

# The influence of cathodic decomposition of compound substrates on electrodeposition of metals from solutions

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## ABSTRACT

Peculiarities of cathodic decomposition (solid-state reduction) products of compound semiconductors such as CdSe, CdS, InP, CuO, etc. are reviewed and analyzed. Such products are either metals, metal-like (rich in metal) non-stoichiometric compounds with disordered structure, their mixtures, or their solid solutions. Their presence on the substrate surface can substantially accelerate subsequent electrodeposition of metals from the solutions containing their salts because these products improve the conditions for the initial stages of this process (accumulation of adatoms and nucleation). A brief explanation of this process is presented.

**KEYWORDS:** cathodic decomposition, solid-state reduction, electrodeposition, binary semiconducting compound, metal, anodic ionization

## ABBREVIATIONS

ASV – anodic stripping voltammogram  
BSC – binary semiconducting compounds  
CVA – cyclic voltammogram  
SHE – standard hydrogen electrode

## INTRODUCTION

Many experimental investigations reveal that strong cathodic polarization of electrodes consisting of binary semiconducting compounds (BSC) such as CdS, CdSe, InP, GaAs, ZnO, SnO<sub>2</sub>, CuO, etc. in

indifferent electrolytes (for example, aqueous solutions of KCl, Na<sub>2</sub>SO<sub>4</sub>) leads to their reduction (cathodic decomposition) [1-14]. In many cases such processes proceed in solid phase, and the surface layers of the electrode materials undergo significant changes in composition, structure, and physical and electrochemical properties. Products of these decomposition processes contain high quantities of the metal and have structural defects such as anion vacancies and pores; that is, they have disordered structures [6, 7, 15-17]. Undoubtedly, these changes should strongly influence the initial stages of the subsequent process of electrodeposition of metals from solutions on adding the corresponding metal salt to the electrolyte. This subject is interesting both from the point of view of fundamental sciences and also from the point of view of its practical applications such as electrochemical metallization of compound semiconductor samples and of metallic substrates with thin oxide surface layers which can be reduced cathodically before electrodeposition of the metal from the solution. However, although a very many number of studies have been done on solid-state reduction of BSC samples and on electrodeposition of metals on them, the authors of most of such investigations considered these two types of cathodic processes independent of each other, without noticing their connection. Only a few studies have been devoted to this topic and quite insufficient attention has been paid to it yet. Generally, many important studies (not published in English language) in this field are little-known world wide till now.

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Therefore, the purpose of this mini-review is to update electrochemists about the main results of such studies and attract their attention to the relationship between the above-mentioned cathodic processes on BSC crystals.

### **Some peculiarities of cathodic decomposition of binary semiconducting compounds that influence the structure and properties of its products**

#### **A. Specific features of cathodic reduction of BSC**

Numerous investigations of cathodic reduction of binary compounds [1-24] have revealed that these processes may result in the formation of either metals [18, 20-22] or non-stoichiometric compounds [23, 24]. Among several of such investigations, many detailed and important studies of mechanisms of these processes have been performed by Russian scientific schools during the period of 1960-1990 [17, 23-30].

They established that the processes of reduction (cathodic decomposition) of many slightly soluble semiconducting metal oxides in aqueous electrolytes proceed in the solid phase by the electron-protonic mechanism, including passing some protons from the solution into the surface layers of the oxide crystalline lattice, and their insertion in them results in the formation of  $\text{OH}^-$  anions [24]. At the same time, electron transfer to the surface layers of the semiconducting cathode results in the reduction of the metal ions on the surface. Irrespective of proton involvement in the processes of solid-state reduction of other binary semiconducting compounds, these processes have to include the stage of gradual movement of anions from the compound crystal lattice to the surface of the cathode, their subsequent solvation at the interphase boundary and passage into the solution. This movement of anions inside the crystal may be caused either by the process of their diffusion [14] or by their electromigration in the electric field of the space-charge region of the semiconducting cathode [7, 31] if the electrode potential is more negative than the flatband potential value. This must be possible, for example, in CdS crystals [7] because they have the properties of solid electrolyte and their sulphur anions have noticeable mobility in electric fields [32].

