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Comparison of Structural and Optical Properties of CdSe Films Grown by CSD and CBD Methods

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Cadmium selenide (CdSe) films were synthesized on glass substrates via chemical surface deposition (CSD) and chemical bath deposition (CBD) methods. Aqueous solutions of cadmium chloride, thiourea, sodium selenosulfate, trisodium citrate and ammonia hydroxide were used. Theoretical calculations of the boundary conditions for the formation of cadmium selenide and cadmium hydroxide were carried out in the cadmium-selenosulfate and cadmium-selenosulfate-citrate-ammonia systems. The phase composition, optical transmission spectra and surface morphology of deposited CdSe films were investigated. According to the X-ray analysis, the film samples are single phase and consist of CdSe compound in its typical cubic modification. The film surface is solid, smooth and has a small number of surface defects. The optical transmission of CdSe films increases in the investigated wavelength area from 340 to 900 nm. The transmission curves have bends in the 650 nm region, which is typical for cadmium selenide. The optical band gap values of CdSe films are found to be in the range of 1.82-1.88 eV.

Keywords: Cadmium selenide, Semiconductor films, Chemical deposition, XRD, Optical band gap.

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1. INTRODUCTION

Cadmium selenide (CdSe) films are of interest for the fabrication of large-area products. These are solar selective coatings, solar cells, photoresistors, etc. Also, the realization of deposition of silver [1, 2] or gold [3, 4] nanoparticles with CdSe allows obtaining photocatalysis [5-7] and photoluminescence [8-10] materials. But sophisticated equipment, power- and cost-consumption of CdSe films-based products preparation hinder their industrial fabrication. So, an effective and profitable film deposition method that allows to decrease the value of manufacturing cost is an actual task.

There are two methods to obtain CdSe films simply and cost-effectively: chemical bath deposition (CBD) and chemical surface deposition (CSD). The CBD method has been known for a long time [11, 12]. In this method, the reaction takes place in a bath between the dissolved chemical reagents in an aqueous solution at a temperature below the boiling point of water. Deposition of CdSe films occurs on substrates immersed in a bath with the working solution during a certain duration of the CBD process. The newer CSD method was proposed in [13, 14]. This method is also based on the reaction between dissolved chemicals in an aqueous solution. But it takes place only on the preheated substrate surface. This significantly reduces the amount of used working solutions to obtain the same amount of CdSe coatings. As a result, there is less waste. However, a long process duration of CSD is undesirable because it leads to complete evaporation of the working solution from the substrate surface. This requires the use of a smaller number of reagents in the working solution in order to accelerate the CdSe formation and, accordingly, reduce the CSD process duration.

The work is aimed at investigating and comparing the phase composition, optical properties, and surface morphology of CdSe films obtained by CSD and CBD.

2. EXPERIMENTAL DETAILS

2.1 Materials

To obtain CdSe films, we used the following chemical reagents: cadmium chloride ($CdCl_2$), sodium selenosulfate (Na_2SeSO_3), trisodium citrate ($Na_3C_6H_5O_7$), ammonia hydroxide (NH_4OH) and thiourea ($(NH_2)_2CS$). Glass plates were used as the substrate material with unit dimensions of 18 mm × 18 mm.

2.2 Methods

The CBD and CSD methods were used to obtain CdSe films. The conditions for CdSe film deposition by these two methods are given in Table 1. The necessary amounts of chemicals were dissolved in distilled water to obtain working solutions. Then the required volumes of working solutions were poured into the bath or on the substrate surface and heated for a specified process duration at a given temperature. The scheme for obtaining CdSe films by CBD and CSD methods is shown in Fig. 1. After the end of the deposition process, the substrates were cleaned with distilled water.

Table 1 – The conditions for the CdSe film deposition

Index	CSD method	CBD method
$C(CdCl_2)$, mol/L	0.005	0.005
$C(Na_2SeSO_3)$, mol/L	0.05	0.05
$C(Na_3C_6H_5O_7)$, mol/L	–	0.25
$C(NH_4OH)$, mol/L	–	0.10
$C((NH_2)_2CS)$, mol/L	–	0.05
Volume of working solution, ml	0.5	100
pH of working solution	9.6	10.7
Process duration, min	3-12	15-40
Temperature, °C	70	70

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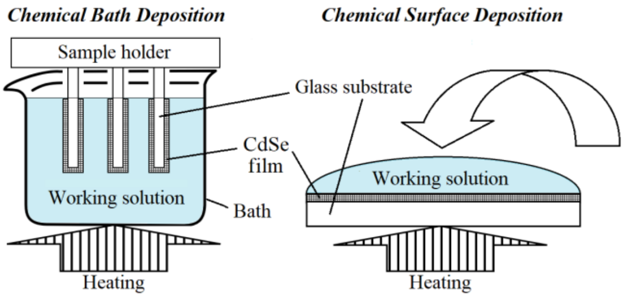


