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CHEMICAL DEPOSITION OF CDS FILMS FROM AMMONIAC-THIOUREA SOLUTIONS

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Досліджений вплив концентрації реагентів на зміну мутності в процесі хімічного осадження плівок сульфіду кадмію з аміачно-тіокарбамідних розчинів. За результатами досліджень зміни мутності розчинів в процесі осадження та морфології одержаного осаду визначені концентрації $CdCl_2$, NH_4OH і $CS(NH_2)_2$ при яких утворюється суцільна плівка CdS. Проведена робота дозволила встановити умови формування суцільних плівок CdS, що є передумовою для розробки контрольованого процесу виготовлення фотоелектричних перетворювачів

Ключові слова: фотоелектричні перетворювачі, сульфід кадмію, хімічне осадження, мутність, аміачно-тіокарбамідні розчини

Исследовано влияние концентрации реагентов на изменение мутности в процессе химического осаждения пленок сульфида кадмия из аммиачно-тиокарбамидных растворов. По результатам исследований изменения мутности растворов и морфологии полученного осадка определены концентрации $CdCl_2$, NH_4OH и $CS(NH_2)_2$, при которых происходит образование сплошной пленки CdS. Проведенная работа позволила установить условия формирования сплошных пленок CdS, что является предпосылкой для разработки контролированного процесса изготовления фотоэлектрических преобразователей

Ключевые слова: фотоэлектрические преобразователи, сульфид кадмия, химическое осаждение, мутность, аммиачно-тиокарбамидные растворы

1. Introduction

Interest in renewable energy sources (RES) that work based on the conversion of solar energy is predetermined by the negative trends in the development of traditional energy generation, which imply rapid depletion of natural resources and environmental pollution. A not less important driver for the development of RES is the grown of population on Earth, causing an annual increase in energy consumption at the level of 4–8 %. Increasing energy generation at such a pace, by burning hydrocarbon fuels, leads to serious environmental consequences. Emissions of CO_2, SO_2, SO_3, NO_x, as well as other substances, into the atmosphere lead to the deterioration of the environment. Along with gaseous emissions, energy generation is a producer of huge masses of solid wastes – tails, ash, and slag.

Photoelectric converters (PEC) have an almost unlimited resource of raw material in the form of solar radiation. PEC have no moving parts, hence their longevity. PEC are devices that are reliable and stable, which do not pollute the environment. Among the materials that can be used to create PEC, an important role belongs to CdS. Physical-chemical properties of CdS define its use in electronics as an active medium of semiconductor lasers, the base for photovoltaics, solar panels, photo- and light-emitting diodes, luminophores. CdS has a good light sensitivity and high adsorption capacity, reasonable width of forbidden zone, does not change its characteristics at high temperatures, which is important as PEC heat during operation.

To fabricate PEC based on CdS, sulfide films are deposited onto the substrate made of a metal or glass. Several

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methods were developed for obtaining CdS in the form of compact coatings using sophisticated techniques, which makes the films rather costly. From an economic and technological points of view, of interest is the method of chemical deposition of CdS films from solution. Technical implementation of the method is simple, which results in low cost of the films received. An important stage in the introduction of this method is to determine the mode of deposition of films, which primarily implies the establishment of optimal concentrations of chemical reagents.

2. Literature review and problem statement

In PEC, cadmium sulphide is used in the form of thin films whose structure affects its sensitivity to the effect of radiation. In turn, the structure of the film is determined by the size and shape of the CdS particles [1, 2]. Characteristics of the CdS particles depend on the method and mode applied for obtaining. The CdS films are derived by the following methods: vacuum evaporation, epitaxy, ion spraying, pyrolysis, chemical deposition, screen printing, deposition from the vapor phase, electrolysis.

Vacuum deposition method is implemented at high temperature in vacuum [3]. The CdS films obtained by this method have a thickness of 15–30 μm. The process requires the use of specialized equipment, rather costly and energy-intensive. Disadvantages of the method are uneven distribution of CdS at the substrate surface and solving the issues related to the contamination of a vacuum system with toxic cadmium.

Epitaxial deposition makes it possible to obtain films with large (≈1 μm) oriented grains. The application of a given method is limited to research purposes and obtaining films for special-purpose PEC [4]. Electrical properties of epitaxial CdS films are largely dependent on the conditions for their growth. The disadvantage of this method is the use of sophisticated apparatus design, which should include a vacuum system and specially prepared samples.

