Journal of Nano- and Electronic Physics
Vol. **15** No 2, 02009(5pp) (2023)

Журнал нано- та електронної фізики
Том **15** № 2, 02009(5cc) (2023)

Chemical Deposition of CdS Films from Aqueous Solution Containing Triethanolamine

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(Received 05 February 2023; revised manuscript received 15 April 2023; published online 27 April 2023)

Cadmium sulfide (CdS) films were obtained on glass substrates via two chemical deposition methods: in the aqueous bath (chemical bath deposition) and directly on the substrate surface (chemical surface deposition). The aqueous solutions of cadmium chloride, thiourea and triethanolamine were used to prepare working solutions. The theoretical calculations of boundary conditions for the formation of cadmium sulfide and cadmium hydroxide were made in the cadmium-triethanolamine-thiourea system. The phase composition, surface morphology and optical transmission spectra of deposited CdS films were investigated. The X-ray diffraction analysis showed that the obtained films were single-phase and contained the CdS compound in its typical cubic modification (ZnS structural type). The film's surface was sufficiently homogeneous, solid and smooth and contained a small amount of fine precipitate particles. The elemental analysis showed the almost stoichiometric molar ratio of cadmium and sulfur in films. The optical transmission of CdS films increases with increasing wavelengths in the measured area from 340 to 900 nm. There are bends on the transmission curves in the 450-500 nm region, which is characteristic for the cadmium sulfide compound. The values of optical band gaps of CdS films were defined to be in the range of 2.41-2.58 eV.

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

DOI: 10.21272/jnep.15(2).02009 PACS numbers: 81.15.Lm, 78.66.Hf, 68.55.ag, 61.05.cp

1. INTRODUCTION

Cadmium sulfide (CdS) belongs to the A_2B_6 semiconductor group. It is interesting in the form of film and has wide use in electronic products: solar cells, semiconductor lasers, photoresistors, etc. In addition, a combination of the deposition of silver [1], gold [2] or platinum [3] nanoparticles with CdS allows obtaining electrocatalysts [4], photocatalysts [5] and photoluminescence [6] materials or nanocomposite for removal of azo dyes under UV and solar light [7].

One of the simplest and cost-effectiveness way to obtain CdS films is by the chemical deposition. In this case, the reaction takes place in an aqueous working solution between the dissolved chemical compounds at a temperature below the boiling point of water. There are two varieties of chemical deposition of CdS films: in the aqueous bath [8, 9] and directly on the substrate surface [10]. These varieties are called chemical bath deposition (CBD) and chemical surface deposition (CSD), respectively. The specificities of CBD and CSD we described earlier in [11].

Aqueous working solution for chemical deposition of CdS films contains cadmium salt, sulfurizing agent, complexing agent and if, necessary, pH-regulator. The complexing agent binds cadmium ions into Cd-complexes, preventing the rapid formation of an insoluble CdS precipitate. In literature, as complexing agents for chemical deposition of CdS were used such chemicals as: ammonia hydroxide (ammonia) [9], triethanolamine [12], sodium citrate [8], hydrazine [13], potassium hydroxide [14] etc. In case of ammonia hydroxide use [9], it provides itself the necessary pH of the working solution. In cases of triethanolamine, sodium citrate and hydrazine [8, 12, 13] some amount ammonia hydroxide was added to the working solution as pH-regulator to reach necessary pH value. In case when working solution contains potassium hydroxide [14], authors add ammonia salt, which leads to generation of ammonia hydroxide directly in the working solution as a weak base. The use of ammonia hydroxide in the deposition of CdS films creates its sharp odour over the working solution, especially when using the CBD with a larger solution volume in the bath (usually hundreds of millilitres). Considering this, the deposition of CdS films with smaller volumes of working solution (around 0.5-1 ml per 5 cm^3 of the substrate), which is possible using the CSD method, and without the use of ammonia hydroxide, is an actual task.

The work is aimed at investigating and comparing the phase composition, surface morphology and optical properties of CdS films obtained by CSD and CBD from aqueous solutions containing triethanolamine and not containing ammonia hydroxide.

2. EXPERIMENTAL DETAILS

2.1 Materials

To deposit CdS films, the following chemical compounds were used: cadmium chloride ($CdCl_2$), triethanolamine (TEA, $N(CH_2CH_2OH)_3$) and thiourea ($(NH_2)_2CS$).

The glass plates were used as substrate material with an area of 3.24 cm^2.

