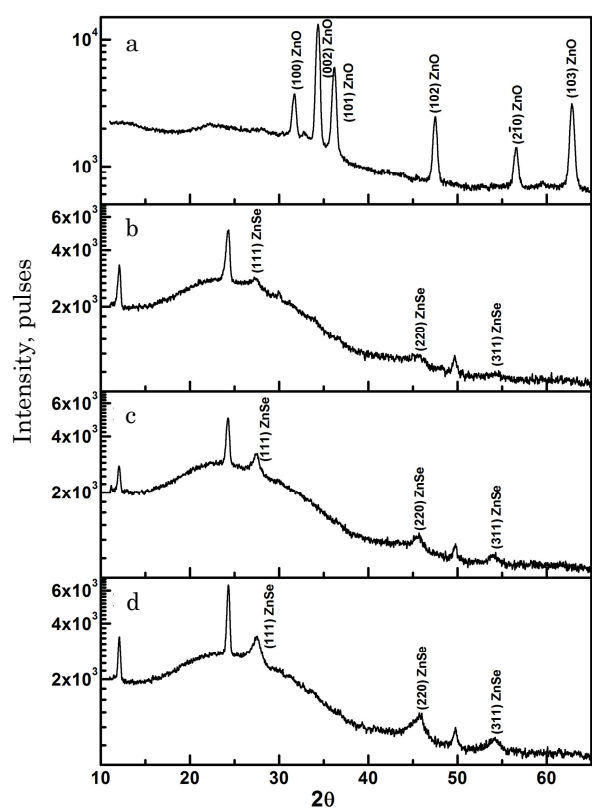
Spectral dependences of the reflection  $R(\lambda)$  and trans-

mission  $T(\lambda)$  coefficients of condensates were measured by spectrophotometer SF-26 in the wavelength range of  $\lambda = 360-1200$  nm. To obtain the  $R(\lambda)$  spectra the add-on PZO-2, which provided double light reflection from the surface of the experimental samples, was used. The film thickness was measured by the Linnik microinterferometer MII-4 [17].

### 3. RESULTS AND DISCUSSION

Light yellow films were obtained during the deposition from ammonia solutions and yellow films with tints of granite – from NaOH solutions. We have to note that the films obtained from ammonia solution had larger thickness ( $0.30 \mu\text{m}$ ) in comparison with the films deposited from sodium hydroxide solutions ( $0.15-0.20 \mu\text{m}$ ).

In Fig. 1 we show the diffraction patterns of the condensates obtained from ammonia and alkaline solutions.

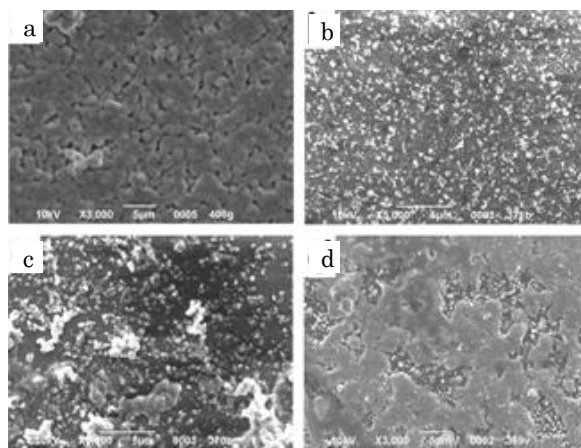


**Fig. 1** – Diffraction patterns of ZnSe films deposited from ammonia (a) and alkaline solutions at the concentration of NaOH in the solution of 0.5 M (b), 1 M (c) and 3 M (d)

Analysis of the diffraction patterns (Fig. 1a) implies that film synthesis from ammonia solution leads to the formation on the substrate surface of zinc oxide (ZnO) layers with hexagonal structure. Together with this, reflexes which belong to the cubic modification of ZnSe (Fig. 1b-d) are found on the diffraction patterns from the films obtained from NaOH solutions. In accordance with the data of the X-ray diffractometry investigations, increase in the concentration of alkali in the solution leads to the increase in the intensity of reflexes of zinc selenide (Fig. 1b-d). We should note that on the diffraction patterns of the films obtained from sodium hydroxide solutions (Fig. 1b-d) besides diffraction maximums belonging to ZnSe the additional reflexes from unascer-

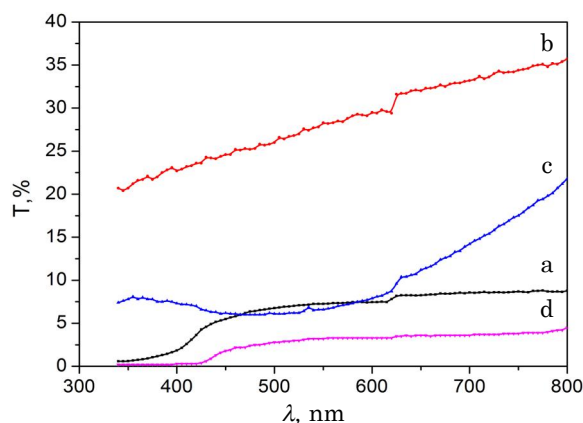
tained phase are discovered.

