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## CADMIUM ELECTROCHEMICAL REDUCTION IN $\text{CdCl}_2$ SOLUTIONS IN DIMETHYLSULFOXIDE AND MORPHOLOGY OF CATHODE DEPOSIT

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**Abstract.** Cadmium reduction in solutions at steady-state and pulse electrolysis has been studied. It was established that polarization results in cadmium formation at potentials  $\sim 1$  V larger than equilibrium one. In 0.25-1.0 molar solutions of  $\text{CdCl}_2$  concentrated depolarization leads to removal of the beginning of cadmium reduction by  $\sim 0.3$  V. Photographs of SEM are presented and effect of electrolysis characteristics on the morphology of cathode deposit is shown.

**Key words:** cadmium, DMSO, electrolysis, pulse current, morphology

### 1. Introduction

Last decade polycrystalline semiconductor films cause the great interest due to the possibility of their use for production of large areas sun energy transformers and lower cost value in comparison with single-crystal ones [1-3]. Among well known obtaining methods of polycrystalline films (physical, physical-chemical and chemical methods), electrochemical formation has a number of advantages. First of all, it is cheap technological equipment and low cost value of the process [1, 2]. We should also mention the development of the new trend in semiconductor electrochemistry: semiconductor obtaining and operation in the medium of organic solvents [4-7]. The latter allows to prevent a range of by-side chemical and electrochemical processes results in obtaining of cathode deposit of high purity and proceeding of electrode reactions which are impossible or difficult in aqueous solutions [8, 9]. The aim of this work is investigation of electrochemical deposition of cadmium, which is substantial component in formation of semiconductor films, namely CdTe in aprotic solvents. This work continues systematic researches concerning metals [10, 11] and semiconductors [12] obtaining by electrolysis in nonaqueous medium.

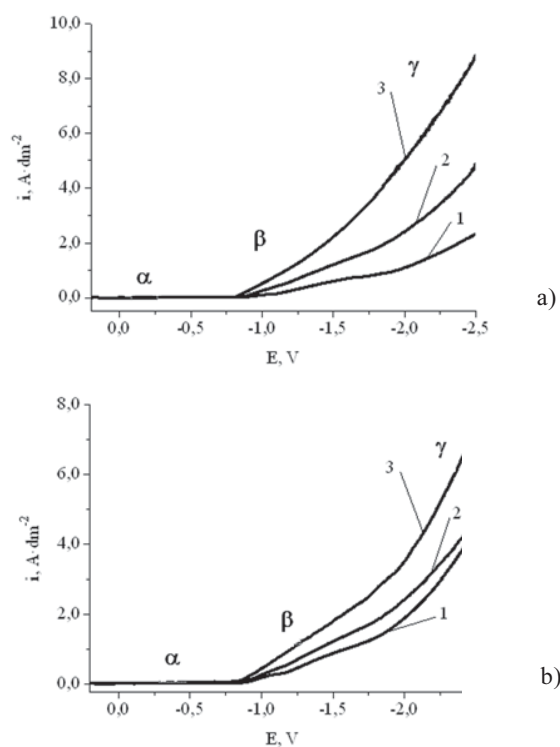
### 2. Experimental

Experiments were carried out in 0.25-1.0 molar solutions of  $\text{CdCl}_2$  in dimethylsulfoxide (DMSO) within temperature range of 293-333 K. Cadmium chloride and organic solvents used were chemically pure. The research of electrode processes was carried out using IPC-Pro potentiostat with standard electrochemical compartment, auxiliary cadmium electrode and comparative chloride-silver electrode. Polarization curves were photographed with scanning rate  $2 \text{ mV}\cdot\text{s}^{-1}$ . Graphite rod with diameter 6 mm and fluoroplastic insulation was the main electrode. Before every experiment graphite samples were scraped with fine-grained emery paper, then polished with velvet and washed with isopropanol. The morphology of cathode cadmium was studied using samples obtained by electrolysis in hydrostatic mode with soluble cadmium anode. The current was steady-state ( $E=\text{const}$ ) and intermittent with pulse duration 0.01-0.1 s and pause duration 0.1-1.0 s. Pulses had squared shape. Cathode cadmium was rinsed with DMSO and isopropanol and dried with air at 323 K staying over graphite sample. The cadmium surface was studied using REMMA-102-02 scanning microscope.