2.2 Methods

The chemical depositions of CdS films were carried out from the aqueous solutions by the CBD method and directly on the substrate surface by the CSD method. The conditions for CdS film deposition by these two methods are given in Table 1. The working solutions

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were prepared by dissolving the necessary amounts of chemical compounds in distilled water. Then the required volumes of working solutions were poured into the bath or on the substrate surface and heated for a specified process duration and temperature. The schemes for obtaining films by CBD and CSD methods we have shown earlier in a previous study [11]. After the end of the deposition process, the substrates were cleaned with a jet of distilled water and analyzed by the methods given below.

Table 1 – The conditions for the CdS film deposition

Index	CBD method	CSD method
$C(CdCl_2)$, mol/L	0.005	0.005
$C(N(CH_2CH_2OH)_3)$, mol/L	1.0	1.0
$C((NH_2)_2CS)$, mol/L	0.05	0.05
Volume of working solution, mL	200	0.7
Process duration, min	7-25	5-15
pH of working solution	10.6	10.6
Temperature, °C	70	70

2.3 Analysis

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

The optical transmission spectra of the CdS films were recorded on a Xion 500 spectrophotometer in the 340-900 nm wavelength range. The accuracy of optical transmission measurement was ±0.5 %. To define the direct optical band gaps (E_g) of the deposited CdS films, the Tauc relationship was used, as shown in [16].

The surface morphology images of the CdS films were made using a REMMA-102-02 scanning electron microscope (SEM) with an elemental 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 conditions of CdS film depositions (according to Table 1), there is a system of cadmium-triethanolamine-thiourea. In this system, the formation of cadmium soluble complexes with TEA and hydroxide are possible, as well as cadmium hydroxide ($Cd(OH)_2$) as an insoluble by-product. Accordingly, the minimum concentrations of cadmium salt required to form insoluble CdS and $Cd(OH)_2$ phases were calculated using the following equations, respectively [8, 17, 18]:

$$pC_{Cd^{2+}}^{\min} = pSP_{CdS} - p\alpha_{Cd^{2+}} - \left(pK_{H_2S}^{1,2} - 2pH + \frac{1}{2} pK_{(NH_2)_2CS} + p[(NH_2)_2CS] - p\frac{\beta_{H_2CN_2}}{\beta_{H_2S}} \right) \quad (1)$$

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

Where $\beta_{H_2S} = \left[H^+\right]^2 + K_{HS^-}^1 \left[H^+\right] + K_{H_2S}^{1,2}$;

$\beta_{H_2CN_2} = \left[H^+\right]^2 + K_{HCN_2^-}^1 \left[H^+\right] + K_{H_2CN_2}^{1,2}$;

p is a negative decimal logarithm (exponent); $C_{Cd^{2+}}^{\min}$ is the minimum Cd^{2+} salt concentration required for forming an insoluble phase; SP_{CdS} is the solubility product of CdS; $\alpha_{Cd^{2+}}$ is the mole fraction of the free Cd^{2+} ions in the solution. $K_{H_2S}^{1,2}$, $K_{H_2CN_2}^{1,2}$, $K_{(NH_2)_2CS}$, K_{H_2O} are constants of hydrogen sulfide, hydrogen cyanamide, thiourea, and water dissociation, respectively; The $\alpha_{Cd^{2+}}$ value can be found from the following equation:

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

where $[L]$ is the free ligand (L) concentration of the complexing agent; $K_L^{1,2,\ldots n}$ are the instability constants of cadmium complexes with triethanolamine and hydroxide. According to [19] cadmium forms with TEA two complexes of the compositions $[Cd(TEA)]^{2+}$ and $[Cd(TEA)_2]^{2+}$, and their logarithms of stability constants are $\log \beta_1 = 3.0$ and $\log \beta_2 = 5.17$, respectively. So, the instability constants will be $K_{TEA}^1 = 10^{-3}$ and $K_{TEA}^{1,2} = 10^{-5.17}$.

Based on equations (1) and (2), the dependences of the minimum Cd^{2+} salt concentration required for forming insoluble CdS and $Cd(OH)_2$ phases at various pH values of the working solution were plotted (Fig. 1). The calculations were performed for the cadmium-triethanolamine-thiourea system using the initial concentrations of chemical compounds, which are given in Table 1. The other thermodynamic constants values used in calculations were taken from [18, 20].

According to Fig. 1, the value of $C_{Cd^{2+}}^{\min}$ is around 10^{-15} mol/L in alkaline area. In practice, at such very low Cd-salt concentrations, when $C_{Cd^{2+}}^{\min}$ is between 10^{-3} and 10^{-15} mol/L, only a weak CdS turbidity of the solution can be obtain with no formed CdS coatings on the substrate. Similarly as in [11], the film is formed at cadmium salt concentrations ranging from 10^{-3} mol/L.

