

## Electrodeposition kinetics, structure and optical properties of cadmium sulfide films

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The selection of the optimal regimes for electrodeposition of near-stoichiometric cadmium sulfide (CdS) layers has been provided by means of voltammetric studies of cadmium and sulfur separate and joint electrodeposition kinetics in aqueous chloride solutions. Optical analysis has discovered that the deposited films were transparent, characterized by straight allowed optical transitions and band gap typical for cadmium sulfide. X-ray diffraction results have shown that these films consist mainly of hexagonal modification CdS nanocrystals.

С помощью вольтамперометрических исследований процессов отдельного и совместного электроосаждения кадмия и серы из водных хлоридных растворов обеспечен выбор оптимальных режимов получения близких к стехиометрическим слоев сульфида кадмия (CdS). Оптический анализ обнаружил, что электроосажденные пленки были прозрачными, характеризовались прямыми разрешенными оптическими переходами и шириной запрещенной зоны, типичными для сульфида кадмия. Результаты рентгенодифрактометрического анализа показали, что полученные пленки состояли преимущественно из нанокристаллов CdS гексагональной модификации.

Recently, the electrochemical cathodic deposition of semiconductors is used widely in production technologies of thin film devices, in particular, photovoltaic devices (PVD). By controlling the process parameters such as electrolyte composition and working electrode potential, it is possible to obtain semiconducting layers with pre-specified properties. For example, the electrodeposition of cadmium sulfide (CdS) films is believed to be among the most prospective ways to buffer layers for PVD on the base of cadmium telluride or copper indium diselenide [1–5].

At the same time, the investigation of electrochemical mechanisms involved in the cadmium sulfide electrodeposition was not an object of sufficient attention yet. As a consequence, an empirical choosing of the regimes providing stoichiometric layers of cadmium sulfide [1, 2] required optimization of electrodeposition regime in the case of even insignificant deviations of techno-

logical process. So, the aim of this work is to study in detail the CdS electrodeposition process kinetics basing on voltammetric investigations of separate and joint cathodic reduction of cadmium and sulfur to provide a scientific approach for optimization of the cadmium sulfide crystal film electrodeposition.

The kinetics of CdS electrodeposition was studied using a potentiostat by voltammetric analysis with lineal potential scanning (VA) and by cyclic voltammetric analysis (CVA) [6, 7]. To that end, glass plates of 1 cm<sup>2</sup> area coated by reactively sputtered 500 nm thick titanium nitride that had layer resistance less than 1 Ohm were used as cathodes in three-electrode electrochemical cell. As the reference electrode and counter electrode, were used saturated Ag/AgCl electrode (SAE) and platinum electrode of 30 cm<sup>2</sup> area, respectively. The electrolyte temperature was maintained at 50°C using a thermostat. The solutions were pro-

tected against mixing to prevent the convective transfer (except the especially mentioned cases). To avoid the migration during the voltammetric experiments, all the solutions contained 0.1 M  $\text{Na}_2\text{SO}_4$ . Electrochemical processes were studied in the following solutions: 1) solution corresponding to electrolyte for cadmium sulfide deposition containing 0.2 M  $\text{CdCl}_2$ , 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ ; 2) partial cadmium solution: 0.2 M  $\text{CdCl}_2$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ ; 3) partial sulfur solution: 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ ; 4) background solution: 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ . The polarization voltage scanning rates ( $\nu$ ) were from 2 mV/s up to 500 mV/s, the potential scanning range  $E_c$  was from 0.2 V up to -1.4 V or from 0.2 V up to -1.0 V (here and below, all potentials are displayed with regard to SAE).

The CdS films were electrodeposited in potentiostatic regime in the same three-electrode cell without any stirring of the electrolyte that consisted of 0.2 M  $\text{CdCl}_2$ , 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.01 M  $\text{H}_2\text{SO}_4$  (pH 2). As substrates, were used glass plates coated with the above-mentioned titanium nitride layers or by magnetron-sputtered transparent indium-tin oxide (ITO) conductive layers. The electrolyte temperature was 50°C, the cathode potential  $E_c = -0.65$  V, the electrodeposition time was 15 min.