The process of ion spraying enables easy precise control over a film deposition rate. The process is inefficient in energy terms, because its main part is transformed into heat. This leads to a decrease in the deposition rate of films [5]. The films obtained by this method are composed of grains the size ≈0.1–0.5 μm.

Pulverization method followed by pyrolysis implies spraying of the solution containing soluble components onto the heated substrate. Grain size in the CdS films obtained by this method is 0.1–0.5 μm. A distinctive feature of films is their high adhesion to the substrate and continuity even at a small thickness [6]. The disadvantage of the method is in the large consumption of reagents to conduct the deposition and the need for rigorous safety measures during work.

Chemical deposition from the vapor phase implies that a substrate is exposed to the action of vapors from one or several compounds. Vapor phase components are the components of substance that condenses on the substrate as the product of a chemical reaction. At a high temperature of the substrate and a low density of the vapor, the films form that consist of large crystals; at a low temperature of the substrate and a high density of the vapor, the amorphous and microcrystalline layers are deposited [7]. The disadvantages of this method are the need for careful and continuous monitoring of the temperature, the concentration of components in the gas phase, and other process parameters. The type, size of the crystals, and the degree of contact between them, are sophistically dependent on the nature of a seeding surface, pressure, and temperature of the substrate.

Electrochemical method of obtaining CdS is divided, according to the type of the electrodes used, into electrolysis on inert electrodes and electrolysis with a soluble anode [8]. The use of inert anodes complicates the process because there is a need for constant monitoring of the composition of the electrolyte. Disadvantages of this method include hydrolysis of compounds, gassing on electrodes (including H_2S), porosity, and a low adhesion of films.

Screen printing makes it possible to receive cheap polycrystalline and uniformly-thick films [9]. The process is characterized by long duration and high temperatures. Thus, the described physical-chemical methods for obtaining thin CdS films have a number of shortcomings that contribute to the difficulty of obtaining films, uniform in composition and thickness, at large areas. First of all, it is the use of sophisticated technological equipment, large energy consumption, the need for precise control over process parameters.

Chemical deposition of CdS films from solution can be considered as a promising method [10, 11]. The process of a film formation implies the deposition of sulfide at the active regions in a substrate. Deposition rate and the resulting film thickness depend on the number of active centers and the degree of supersaturation of the solution. The repeated immersion of the sample in a fresh solution leads to that the further deposition takes place on the film, which has been already applied.

Despite the advantages of the method, data on the structure of CdS films, obtained by chemical deposition, are fragmented. There are no data on the impact of separate process parameters on the peculiarities of a film formation. Determining the conditions for the growth of CdS films is a prerequisite for the development of a controlled process of PEC fabrication.

3. The aim and objectives of the study

The aim of present work was to study influence of the concentration of reactants on the process of CdS film formation from ammonia-thiourea solutions.

To accomplish the aim, the following tasks have been set:

– to investigate effect of the composition of solution on a change in the turbidity of solution during formation of CdS;

– to determine working concentrations of reagent solutions at which deposition of continuous CdS films with a good adhesion to the substrate occurs.

4. Procedure for conducting experimental research

The process of CdS deposition was performed in a glass reactor with a periodic action. In the reactor, we fixed the sample manufactured by applying a titanium film on the glass substrate using vacuum evaporation. To obtain a film, certain amounts of reagent solutions ($CdCl_2$, NH_4OH, $CS(NH_2)_2$) were heated in separate containers. After reaching the required temperature, they were pumped into the reactor with a degreased sample. To prepare solutions, we used chemically pure reagents. The course of the process was controlled by measuring turbidity of the solution using the nephelometer NMF (lens No. 4, red light filter). Turbidity values in figures are given in relative units. In parallel with the measurement of turbidity, we conducted visual observations of changes in the sample surface and the solution. We acquired microphotographs of surface of the samples. A working reagent concentration in a solution was believed to be such as to ensure the formation of a solid CdS film with a thickness not less than 100 μm with a good adhesion to the substrate.