Fig. 1 – The scheme of obtaining CdSe films by CSD and CBD methods

2.3 Analysis

X-ray diffraction (XRD) analysis of the synthesized CdSe film samples was made using an Aeris Research X-ray diffractometer (Cu$K\alpha^-$ radiation). The preliminary processing of the experimental diffraction arrays in order to identify the phases was carried out using the PowderCell program [15].

The optical transmission spectra of CdSe films were recorded on a Xion 500 spectrophotometer in the 340-900 nm wavelength range. The optical transmission detection accuracy was ± 0.5 %. The optical band gaps (E_g) were determined from $(\alpha h\nu)^2$ vs. $h\nu$ dependences by extrapolating the linear parts of $(\alpha h\nu)^2$ curves to the intersection with the $h\nu$ (energy axis) [16].

The surface morphology of CdSe films was investigated using a REMMA-102-02 scanning electron microscope (SEM) with a microanalysis system.

The pH values of the working solutions were measured with a pH-150 MI pH-meter with a glass combined electrode.

3. RESULTS AND DISCUSSION

3.1 Boundary Conditions Calculation

Under the CBD conditions of CdSe films (according to Table 1), the formation of soluble cadmium citrate, ammonia and hydroxo complexes are possible, as well as insoluble cadmium hydroxide ($Cd(OH)_2$) as a by-product. In the case of CSD of CdSe films, the formation of only cadmium hydroxo complexes and $Cd(OH)_2$ as a by-product is possible. In such systems, the minimum concentration of cadmium salt required for the formation of solid CdSe and $Cd(OH)_2$ phases was calculated using the following equations, respectively [17-19]:

$$pC_{\mathrm{Cd}^{2+}}^{\min} = pSP_{\mathrm{CdSe}} - p\alpha_{\mathrm{Cd}^{2+}} - \frac{1}{2}\left(pK_{\mathrm{SeSO}_3^{2-}} - 2pH + 2pK_{\mathrm{H_2Se}}^{1,2} + p[\mathrm{SeSO}_3^{2-}] - p\beta_{\mathrm{H_2Se}}\right), \quad (1)$$

$$pC_{\mathrm{Cd}^{2+}}^{\min} = pSP_{\mathrm{Cd(OH)_2}} + 2pH - p\alpha_{\mathrm{Cd}^{2+}} - 2pK_{\mathrm{H_2O}}, \quad (2)$$

where $\beta_{\mathrm{H_2Se}} = [H^+]^2 + K_{\mathrm{HSe}^-}^1[H^+] + K_{\mathrm{H_2Se}}^{1,2}$; p is an indicator (negative decimal logarithm); $C_{\mathrm{Cd}^{2+}}^{\min}$ is the minimum concentration of Cd^{2+} ions required for the formation of a solid phase; SP_{CdSe} is the solubility product of CdSe; $K_{\mathrm{H_2Se}}^{1,2}$, $K_{\mathrm{SeSO}_3^{2-}}$, $K_{\mathrm{H_2O}}$ are constants of hydrogen selenide, selenosulfate and water dissociation, respectively; $\alpha_{\mathrm{Cd}^{2+}}$ is the molar fraction of the free Cd^{2+} ions in the solution. The value of $\alpha_{\mathrm{Cd}^{2+}}$ can be found from the following equation:

$$\alpha_{\mathrm{Cd}^{2+}} = \frac{1}{1 + \frac{[L]}{K_L^1} + \frac{[L]^2}{K_L^{1,2}} + \ldots + \frac{[L]^n}{K_L^{1,2,\ldots n}}}, \quad (3)$$

where $[L]$ is the concentration of free ligand (L) of the complexing agent, and $K_L^{1,2,\ldots n}$ are the instability constants of Cd^{2+} complexes with citrate, ammonia and hydroxide.

On the basis of equations (1), (2) and (3), the dependences of the minimum concentration of cadmium salt required for the formation of CdSe and $Cd(OH)_2$ at different pH values of the working solution were plotted (Fig. 2). The calculations were carried out using the following initial concentrations of compounds given in Table 1. The other values of thermodynamic constants used in calculations were taken from [18-20].