X-ray examinations (XRD) of crystal structure of the film samples were carried out using a DRON-4 diffractometer in characteristic radiation  $\text{FeK}_\alpha$  ( $\lambda = 1.93604 \text{ \AA}$ ) according to  $\theta$ - $2\theta$  scheme with Bregg-Brentano focusing. The scanning step was 0.02 deg; the exposure time 1 s. The phases of obtained compounds were identified by comparing the experimental data with crystal lattice parameters of cubic (sphalerite) and of hexagonal (wurtzite) CdS modifications in accordance with JCPDS No.10-454 and No.6-0314, respectively. To measure the optical transmittance  $T$  of electrodeposited films, an SF-18 spectrophotometer was used. The thicker CdS film on the glass/ITO substrate was placed in the working light channel, while a thinner CdS film on the glass/ITO substrate was placed in the reference channel.

The voltammetric studies have shown that for the background solution, two current peaks are revealed in cathodic branches of cyclic voltammograms ( $I$ - $V$ -curves) (Fig. 1). The first weak current peak corresponds to an irreversible electrochemical

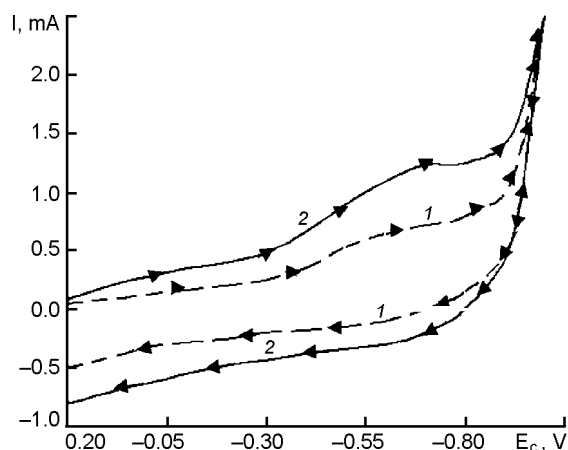
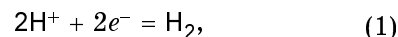


Fig. 1. Cyclic voltammograms of the background solution at potential scanning rates  $\nu$  (mV/s): 50 (1); 100 (2).

process followed by chemical dimerization reaction. First, it shifts to wards negative potentials as the potential scanning rate increases from 2 mV/s to 500 mV/s, so that the cathode half-peak potential  $E_{cp/2}$  changes from -0.4 V to -0.6 V. Second, the differences between potentials of cathodic peaks and cathodic half-peaks are large enough. These differences change depending on  $\nu$ , but is approximately about 0.1 V, thus exceeding more than thrice the value for reversible process. Third, these peaks are absent in anodic branches of cyclic voltammograms of the background solution.

Taking into account that the half-peak potential for the irreversible electrode process followed by chemical dimerization reaction is always shifted towards negative values as compared to the reversible process [6, 7] and in accordance with the standard potential data [8, 9], the first peak in the background solution can be ascribed to the reaction



for which the equilibrium cathode potential in this solution, as calculated using the Nernst equation [8], is -0.33 V. The shift of this peak towards negative potentials is a result of overvoltage, which for irreversible processes followed by dimerization amounts at least 0.1 V [6]. The intensity of this peak is low, because the solution is only slightly acidic (pH 2).