### 3. Results and Discussion

We can see from Fig. 1 that characteristics of polarization curves are similar in the wide range of  $\text{CdCl}_2$  concentration and temperatures and have three express zones. The first one (zone  $\alpha$ ) represents a plateau at interval of cathode potentials from stationary value ( $E_s$ ) to  $-0.8 - -1.2$  V and corresponds to low current values (up to  $0.02 \text{ A}\cdot\text{dm}^{-2}$ ) caused by considerable cathode polarization. The second and third zones correspond to the sharp growth of cathode currents within potential ranges from  $-0.8 - -1.0$  V to  $-1.7 - -1.8$  V (zone  $\beta$ ) and over  $-1.7 - -1.8$  V (zone  $\gamma$ ). The last zone characterizes cathode depolarization. The reason of depolarization is that polar O-donor molecules of DMSO are adsorbed over

undercoat surface resulting in electrode polarization. The increase of cathode potential shifts the *adsorption of DMSO molecules!desorption* equilibrium to the right. At definite E value (passage between a and b zones) repulsion forces between molecules of aprotic solvent and cathode surface predominates attraction forces resulting in decrease of adsorption factor. Taking into consideration weak donor-acceptor bond between Cd-ion and DMSO in  $[\text{Cd}(\text{DMSO})_n]^{2+}$ , the effect of organic solvent is diminished essentially at values of cathode potentials higher than -0.8 – -1.0 V. It causes formation of heterogeneous deposit with fragments of compact and friable cadmium (zone  $\beta$ ) or formation of only dispersed deposit (zone  $\gamma$ ).

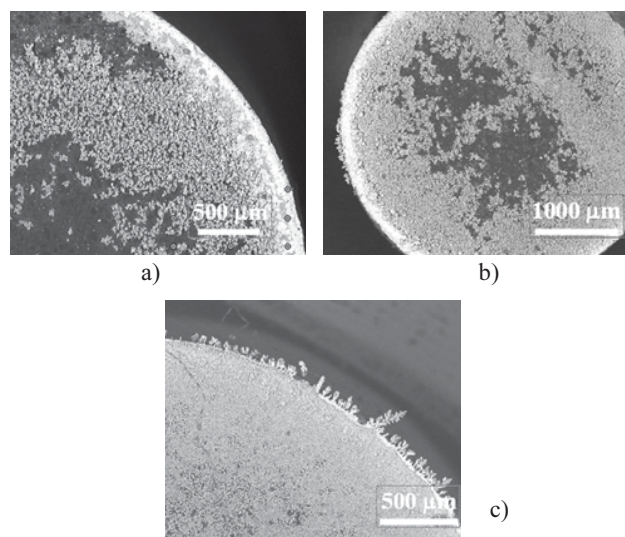


**Fig. 1.** Cadmium cathodic polarization curves in solutions of  $\text{CdCl}_2$  in DMSO

- a)  $T = 313 \text{ K}$  in  $\text{CdCl}_2$  concentrations ( $\text{mol}\cdot\text{dm}^{-3}$ ):  
 1 – 0.25; 2 – 0.5; 3 – 1.0;  
 b)  $0.5 \text{ M CdCl}_2$  at temperatures (K):  
 1 – 293; 2 – 313; 3 – 333

The increase of  $\text{CdCl}_2$  concentration removes the beginning of active cadmium reduction to less cathode potentials (Fig. 1a). So, if in  $0.25 \text{ M CdCl}_2$  breakpoint of polarization curve is at  $E = -0.95 \text{ V}$ , then in  $0.5$  and  $1.0 \text{ M}$  solution breakpoints are at  $E = -0.85$  and  $-0.8 \text{ V}$ , respectively. This fact indicates the considerable part of concentrated polarization in total cathode polarization of cadmium. The temperature slightly influences the displacement of passage from polarization to active cadmium deposition (Fig. 1b), indicating the process proceeding in diffusion area. The analogous influence of