In practice, it was impossible to obtain coatings exactly at the minimum calculated concentrations ($C_{\mathrm{Cd}^{2+}}^{\min}$ = 10^{-18}-10^{-19} mol/l) in an alkaline area. So, an

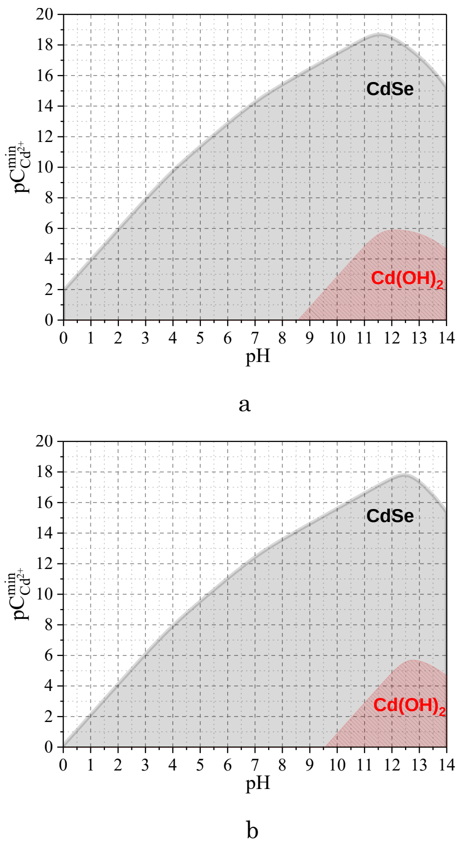


Fig. 2 – Boundary conditions of the CdSe and $Cd(OH)_2$ solid phase formation in the cadmium-selenosulfate (a) and cadmium-selenosulfate-citrate-ammonia (b) system

additional experimental selection of the Cd-salt concentration was performed to find out when CdSe is formed on the film substrate. This occurs at Cd-salt concentrations ranging from 10^{-3} mol/l. At concentrations lower than 10^{-3} mol/l, CdSe appears only in the form of weak turbidity of the solution. In addition, it was necessary to choose such a Cd-salt concentration and pH at which the rate of formation of the final product leads to a better quality of formed CdSe films. We experimentally established that this concentration value is $5 \cdot 10^{-3}$ M at pH = 9.6 (in the case of the cadmium-selenosulfate system) or at pH = 10.7 (in the case of the cadmium-selenosulfate-citrate-ammonia system). These parameters are used in this work (Table 1). It is close to the region of $Cd(OH)_2$ formation, but its presence as a by-product will not be confirmed in experimental studies of the work below.

3.2 Structural and Morphological Properties

XRD analysis of the deposited film samples was carried out. It can be seen from Fig. 3 that the XRD patterns of films obtained by CSD and CBD methods have one prominent peak at 25.7° and two weak peaks at 42.6° and 50.4°. These peaks correspond to the (111), (220) and (311) planes of the cubic CdSe phase (ZnS structural type), which is a typical modification of cadmium selenide compound. $Cd(OH)_2$ was not detected in the film composition.

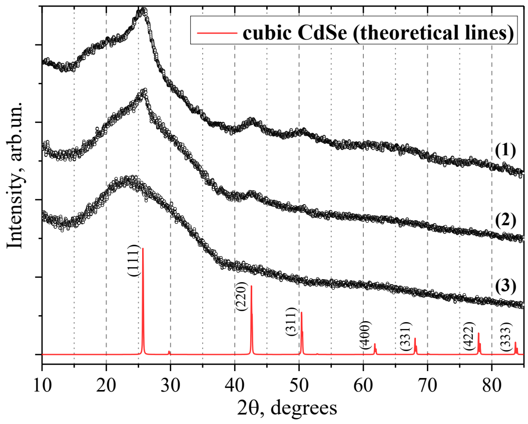
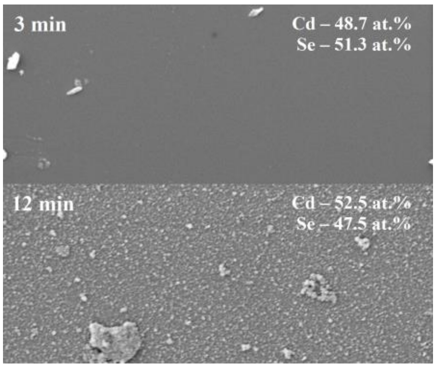