The current increase in the background solution at potentials more negative then -0.9 V is intense enough. According to our calculations, it corresponds to water decom-

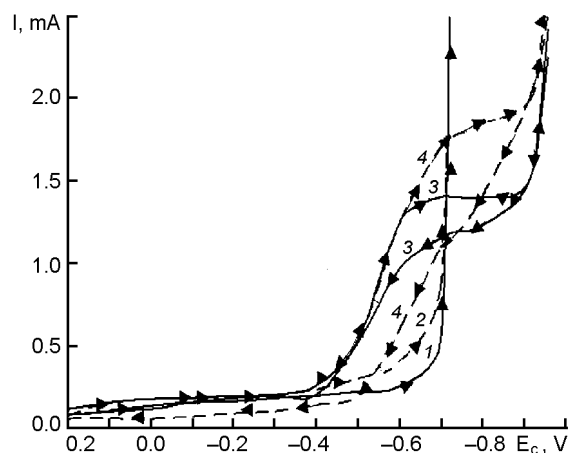
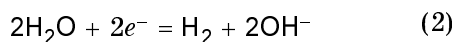


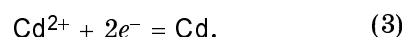
Fig. 2. Voltammograms of cadmium partial solution (0.2 M  $\text{CdCl}_2$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ ) at potential scanning rates  $v$  (mV/s): 5 (1); 50 (2); and cyclic voltammograms of sulfur partial solution (0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ ) at potential scanning rates  $v$  (mV/s): 5 (3); 50 (4)

position with the hydrogen release according to reaction:



for which the standard potential is  $-1.03$  V [8].

In voltammograms for cadmium partial solution (Fig. 2, curves 1, 2), the first weak hydrogen reduction peak corresponding to reaction (1) is also observed. Then, a sharp current increase arises independent from the scanning rate at potentials more negative than  $-0.7$  V, that, according to [7, 8], evidence the reversible cathodic process of cadmium reduction:



According to the Nernst equation [8, 9], the standard potential of reaction (3) is  $-0.63$  V.

Voltammograms of thiosulfate reduction in sulfur partial solution are shown in Fig. 2 (cyclic curves 3 and 4). According to calculations described in [6, 7], the first cathodic curve in sulfur partial solution corresponds to the irreversible electrode process. First, the potential of cathode peak ( $E_p$ ) becomes and more negative as  $v$  increases. Second, the difference ( $E_p/2 - E_p$ ) exceeds 0.1 V. Third, the difference between potentials of cathodic and anodic peaks is a function of the polarization voltage scanning rate.

The most probable electrochemical process in this case is [8],

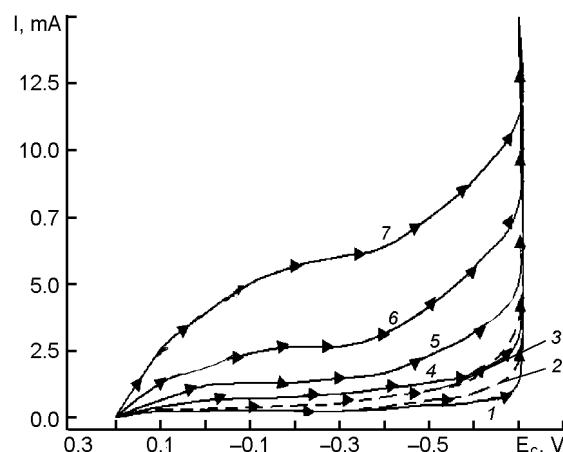
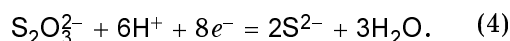


Fig. 3. Voltammograms of solution corresponding to electrolyte for CdS electrodeposition (0.2 M  $\text{CdCl}_2$ , 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 M  $\text{Na}_2\text{SO}_4$ , 0.01 M  $\text{H}_2\text{SO}_4$ ) at potential scanning rates  $v$  (mV/s): 5 (1); 20 (2); 5 with electrolyte stirring (3); 50 (4); 100 (5); 200 (6); 500 (7)

The equilibrium potential for reaction (4) calculated using the Nernst equation [8] is  $-0.22$  V, but, due to irreversibility of electrochemical process (4) in this solution, an overvoltage exceeding 0.2 V is registered. The sharp current increase in the sulfur partial solution occurs at the same potentials (more negative than  $-0.9$  V) as in background solution, so, it corresponds to water decomposition and hydrogen release (2).