Nonetheless, it should be expected that solid-state reduction may not result in the complete extraction of all anions from the surface layer of the compound crystal, but only their partial extraction especially if the duration of the reduction process is not very long. It has to result also in the formation of a great number of anion vacancies in the crystalline lattice of the compound after the departure of anions from the lattice (irrespective of the detailed mechanism of the reduction process). Therefore, these processes may result in the formation of non-stoichiometric compounds or phases of variable composition (solid solutions) containing high quantities of the metal of the compound at the electrode surface. These theoretical conclusions are confirmed by many experimental investigations.

Experimental studies reveal that solid-state reduction of many oxides (for example,  $\text{PbO}_2$  [25],  $\text{CuO}$  [26],  $\text{AgO}$  [18] or  $\text{TiO}_2$  [21]) proceed gradually, as per the following stages:

- 1) The first step of extraction of oxygen ions from the crystal lattice with the formation of anion vacancies and an oxide containing lesser amount of oxygen (such as  $\text{PbO}_{1,34}$  [25],  $\text{Cu}_2\text{O}$  [26],  $\text{Ag}_2\text{O}$  [18],  $\text{TiO}$  [21], etc.).
- 2) Further reduction of these intermediary products resulting in formation of either metals (Pb, Cu, Ag, Ti, etc.) or products which are rich in the metals. These products are either mixtures of all the above-mentioned substances or their solid solutions as predicted by the above theoretical considerations.

The products of cathodic decomposition of binary semiconducting compounds have usually metal-like appearance (metallic lustre) which is evident even by visual observations of the electrode surfaces. Therefore, many previous authors [1, 9, 16] considered that these products were simply metals. But the following more detailed investigations reveal that they may not be pure metals in many cases.

Gorochoy and Stoicoviciu [12] analyzed the composition of cathodically reduced p-InP single-crystal wafers at small depths from their surfaces using SIMS method. They revealed that their near-surface layers were enriched in the metal (indium) as compared to the bulk electrode material

but they contained also noticeable amounts of phosphorus (although its concentration was minimal at the very surface of this electrode). Menjeritsky [27] performed X-ray investigations of the products of reduction of CuO. He revealed that they did not consist of pure copper but of its solid solution in copper oxide. Gorbunova *et al.* [26] revealed that the products of solid-state reduction of CuO powder consist of the original oxide, intermediary oxide Cu<sub>2</sub>O and of copper metal.

However, microcrystals of elemental metals such as Zn and Ag are formed as a result of cathodic reduction of ZnO and AgO films, respectively [20, 18].

It was revealed that the rates of cathodic reduction of polycrystalline films of binary compounds such as CdS [9] and Nb<sub>2</sub>O<sub>5</sub> [28] are much greater than those of single-crystals of the same materials. It is caused by much higher density of structural defects such as intergrain boundaries in polycrystalline materials [9, 28] and it is an explicit evidence of the role of these lattice defects in the solid-state reduction processes; their presence reduces the overpotential of cathodic decomposition substantially [9].

Many investigators confirmed experimentally the fact predicted by the above theory that a great number of anion vacancies arises in compound crystals such as CuO [29] and Nb<sub>2</sub>O<sub>5</sub> [28] during their cathodic reduction. It undoubtedly facilitates the subsequent movement of anions in the crystal both by diffusion and by electromigration processes.

If the concentration of vacancies reaches higher values at the subsequent stages of the process, their coalescence may become possible. It results in the formation of multiple pores in the layers of reduction products [7, 15, 16, 30]. Formation of this porosity may be explained also by the fact that the reduction process leads to decreasing of mass and volume of the electrode material (without the volume of pores), but the external shape and dimensions of each sample would remain almost constant during the process [30].