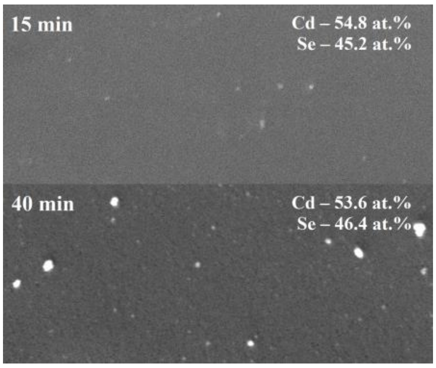
Fig. 3 – Experimental XRD patterns of CdSe films on glass substrates obtained by CSD (1) and CBD (2) methods and XRD pattern of a glass substrate (3) without CdSe film for comparison

The results of the surface morphology investigation of CdSe film samples are shown in Fig. 4. The microphotographs indicate that CdSe films obtained by CBD and CSD at various durations are solid, smooth and uniform over the whole area and reveal a small amount of precipitate and defects on their surfaces. But, in the case of CSD, larger precipitate particles are observed at the maximum process duration. This can be explained as follows: since substrates are arranged horizontally in the CSD method, this, under the influence of gravity, contributes to precipitating and fixing of some larger particles. It was difficult to remove them by cleaning the films with distilled water after the end of the deposition process. The CBD method does not have this drawback because substrates are arranged vertically there.

Microanalysis of CdSe films (Fig. 4, inset) shows that CdSe films obtained at various durations consist practically of cadmium and selenium in a ratio of 1:1.



a



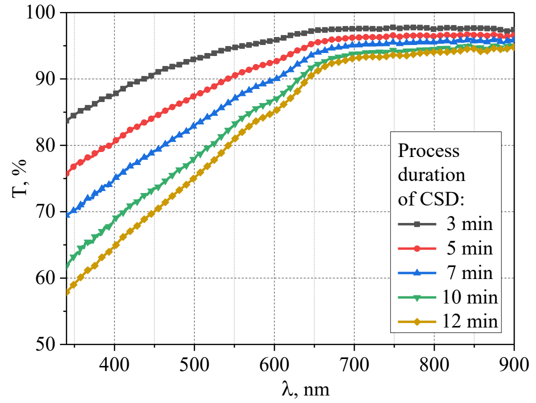
b

Fig. 4 – Surface morphology (×5000 magnification) and atomic composition of CdSe films obtained by CSD (a) and CBD (b) methods at various process durations

3.3 Optical Properties

The optical transmission spectra $T(\lambda)$ of CdSe films obtained by CSD and CBD methods with different process durations were measured in the wavelength (λ) region of 340-900 nm (Fig. 5). The minimum and maximum light transmission is observed at the beginning and end of the studied wavelength range, respectively. An increase in light transmission is seen with bends located in the wavelength range of 600-650 nm, which is characteristic of CdSe films. The spectral curves are shifted down towards lower transmission values with an increase in deposition duration. That is due to a rise in the amount of deposited CdSe over time.

The shape of spectral curves of CdSe films obtained by CSD and CBD methods is generally similar. However, in the scale of transmission (T), CdSe films obtained by the CSD method have lower maximum transmission values at maximum deposition duration than CdSe films obtained by the CBD method. For example, in the case of CSD, the maximum T value is 58 % at λ = 340 nm, and in the case of CBD, the maximum T value is 42 % at the same λ. Accordingly, this shows that the CBD method makes it possible to deposit a larger film amount of CdSe on glass substrates than the CSD method.



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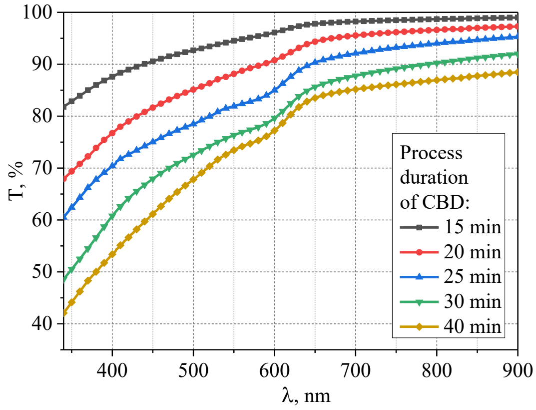
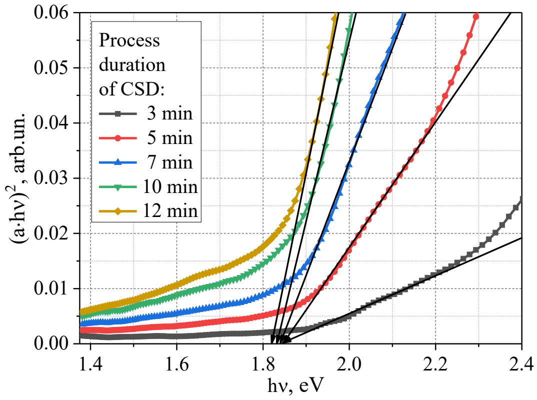


b

Fig. 5 – Spectral dependences of the optical transmission of CdSe films obtained by CSD (a) and CBD (b) methods at various process durations