5. Results of studying the chemical deposition of CdS

Chemical reactions occurring in line with the heterogeneous mechanism are always accompanied by a qualitative and quantitative change in the composition of the liquid phase – a solution. It inevitably causes a change in the physicochemical characteristics of a solution, which can be used both for research purposes and to monitor the progress of the process. Different characteristics (potential, density, conductivity, turbidity) can be used as a tool to study chemical reactions in solutions. Examples include a study in which measuring the potential made it possible to track the progress of the process and boundaries of possible utilization of the heterophase system formed by a solid deposit and a liquid medium [12]. In this paper, a parameter that made it possible to track the course of CdS formation was chosen to be turbidity of the solution. A prerequisite for this choice were the data from visual observations, which showed that the CdS deposition is accompanied by a change in the transparency and color of the solution. It was suggested that this observation could be used to monitor the process by measuring the turbidity of a solution, which would make it possible to associate its change with certain stages of the course of the process. CdS deposition is conducted from multicomponent solutions, which is why the influence of the following reagents was investigated: $CdCl_2$, NH_4OH, and $CS(NH_2)_2$. The study produced dependences of turbidity of a solution on time of aging the samples in the solution, which, together with the results of visual observations, made it possible to identify patterns in the CdS formation and establish working concentrations of components in solution.

The most important stage in forming a film, which defines its structure, is the emergence of primary CdS particles. As a result of this process, the sites of substrate growth undergo the formation of two- and three-dimensional CdS embryos. Usually, growth sites are the regions of a surface with an elevated value of free energy, for example, structural defects, inclusions, intra-grain boundaries. Due to the formation of zones of supersaturation, in the vicinity of growth sites, simultaneously with the emergence of particles at the surface, there is the formation of colloidal CdS particles Cds in the bulk of solution. The process is accompanied by a change in the physical-chemical characteristics of the solution, specifically turbidity, which one can use to track the progress of a reaction. The obtained results of measuring the turbidity of solution in the process of CdS film deposition at different values of concentrations of $CdCl_2$ are shown in Fig. 1, *a*.

The dependences obtained indicate that an increase in the concentration of $CdCl_2$ causes an increase in the initial rate of a CdS film formation. This is due to the fact that the accumulation of colloid-dispersed CdS in solution proceeds at the initial acceleration, that is, it is autocatalytic. Indeed, visual observations show that depending on the composition of the solution, the initial 50–150 minutes of the process are characterized by a decrease in its transparency and the emergence of yellow coloring, characteristic of the CdS deposit. Decomposition of thiourea in alkaline solution with the formation of S^{2-} ions occurs in the presence of $Cd(OH)_2$, which forms during decomposition of ammonium cadmium complexes. The rate of decomposition increases with an increase in the concentration of $CdCl_2$.

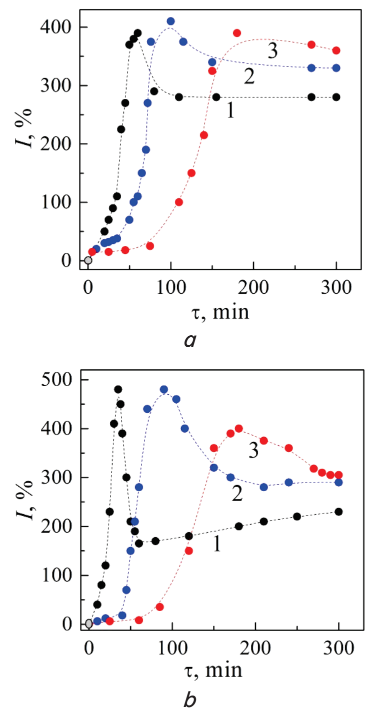

Fig. 1. Change in turbidity of solution at a CdS film deposition; *a* – dependence of turbidity at different $c(CdCl_2)$; $c(CdCl_2)$, g·l^{-1}: 4.0(1); 6.0(2); 7.6(3); *b* – dependence of turbidity at different $c(CS(NH_2)_2)$; $c(CS(NH_2)_2)$, g·l^{-1}: 8.4(1); 7.6(2); 6.8(3). Dots show experimental data; a dotted line, a possible approximation to a functional dependence, was derived using the polynomial approximating function