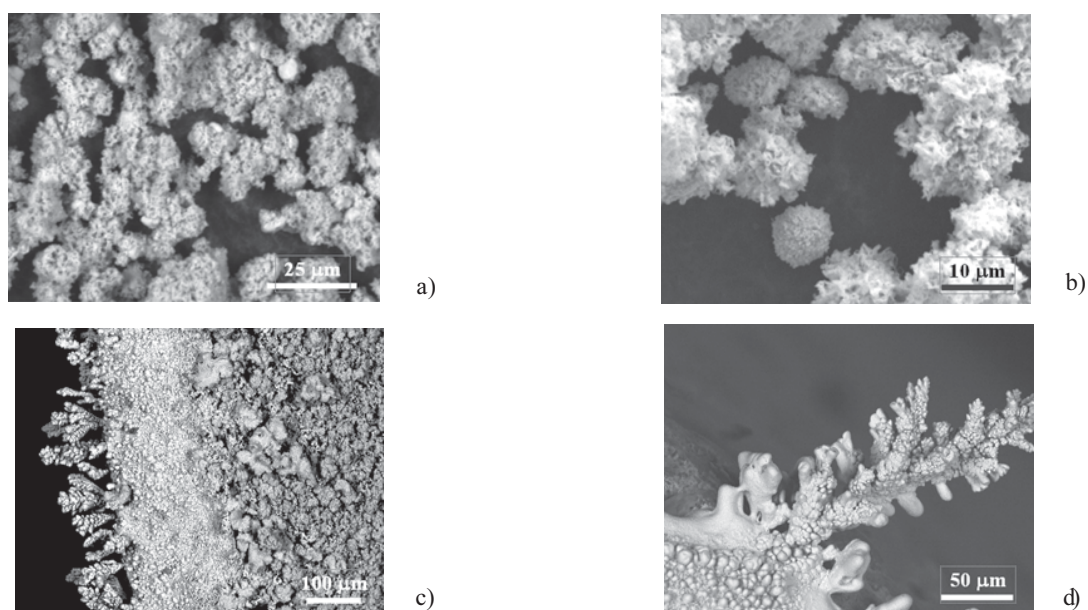
temperature results in high increase of cathode currents in the section of metal active reduction ( $80\% \cdot 10\text{grad}^{-1}$ ). It is connected with decrease of DMSO viscosity at heating and corresponding enhancement of electrolytic convection.



**Fig. 2.** Cadmium deposit distribution over undercoat and its characteristic obtained under steady-state (a, b) and pulse (c) modes of electrolysis in  $1.0 \text{ M CdCl}_2$  in DMSO at  $313 \text{ K}$  at cathode potentials (V): a) 1.5; b) 2.0; c) 2.5

Insignificant polarization influence of dimethylsulfoxide medium becomes apparent on the nature of cathode cadmium. First of all, it is nonuniform distribution of cadmium deposit over undercoat (Fig. 2). In particular, compact packing of the surface with deposit takes place only by perimeter of cathode within wide range of potentials. The part of deposited cadmium decreases with approaching to the center. However, there is tendency towards uniform cadmium deposition over whole cathode surface with increase of cathode potential (Figs. 2a and b), especially at electrolysis under pulse mode (Fig. 2c). We explain this, first of all, by diffusion factor, because at electrolysis under mode of high current density it is better to supply cadmium ions by perimeter of cathode.

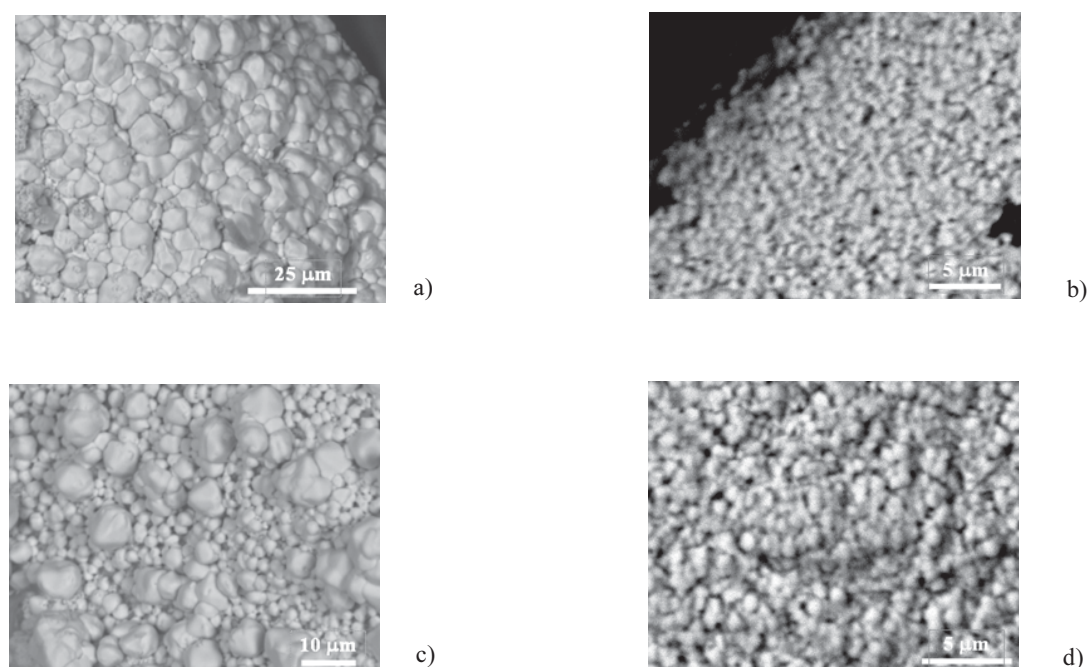
Diffusion factor is also the reason of dispersed cadmium formation even at low values of current density (Fig. 3). Pulse current (Fig. 3a) in comparison with steady-state current (Fig. 3b) forms more homogeneous deposit. This fact is explained by equal concentrations of cadmium ions in near-surface zone at relatively large ratio between pause and pulse duration during electrolysis. The increase of cathode potential (current density) results in formation of compact cadmium by perimeter of cathode and coarsely dendritic cadmium under steady-state and pulse modes of electrolysis (Figs. 3c and d).