Flerov [17, 33] was one of the first investigators who paid due attention and gave significance to the fact that metals or metal-like products formed after the solid-state reduction of binary compounds (such as CuO, Cu<sub>2</sub>O, AgO) may have highly

unstable, non-equilibrium structures. He proposed and expressed the reasonable idea that metal atoms of all these products remain initially at the same positions as those in the crystal lattices of the original compounds [17]. Therefore, the distances between adjacent metal atoms of this product correspond to the lattice parameters of the original compound, but they are greater than those of the crystal lattice of the stable modification of the same pure metal [17, 7]. In other words, metal atoms of this product are not located in their equilibrium positions which are characteristic for the pure metal crystal lattice. Therefore, such reduction products have excessive molar Gibbs energy compared to that of the same pure metals in their stable equilibrium modifications. Theoretically, it must lead to relaxation processes in the layers of these products (because metal atoms have to move to their equilibrium positions in the crystal lattice [17]), arising high internal stresses in them [7]. These theoretical predictions have been confirmed completely by our experimental examinations of the metal-like product of solid-state reduction of CdSe single crystals; explicit signs of the presence of these stresses such as emergence of multiple ruptures in these layers and tightening of some segments of them were clearly visible through a microscope [7].

## B. Experimental investigations using cyclic voltammetry

Typical cyclic voltammograms registered for a rather perfect n-type CdSe single crystal in indifferent aqueous electrolytes in darkness in our experiments are shown in Figure 1 as curves 1 and 2 [34]. Cyclic voltammograms registered for n-type CdS and CdSe single-crystal electrodes in analogous indifferent electrolytes by other investigators [9, 35] are very similar to our results in many respects.

As can be seen from the curves 1 and 2 (Figure 1), cathodic current density increases very slowly during the cathodic potential sweep of the CdSe electrode without forming of any cathodic peaks. Hydrogen evolution is the predominant cathodic process in these conditions [35]; only a small part of the electric charge passed is involved in the CdSe reduction process (the onset potential of this process is equal to approximately  $-0.71$  V vs. SHE [2]). This is evident from the fact that the

subsequent anodic sweep proceeds with even smaller current densities, producing only a tiny, low and broad anodic peak (designated as **A0**) at the potential value of approximately  $-0.5$  V vs. SHE. Its height is so small for such electrodes that it can hardly be noticed at low sweep rates ( $\leq 0.05$  V/s) in many cases (see curve 1 in Figure 1 and other similar voltammograms presented in [6, 7, 34]). Therefore, increasing the potential sweep rate up to the values of  $\geq 0.1$  V/s is necessary in order that this anodic peak become somewhat higher and better noticeable (curve 2 in Figure 1). This small peak is caused by anodic ionization of the product of cathodic reduction of CdSe. The amount of this product (estimated by the value of electric charge which is spent for its ionization) is very small in these conditions.

Somewhat similar cyclic voltammograms registered for a polycrystalline  $\text{SnO}_2$  film in indifferent aqueous electrolyte have been described by Canava and Lincot [10]. They pointed out that the redox potential of the couple  $\text{SnO}_2/\text{Sn}$  is equal to  $-0.71$  V vs. SCE at the pH value 6, but the reaction of cathodic reduction of  $\text{SnO}_2$  to metallic tin proceeds with substantial overpotential, and it leads to blackening of the film. The blackening was observed also by Liu *et al.* [11] who ascribed this colouration to formation of a thin layer of the non-stoichiometric compound with the composition of  $\text{SnO}_x$  (where  $x$  is less than 2). Subsequent anodic scan resulted in three peaks with unequal heights [10].

### C. Experimental investigations using anodic stripping voltammetry

The above-mentioned low and broad anodic peak **A0** (caused by ionization of the products of cathodic decomposition of the compound) exists also on anodic stripping voltammograms registered for a CdSe single-crystal electrode in indifferent electrolytes in experiments in which potentials of the cathodic stage are more negative than  $\approx -0.75$  V [7, 15] (curve 1 in Figure 2).