The dependences obtained, along with performed visual observations of the solution and the surface of samples, suggest that the process of a film formation consists of the following stages. The first stage corresponds to the formation of colloidal CdS particles. Turbidity of solution in this case increases sharply (Fig. 1). The concentration of reactants in the layer of solution, adjacent to the sample's surface, reduces. This leads to a decrease in the rate of formation of new particles and the formation of large agglomerates from the CdS particles already formed. When looking at the substrate, its surface reveals separate grains of CdS. This process is matched in time by a maximum on dependences. Subsequent formation of a film enters a stationary mode, characterized by equality of rates in the consumption of reagents for the formation of CdS and diffusion of reagents from the bulk of solution. A sample's surface is gradually covered by a CdS film; turbidity of the solution decreases to a certain value and remains approximately constant afterwards. In the process of a film formation, important role belongs to the rate of accumulation in the solution of colloid-dispersed CdS. It was established that an increase in the rate of particle accumulation leads to a decrease in the film thickness. For a series of $CdCl_2$ concentrations, the following relations are found (*s*, g·l^{-1} –

δ, μm): 4.0–61; 6.0–96; 7.6–112. To obtain a thick film, it is necessary to use solutions with a lower value of $c(CdCl_2)$. A decrease in the concentrations of $CdCl_2$ below 6.0 g·l^{-1} is impractical as it leads to forming the films in the form of a mixture of dense crystalline agglomerates and a powder of CdS. An increase in $c(CdCl_2) > 7.0$ g·l^{-1} is accompanied by the hydrolysis of chloride with a $Cd(OH)_2$ precipitate.

The concentration of thiourea also affects the formation of a CdS film (Fig. 1, *b*). The Figure shows that an increase in the concentration of $CS(NH_2)_2$ predetermines the growth of rate in the formation of colloidal CdS particles. This is explained by that $CS(NH_2)_2$ is the source of the S^{2-} ions. Studying the films obtained showed that an increase in the concentration of $CS(NH_2)_2$ above g·l^{-1} is detrimental. The films received under these conditions are a mixture of crystals and amorphous powder whose share increases with an increase in the concentration of thiourea.

An important parameter is the concentration in a solution of ammonia. In an ammonia solution, cadmium is in the form of a series of complexes of the $[Cd(NH_3)_6]^{2+}$ type. Deposition of CdS is accompanied by the dissociation of these ammonia complexes. Because ammonia participates in ionic equilibria, its concentration has an impact on the process. The results of studying a change in the turbidity of solutions at different values of $c(NH_4OH)$ are shown in Fig. 2. The rate of deposition process at $c(NH_4OH) = 0.3$ g·l^{-1} almost does not differ almost from the rate of the process at 0.6 g·l^{-1}, and at concentrations of 1.0 g·l^{-1} it is twice large. It was established that the working concentration is $c(NH_4OH) = 0.6$ g·l^{-1}. At $c(NH_4OH) =$ $= 0.3$ g·l^{-1} the process is faster and is accompanied by solution turbidity and a white precipitate of $Cd(OH)_2$ due to a lack of NH_4OH for the formation of ammoniate. The CdS films in this case are of poor quality. Increased concentration of NH_4OH to 1.0 g·l^{-1} leads to the overconsumption of a reagent.

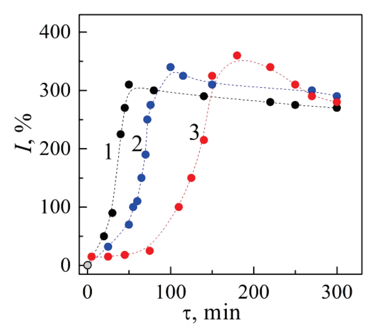

Fig. 2. Change in the solution turbidity during a CdS film deposition. $c(NH_4OH)$, g·l^{-1}: 1.0(1); 0.6(2); 0.3(3). Dots show experimental data; a dotted line, a possible approximation to a functional dependence, was derived using the polynomial approximating function

6. Discussion of results of studying the deposition of CdS films

There were proposed several possible schemes for the formation of cadmium sulfide. The most widespread is the mechanism based on the assumption on interaction between Cd^{2+} and $CS(NH_2)_2$ at which Cd^{2+} reacts directly with the S^{2-} ion. The result of the process is the formation of cyanamide, cyanide, thiocyanate, and hydrogen sulphide. The process of transition of $CS(NH_2)_2$ into NH_4SCN implies that three out of the four molecules of $CS(NH_2)_2$ are isomerized, and one is decomposed. The proposed scheme does not take into consideration the formation of complexes of cadmium with $CS(NH_2)_2$, characteristic of these solutions [13]. The most probable is the mechanism of CdS formation via an intermediate formation of thiourea, which is consistent with the results of chemical analysis of the working solution (Table 1).