**Fig. 3.** Morphology of dispersed cadmium deposit obtained under steady-state (a, c) and pulse (b, d) modes of electrolysis in 1.0 M  $\text{CdCl}_2$  in DMSO at 313 K at cathode potentials (V): a), b) 1.5; c) 2.0; d) 2.5

The researching results show that current form considerable affects the morphology of compact cadmium and crystallite sizes. At steady-state electrolysis deposit is characterized with great divergence of grain sizes and conglomerate formation on their bases (Figs. 4a and c). At the same time grain sizes are changed insignificantly. Pulse

current favors deposit formation at the absence of agglomerates and uniform graininess (Fig. 4 b and d). Moreover agglomerates have less size by order. At steady-state electrolysis and  $E = -1.5$  V crystallites sizes are within the range of 2–10  $\mu\text{m}$ , and at pulse electrolysis and the same value of  $E$  the sizes are in the range of 0.5–1.5  $\mu\text{m}$ .



**Fig. 4.** Morphology of compact cadmium deposit obtained under steady-state (a, c) and pulse (b, d) modes of electrolysis in 1.0 M  $\text{CdCl}_2$  in DMSO at 313 K at cathodic potentials (V): a), b) 1.5; c) 2.0; d) 2.5

## 4. Conclusions

1. In 0.1–1.0 M CdCl<sub>2</sub> in DMSO solution cadmium active reduction takes place at potential values greater than equilibrium value by 1 V owing to cathode polarization. Increase of cadmium salt content results in concentrated depolarization, what means displacement of beginning of metal reduction by 0.3 V.

2. Temperature increase from 293 to 333 K actually is not the reason of cathode depolarization. Increase in cathode current indicates the diffusion area of process proceeding.

3. Non-stationary electrolysis mode with duration of pulse/pause 1/100 is the main factor of its influence on formation of monolithic cathode cadmium, which is homogeneous by dispersion and grain sizes. At equal potential values the application of pulse mode gives the possibility to obtain compact coatings with crystallite sizes less by 2–4 times than those obtaining at steady-state electrolysis.

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### ЕЛЕКТРОХІМІЧНЕ ВІДНОВЛЕННЯ КАДМІЮ У РОЗЧИНАХ CdCl<sub>2</sub> В ДИМЕТИЛСУЛЬФОКСИДІ ТА МОРФОЛОГІЯ КАТОДНОГО ОСАДУ

*Анотація.* Досліджено відновлення кадмію в розчинах за стаціонарного та імпульсного електролізу. Встановлено, що поляризація спричиняє формування кадмію за потенціалів більших за рівноважний на ~1 V. Показано, що у 0,25...1,0 M CdCl<sub>2</sub> концентраційна деполаризація призводить до зміцнення початку відновлення кадмію на ~0,3 V. Наведено фотографії SEM і показано вплив параметрів електролізу на морфологію катодного осаду.

*Ключові слова:* кадмій, DMSO, електроліз, імпульсний струм, морфологія.