Micrographs of the surface of the obtained films are illustrated in Fig. 2. The film deposited from ammonia solution (Fig. 2a) is formed by coalescent spherical particles with sizes of  $1.0-1.5 \mu\text{m}$ . The layers deposited from NaOH solution with concentration of 0.5 M (Fig. 2b) also consist of spherical particles but with sizes of  $0.15-0.2 \mu\text{m}$ . Increase in the concentration of alkali (Fig. 2c, d) does not result in the change of the size of spherical particles. Deposit of unknown origin, possibly, remains of precursors are observed on the film surface.



**Fig. 2** – Micrographs of the films deposited from ammonia (a) and NaOH solutions with concentration of 0.5 M (b), 1 M (c) and 3 M (d)

In Fig. 3 we represent the transmission spectra of the obtained films. As seen from the figure, the films are characterized by low transmission coefficient in the visible spectral region, which further decreased while shifting towards the UV-region. The film obtained from 0.5 M solution of sodium hydroxide ( $\approx 35\%$  at  $\lambda = 800$  nm) had the maximum transmission coefficient.



**Fig. 3** – Transmission spectra of the films deposited from ammonia (a) and NaOH solutions with concentration of 0.5 M (b), 1 M (c) and 3 M (d)

Reflection of light from the films because of the developed surface relief was on the level of sensitivity limit of detector, and therefore constant value which is equal to the threshold of sensitivity of the device was used in further calculations. To determine the optical band gap  $E_g$  of the material, the following correlation for the direct band semiconductors was applied [18]:

$$ahv = A(hv - E_g)^{1/2}, \quad (1)$$

where  $A$  is the constant depending on the effective mass of charge carriers in material;  $h\nu$  is the energy of optical quanta;  $a$  is the material absorption coefficient.

As follows from (1), extrapolation of the linear part of the graph on the energy axis allows to determine the band gap of the material. Spectral dependences of the film absorption coefficients, which are necessary for the calculation of  $E_g$ , were found by the transmission spectra taking into account constant, close to zero reflection coefficient from the relation

$$a = -\frac{1}{d} \ln \left\{ \frac{1}{R^2} \left[ -\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^4} + R^2} \right] \right\}, \quad (2)$$

where  $d$  is the film thickness.

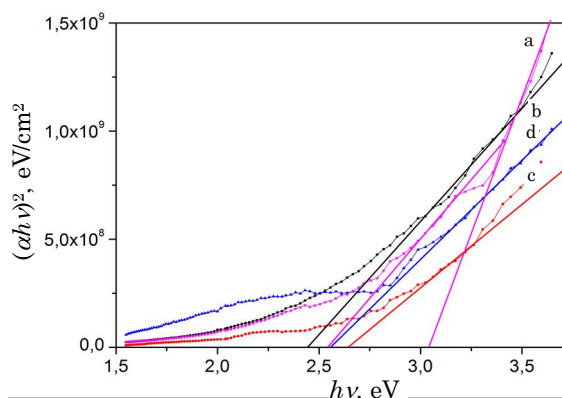
In Fig. 4 we show the dependences  $(ah\nu)^2 - hv$  which we use in the sequel for the determination of the band gap of materials. Approximation of the linear regions of these dependences on the energy axis allows to define  $E_g$  of the phases present in the film. In the case of the film obtained from ammonia solution two characteristic regions giving energies of 2.55 and 3.04 eV (Table 1) are observed on the  $(ah\nu)^2 - hv$  dependence. The value  $E_g = 3.04$  eV indicates the presence of zinc oxide in the sample (an information value is 3.37 eV [2]) that agrees with the data of the X-ray investigations. The energy  $E_g = 2.55$  eV corresponds to the band gap of zinc selenide (an information value is 2.67 eV [2]). The energy  $E_g = 2.45$ -2.65 eV typical for the band gap of zinc selenide is obtained from the  $(ah\nu)^2 - hv$  dependence from the films deposited from NaOH solution.

**Table 1** – Values of the film thickness obtained from different solutions and band gap  $E_g$  of the corresponding material

№	Deposition solution	Film thickness, $\mu\text{m}$	$E_g$ , eV
1	NH <sub>4</sub> OH	0.30	2.55 3.04
2	0.5 M NaOH	0.20	2.45
3	1 M NaOH	0.15	2.65
4	3 M NaOH	0.15	2.57

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**Fig. 4** – Dependences of the absorption coefficient of the films obtained from ammonia (a) and NaOH solutions with concentration of 0.5 M (b), 1 M (c) and 3 M (d)

## 4. CONCLUSIONS

Films are obtained by the hydrochemical deposition method by interplay of zinc ions with selenium in the presence of hydrazine on the surface of glass substrates. It is established that layers, which are the mixture of two phases – oxide (master phase) and zinc selenide, are formed from the ammonia solution. Films of zinc selenide with sphalerite structure are obtained during the deposition from NaOH solutions irrespectively of their concentration.

The layers deposited from the alkaline solutions are formed by spherical particles with the sizes of 0.15-0.20  $\mu\text{m}$ . Change in the concentration of NaOH in the range of 0.5-3.0 M does not significantly influence the morphological characteristics of the films. The purest in phase composition layers are formed from NaOH solutions with concentration of 1-3 M; the corresponding material is characterized by the band gap of 2.57-2.65 eV that corresponds to zinc selenide.

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