Additionally, it was necessary to define such parameters of the cadmium salt concentration and pH at which the final product's formation rate leads to a better quality of deposited CdS films. We experimentally determined that this Cd-salt concentration is $5 \cdot 10^{-3}$ M at pH = 10.6. These values are used in this research (Table 1). It's close to the hydroxide formation region, but the presence of $Cd(OH)_2$ as a by-product will not be confirmed in the experimental results below.

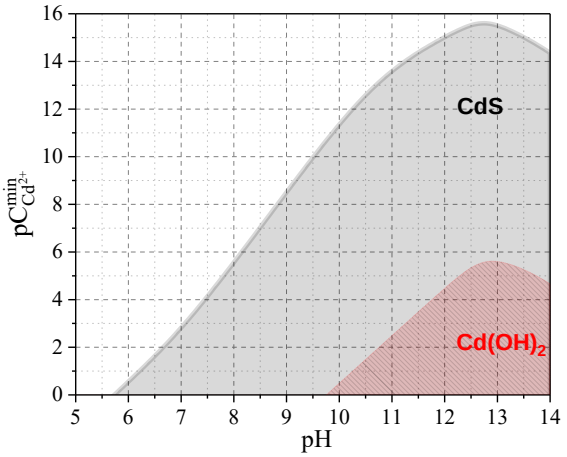


Fig. 1 – Boundary conditions of the CdS and $Cd(OH)_2$ solid phase formation in the cadmium-triethanolamine-thiourea system

3.2 Structural and Morphological Properties

An X-ray phase analysis of the obtained films was made. The experimental XRD patterns are shown in Fig. 2. According to these results, the cubic CdS phase (ZnS structural type) was identified by one prominent peak at 26,6° and two weak peaks at 44,0° and 52,1° in both diffraction patterns of films samples obtained by CSD and CBD. A clean glass substrate did not show these peaks, but an amorphous halo is present, indicating that the substrate is in an amorphous state. The $Cd(OH)_2$ phase was not detected in the film's composition.

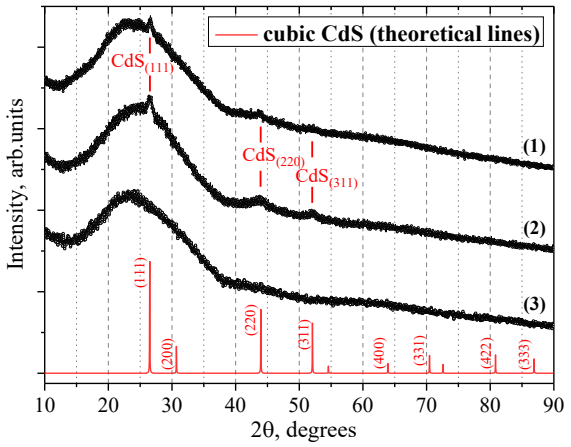


Fig. 2 – XRD patterns of CdS films samples obtained on glass substrates by CSD (1) and CBD (2) and XRD pattern of the clean glass substrate (3) for comparison

The SEM images of the surface morphology of CdS films are shown in Fig. 3. It can be seen that CdS coatings, obtained at various CBD and CSD durations, fully cover the substrate and are sufficiently homogeneous, solid and smooth. The films surfaces contain a small amount of precipitate, but there are no large precipitate particles, as seen in the case of CSD of CdSe films earlier [11]. It can be explained as follows: CdS is lighter than CdSe, and the remains of the precipitate and working solution are washed out better by a jet of distilled water after the end of the deposition.

The microanalysis of CdS films (Fig. 3, inset) shows that CdS films obtained at various durations consist practically of cadmium and sulfur in a 1:1 atomic (molar) ratio, which confirms the data of XRD analysis.

3.3 Optical Properties

The optical transmission spectra $T(\lambda)$ of CdS films obtained at different process durations of CSD and CBD methods were measured (Fig. 4). The character of the spectral curves is such that the transmission (T) increases from the beginning to the end of the measuring wavelength range (340-900 nm). There are sharper rises, like bends, located at the wavelengths near 450-500 nm. Such bends in different regions of the $T(\lambda)$ curve are typical for films of the A_2B_6 semiconductors, and depend on the nature of A_2B_6 compound – chalcogenide of the zinc subgroup [21-23]. The shape of $T(\lambda)$ curves of CdS films are generally similar in both cases of used deposition method (CSD and CBD). The CdS films transmission are shifted to the lower T values over time of deposition. That's because the amount of deposited CdS increases. However, on the transmission scale, CBD-obtained CdS films can reach lower T values at the end of deposition duration than CSD-obtained CdS films. For example, in the case of CBD, the maximum T value is 32 % at $\lambda = 340$ nm, and in the case of CBD, the maximum T value is 40 % at the same λ.