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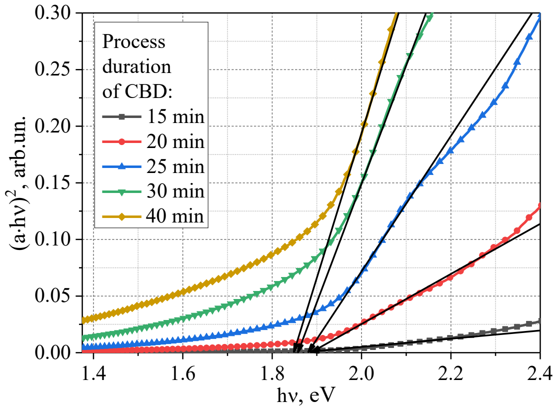

b

Fig. 6 – $(\alpha h\nu)^2 = f(h\nu)$ dependences and determination of the optical band gap values of CdSe films obtained by CSD (a) and CBD (b) methods with different process durations

The defined optical band gaps (E_g) of CdSe films obtained by the CSD method are equal to 1.82-1.85 eV, and the optical band gaps of CdSe films obtained by the CBD method are E_g = 1.84-1.88 eV (Fig. 6).

4. CONCLUSIONS

Boundary conditions for the formation of CdSe and $Cd(OH)_2$ compounds in the cadmium-selenosulfate and cadmium-selenosulfate-citrate-ammonia system have been constructed and considered. CdSe films have been obtained on glass substrates by two methods of chemical synthesis – CSD and CBD. The CSD was carried out in the cadmium-selenosulfate and the CBD – in the cadmium-selenosulfate-citrate-ammonia system.

It was found that the film samples are single phase and consist of only one CdSe phase, regardless of the deposition method (CSD or CBD). The results of optical transmission measurements of CdSe films show nearly the same shape of the spectral curves of CdSe films obtained by CSD and CBD methods. However, spectral curves of CdSe films obtained by the CBD method have lower maximum transmission values than CdSe films obtained by the CSD method with maximum process durations. This is an advantage of the CBD method, because it allows to deposit a larger film amount of CdSe on glass substrates than the CSD method. This is, at least, in the studied systems of cadmium-selenosulfate and cadmium-selenosulfate-citrate-ammonia.

The optical band gap values of CdSe films were 1.82-1.88 eV with no significant difference between the used CSD and CBD methods for coatings obtaining.

The advantages of the CSD method are that coatings are obtained faster, less working solution is used, as well as the number of chemical reagents. The advantages of the CBD method are that CdSe films with higher optical transmittance can be obtained and the absence of larger precipitate particles on the surface of the coatings as a result of the vertical arrangement of the substrates.

Based on the obtained results of chemical synthesis and studies in this work, the prepared CdSe film samples in terms of their semiconductor properties can be used for simple and cost-effective fabrication of semiconductor materials for various electronic device applications.

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Порівняння структурних та оптичних властивостей плівок CdSe, вирощених методами CSD та CBD

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Плівки селеніду кадмію (CdSe) були синтезовані на скляних підкладках методами хімічного поверхневого осадження (CSD) і хімічного осадження у ванні (CBD). Для цього використано водні розчини кадмій хлориду, тіосечовини, натрій селеносульфату, тринатрійцитрату та амоній гідроксиду. Проведено теоретичні розрахунки граничних умов утворення селеніду кадмію та гідроксиду кадмію в системах кадмій-селеносульфат і кадмій-селеносульфат-цитрат-аміак. Досліджено фазовий склад, спектри оптичного пропускання та морфологію поверхні осаджених плівок CdSe. Відповідно до проведеного рентгенівського аналізу, отримані зразки плівок є однофазними і складаються із сполуки CdSe у її типовій кубічній модифікації. Поверхня плівок була суцільною, гладкою та мала невелику кількість поверхневих дефектів. Оптичне пропускання плівок CdSe зростає в досліджуваній області довжин хвиль від 340 до 900 нм. Криві пропускання мають перегини в області 650 нм, що характерно для кадмій селеніду. Значення оптичної забороненої зони плівок CdSe знаходились в діапазоні 1,82-1,88 еВ.

Ключові слова: Кадмій селенід, Напівпровідникові плівки, Хімічне осадження, XRD, Оптична ширина забороненої зони.