Table 1

Qualitative and quantitative composition of solution

Component	*c*, mg·l^{-1}
S^{2-}	224.0
SO_4^{2-}	55.8
SO_3^{2-}	640.0
CO_3^{2-}	7032
CNS^-	0.011
HCN	0.001
$S_2O_3^-$	3,470

The possibility of thiourea formation, the existence of which cannot be determined experimentally, is confirmed by the high content of carbonates in solution, which are the product of decomposition of unstable thiourea [14].

The preconditions put forward suggest the scheme for CdS formation, in which the formation proceeds via the formation of thiourea. In an alkaline medium, $CS(NH_2)_2$ forms thiourea, which, by interacting with $Cd(NH_3)_6^{2+}$, form a layer of CdS. An increase in the rate of thiourea formation leads to that the rate of its consumption for a CdS film formation becomes less than the rate of a side process – decomposition with the formation of carbonate and sulfide-ion, which leads to the formation of powdered CdS:

$$CS(NH_2)_2 + 3H_2O \rightarrow HCSO^{2-} + OH^- + 2NH_4^+. \quad (1)$$

$$HCSO^{2-} + OH^- \rightarrow HCO^{3-} + HS^-. \quad (2)$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O. \quad (3)$$

In the presence of ammonia, cadmium forms ammoniates that interact with $HCSO^{2-}$ and S^{2-}, forming a film or a crystalline powder of CdS:

$$Cd^{2+} + 6NH_3 \rightarrow [Cd(NH_3)_6]^{2+}. \quad (4)$$

$$[Cd(NH_3)_6]^{2+} + HCSO_2^- + OH^- \rightarrow CdS + HCO_3^- + 6NH_3. \quad (5)$$

$$Cd(NH_3)_6^{2+} + S^{2-} \rightarrow CdS + 6NH_3. \quad (6)$$

The formed by-products include sulphates, sulphites, and thiosulphates, as well as hydrosulfates and hydrosulfites, which are in balance with them. Formation of thiocyanates, cyanides and cyanamide is unlikely, which is confirmed by data on the analysis of these substances in solution.

The films, obtained by chemical deposition from thiocarbamide-ammonium solutions, possess *n*-type conductivity and specific resistance at the level of 10^7–10^9 Ohm·cm, which, upon annealing in vacuum, decreases to 1–10 Ohm·s. Following the annealing, the films demonstrate high photosensitivity. The proposed method has several advantages. These include simple hardware design, cheapness, the possibility of obtaining films with a preset thickness at the samples of a large area.

Thus, the study we conducted shows that the measurement of turbidity can be used to control the process of a CdS film formation from thiourea-ammoniac solutions. The application of turbidity as a parameter to control the process is convenient due to the possibility for operative determining of this characteristic in comparison with the methods to control the process when applying the films by pyrolysis or vacuum spraying where it is necessary to ensure that the equipment is airtight because of the toxicity of cadmium.

Establishing the possibility of using the magnitude of turbidity of solutions to monitor the progress of CdS formation is a prerequisite for the establishment of optimum conditions for obtaining CdS films, which is aimed at ensuring rational technological indicators of the process. The deeper research necessitates the following:

– to establish the effect of solution components on the course of the process;

– to establish the effect of solution components on the physical characteristics of the obtained films;

– to find a relationship between the structure, morphology, and properties of films, as well as the influence of deposition conditions on them.

7. Conclusions

1. We have investigated influence of the concentration of separate components of solution on the process of CdS formation using a method of chemical deposition from ammonia-thiourea solutions. The result of parallel visual observations and measurement of turbidity of solution is that the dependences of turbidity at CdS deposition could be used to monitor the course of the process. The dependences demonstrate a characteristic form, at which one can highlight regions, corresponding to the emergence of colloidal CdS particles, to the particle agglomerate formation, and to the stationary mode in the film formation.

2. Our research determined working concentrations of $CdCl_2$, NH_4OH and $CS(NH_2)_2$, which are close to 7.0; 0.6, and 7.0 $g \cdot l^{-1}$, respectively. At these concentrations, there is the formation of continuous CdS films with a good adhesion to the base. An analysis of the composition of solution allowed us to suggest a CdS formation scheme at which a film formation occurs via the formation of thiourea. In an alkaline medium, $CS(NH_2)_2$ forms thiourea, which, by interacting with $Cd(NH_3)_6^{2+}$, form a CdS film.

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