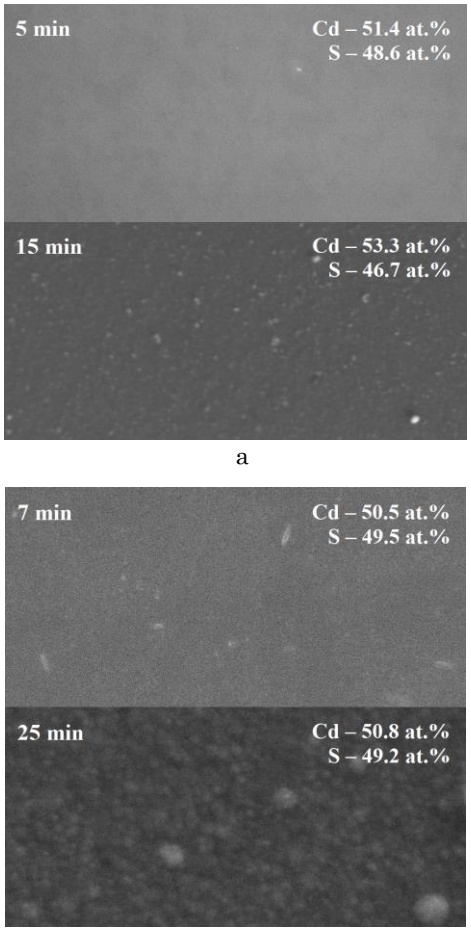
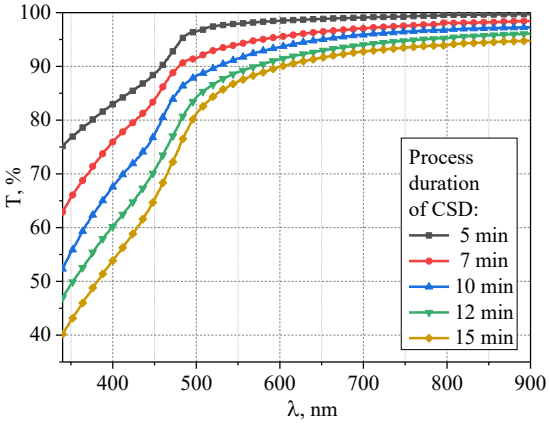
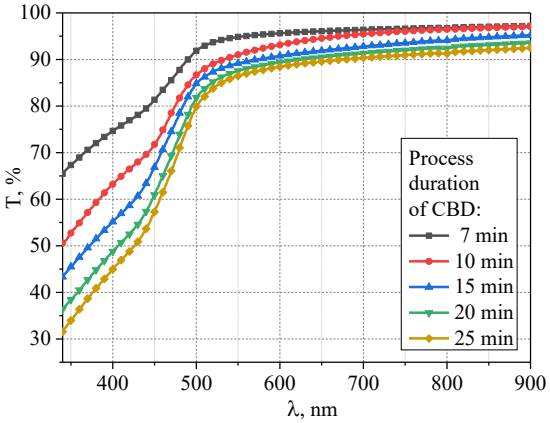


Fig. 3 – SEM images (×5000 magnification) of surface morphology and atomic composition (insets) of CdS films obtained at various process durations of CSD (a) and CBD (b) methods