As is seen from Fig. 3, the  $I$ - $V$ -curves for cathodic processes in the solution corresponding to the electrolyte for cadmium sulfide deposition include waves typical of thiosulfate-ion reduction according to reaction (4) and current increases corresponding to cadmium ion reduction according to reaction (3). Since the potentials at which the reactions (3) and (4) take place are the same in the electrolyte for CdS deposition and in the partial solutions of cadmium and sulfur, we can conclude that at potentials more negative than  $-0.4$  V thiosulfate ions in the electrolyte are reduced into sulfide ions at the titanium nitride electrode surface, the reduction of cadmium ions and the metal film formation on the cathode is possible only at potentials more negative than  $-0.7$  V. Note that forced mixing of the electrolyte by magnetic stirrer results in a regular current increase due to delivery of larger amounts of thiosulfate ions to the cathode surface, but does not change the reduction waves and the potentials at which thiosulfate ions and cadmium ions are reduced (Fig. 3, curve 3). The above allows us to

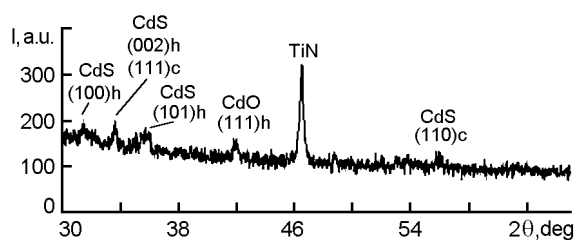
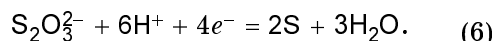


Fig. 4. XRD of CdS on TiN substrate in characteristic radiation  $\text{FeK}\alpha$ .

conclude that in the electrolyte for CdS film deposition, in cathode potential interval from  $-0.4$  V up to  $-0.7$  V the irreversible electrochemical reduction of thio-sulfate ions in accordance with reaction (4) followed by chemical reaction of cadmium sulfide formation take place:



So, comparing the results of separate reduction of cadmium and sulfur in their partial solutions with the processes occurring in the solution corresponding to the electrolyte for CdS deposition, we can conclude that in the electrolyte for cadmium sulfide electrodeposition, the semiconducting material without considerable amounts of impurities can be obtained in the cathodic potential range from  $-0.4$  V to  $-0.7$  V. The rate of CdS electrodeposition increases as the cathodic potential is shifted to more negative values. However, at cathode potential equal to  $-0.7$  V, the electrodeposition of CdS films with cadmium additive is possible. Therefore, the studies of electrochemical mechanisms resulting in formation of stoichiometric cadmium sulfide films, the cathodic potentials most suitable from the technological point of view are from  $-0.45$  V to  $-0.65$  V. At more positive potentials, the electrodeposition of CdS will not occur. According to [8], at these potentials only cathodic electrodeposition of small amounts of sulfur is possible according to reaction:



At cathode potentials more negative than  $-0.7$  V, the films will be enriched in cadmium. On the one hand, the cadmium atoms can be obtained following reaction (3). On the other hand, the reaction (2) will be accelerated at negative potentials and, as a consequence, the  $\text{Cd}(\text{OH})_2$  impurity will appear in the films due to interaction of hydroxyl groups with  $\text{Cd}^{2+}$ :