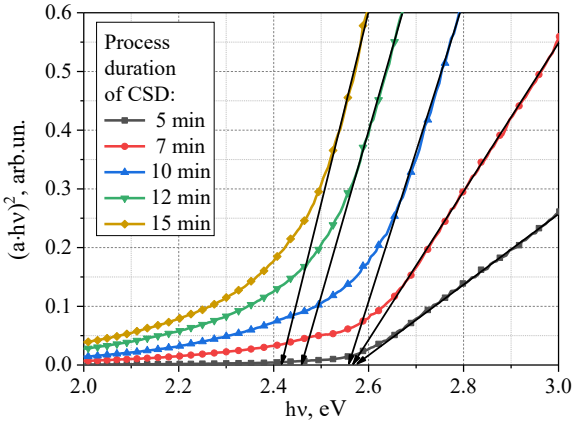


a

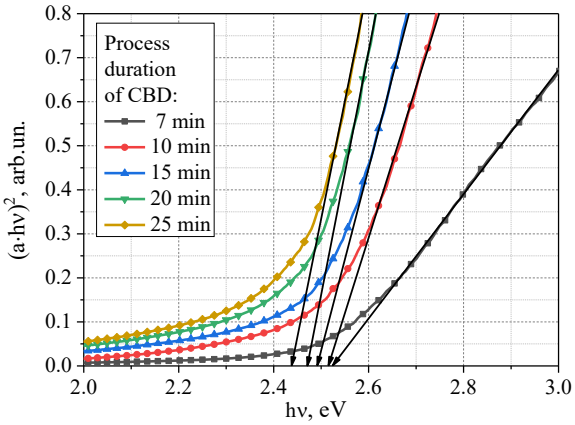


b

Fig. 4 – Optical transmission spectra of CdS films obtained at various process durations of CSD (a) and CBD (b) method



a



b

Fig. 5 – $(\alpha h\nu)^2 = f(h\nu)$ dependences and determination of the optical band gap values of CdS films obtained at various process durations of CSD (a) and CBD (b) methods

The determined optical band gaps (E_g) values of CSD-obtained CdS films are equal to 2.41-2.58 eV. The optical band gaps of CBD-obtained CdS films are E_g = 2.44-2.52 eV (Fig. 5).

4. CONLUSIONS

The boundary conditions for the formation of insoluble CdS and $Cd(OH)_2$ phases in the cadmium-triethanolamine-thiourea system have been constructed and considered.

The CdS films have been obtained on glass substrates by two methods of chemical deposition – CBD and CSD. This was done from aqueous solutions containing triethanolamine and not containing ammonia hydroxide.

It has been established that the obtained CdS films are single-phase and contain only one CdS compound, regardless of used deposition method (CBD or CSD). The studies of optical transmission spectra of CdS films show that they all are similar in shape and have bends of nearly the same shape. But, spectral curves of CdS films obtained by the CBD method have slightly lower maximum transmission values than CdS films obtained by the CSD method with maximum process durations. This shows that a larger amount of CdS film was deposited on glass substrates than in the CSD method. This is at least in the considered system of cadmium-triethanolamine-thiourea.

The E_g values of CdS films were in the range of 2.41-2.52 eV, and there is no significant difference between the used method (CSD or CBD) for obtaining coatings.

The advantages of the CSD of CdS films are that a small amount of working solution is used, and coatings are obtained faster. However, at a longer CSD duration (more than 15 min), the deposition becomes impossible due to the drying of the entire working solution on the heated glass substrate. The advantage of the CBD of CdS films is that we obtained CdS films with lower optical transmittance due to the possibility of longer CBD duration.

In two cases of the CdS deposition (CSD and CBD), there's the absence of large particles of precipitate on the coating's surface, which may be due to good samples cleaning by the jet of distilled water.

Based on the research carried out in this work, the chemically ammonia-free deposited samples of CdS films may be suitable for simple and cost-effective fabrication of semiconductor elements for various electronic products.

ACKNOWLEDGEMENTS

This study was conducted using devices of the Centre of Collective Use of Scientific Equipment: «Laboratory of Perspective Technologies of Creation and Physicochemical Analyses of New Substances and Functional Materials» at Lviv Polytechnic National University (https://lpnu.ua/ckkno).

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Хімічне осадження плівок CdS з водного розчину, що містить триетаноламін

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Плівки сульфіду кадмію (CdS) були отримані на скляних підкладках двома методами хімічного осадження: у водній ванні (хімічне осадження з ванни) та безпосередньо на поверхні підкладки (хімічне поверхневе осадження). Для приготування робочих розчинів використовували водні розчини хлориду кадмію, тіосечовини та триетаноламіну. Проведено теоретичні розрахунки граничних умов утворення сульфіду кадмію та гідроксиду кадмію в системі кадмій-триетаноламін-тіосечовина. Досліджено фазовий склад, морфологію поверхні та спектри оптичного пропускання осаджених плівок CdS. Рентгенівський дифракційний аналіз показав, що отримані плівки були однофазними та містили сполуку CdS у її типовій кубічній модифікації (структурний тип ZnS). Поверхня плівки була достатньо однорідною, суцільною і гладкою та містила невелику кількість дрібних частинок осаду. Елементний аналіз показав майже стехіометричне молярне співвідношення кадмію та сірки в плівках. Оптичне пропускання плівок CdS зростає зі збільшенням довжини хвилі у виміряній ділянці від 340 до 900 нм. На кривих пропускання є перегини в області 450-500 нм, що характерно для сполуки сульфіду кадмію. Визначені значення оптичної забороненої зони плівок CdS знаходяться в діапазоні 2,41-2,58 еВ.

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