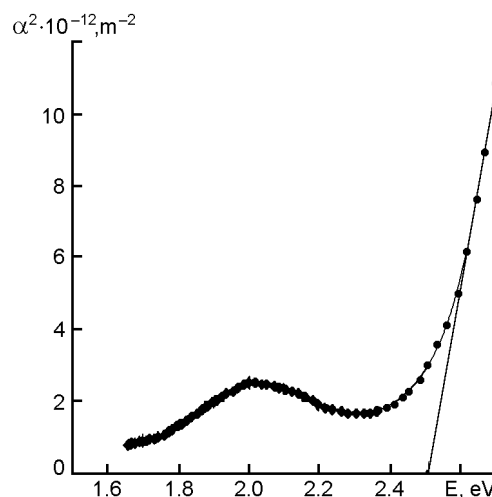
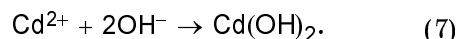


Fig. 5. Absorption coefficient in power index 2 as a function of incident light energy for CdS film on ITO substrate.



Note that at negative potentials, the cadmium sulfide films may be porous due to intensive evolution of gaseous hydrogen on the cathode.

Analyses of structure and optical properties of the films electrodeposited in the optimal potential range have allowed to identify these layers as cadmium sulfide. On X-ray pattern of the CdS/TiN composite film obtained at cathode potential  $-0.65$  V (Fig. 4), one intense peak at  $2\theta = 46.48$  deg and five weak peaks at  $2\theta$ , deg =  $31.36$ ;  $33.66$ ;  $35.64$ ;  $41.98$ ;  $55.97$  are seen. The intense peak seems to correspond to the (111) TiN plane. The weak peak at  $2\theta = 41.98$  deg can be ascribed to the (111) plane of cadmium oxide (JCPDS 5-640). According to literature data and to studies of electrochemical kinetics, the presence of the CdO phase is caused by air oxidation of cadmium sulfide and by reaction (7) and subsequent chemical process of  $\text{Cd}(\text{OH})_2$  decomposition, water release and cadmium oxide formation. The other peaks are formed by planes (100), (002), (101), (110) of CdS hexagonal modification. These peaks are very broad due to nanocrystal structure of electrodeposited cadmium sulfide layers.

Optical analysis of the cadmium sulfide films obtained at the same cathodic potential but on the ITO substrate had shown that the maximum optical transmittance in the wavelength range  $450 \leq \lambda \leq 750$  nm is about 76 %. According to the calculations

made in accordance with the procedure published in [11], thickness of these films is about 0.3  $\mu\text{m}$ . Graphic analysis of  $T = f(\lambda)$  function in  $\alpha^m = f(h\nu)$  coordinates (where  $\alpha$  is the optical absorption coefficient;  $h\nu$ , the incident light quantum energy;  $m$ , power index depending on the optical transition type) (Fig. 5), according to standard procedure [12], allowed to reveal that the films are characterized by straight allowed optical transitions and have the band gap value  $E_g = 2.5$  eV typical of CdS.

So, the XRD and optical analyses confirm that the studied cadmium sulfide electrochemical deposition kinetics has formed a scientific basis for optimal regime that provides manufacturing of sufficiently transparent cadmium sulfide layers that consisting mainly of hexagonal CdS nanocrystals. The main constituents of that regime are the electrolyte composition (0.2 M  $\text{CdCl}_2$ ; 0.02 M  $\text{Na}_2\text{S}_2\text{O}_3$ ; pH 2) and the cathodic potential  $E_c$  range (from -0.45 V to -0.65 V).

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## Кінетика електрохімічного осадження, структура і оптичні властивості плівок сульфїду кадмію

*Н.П.Клочко*

За допомогою вольтамперометричних досліджень процесів окремого та сумісного електроосадження кадмію і сірки з водних хлоридних розчинів забезпечено вибір оптимальних режимів виготовлення близьких до стехіометричних шарів сульфїду кадмію (CdS). Оптичний аналіз виявив, що електроосаджені плівки були прозорими, характеризувалися прямими дозволеними оптичними переходами та шириною забороненої зони, типовими для сульфїду кадмію. Результати рентген-дифрактометричного аналізу показали, що одержані плівки склалися переважно з нанокристалів CdS гексагональної модифікації.