The peak **A0** on ASV (curve 1 in Figure 2) is characterized by a maximum of anodic current density at the same potential value of approximately  $-0.5$  V vs. SHE as that on the above-described CVA. This peak (**A0**) is somewhat higher and better noticeable on CdSe single crystal electrodes

not having very smooth surface, with some visible macroscopic defects (such as scratches) (curve 1 in Figure 2) than that registered for rather perfect crystals with chemically polished surface without any visible macroscopic defects (curve 1 in Figure 1 and many other similar voltammograms [6, 7, 34]). This is the additional evidence of the fact that surface defects substantially facilitate and accelerate the process of cathodic decomposition of CdSe. However, the amount of the product of cathodic reduction of CdSe formed in these conditions (estimated by the value of electric charge which is spent on its anodic ionization) is still much less than that corresponding to one monolayer (ionization of one monolayer of cadmium atoms requires an electric charge value of  $420 \cdot 10^{-6}$  Coulombs/cm<sup>2</sup> [15]). Hence, only a small part of the surface layer was reduced cathodically during the time of these experiments (probably, this process proceeds mainly at the active sites of the electrode such as surface defects).

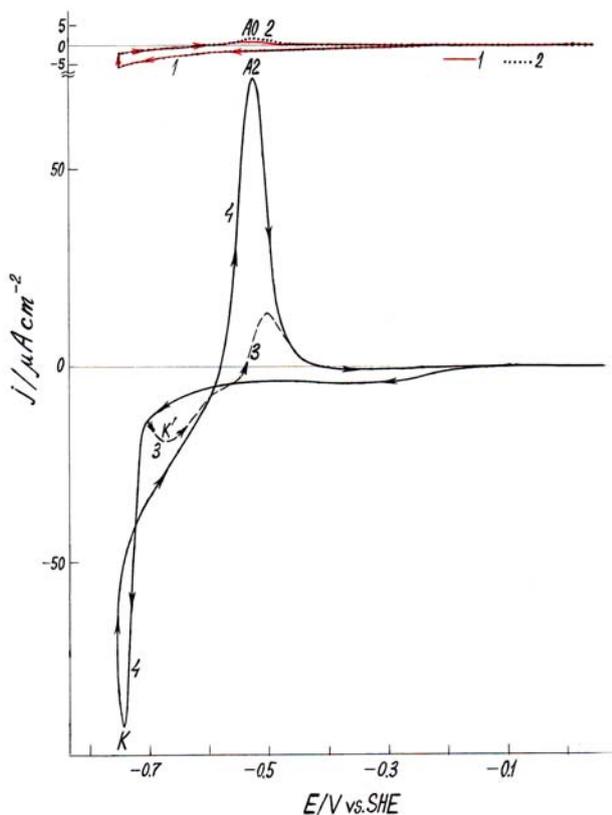
It is evident from the curve 1 in the Figure 2 that the anodic ionization of the product of cathodic reduction of the CdSe single crystals proceeds in a wide interval of potentials. It means that this product is not quite pure cadmium metal although it is undoubtedly rich in cadmium.

The structural peculiarities of the products of solid-state reduction of compound semiconductors are similar to those of metals formed after selective anodic ionization of electronegative components of binary metal alloys which are also characterized by disordered structure and existence of a lot of atomic vacancies and excess of molar Gibbs energy [36].

### Influence of products of cathodic decomposition of binary semiconducting compounds on the subsequent electrodeposition of metals from solutions

#### A. Theoretical considerations

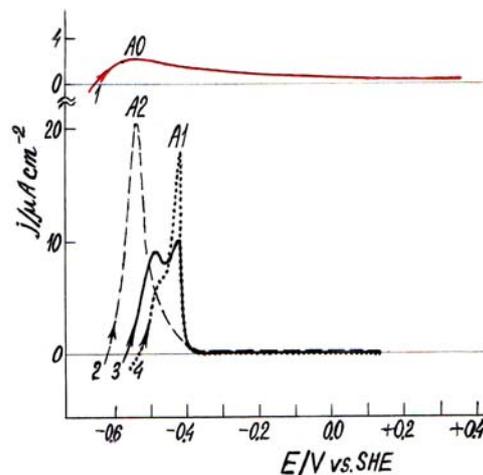
It is known that electrodeposition of metals on bare semiconductor electrodes usually proceeds via the Volmer-Weber mechanism (by the formation of three-dimensional metallic nuclei and their subsequent growth resulting in the formation of 'islands' of metal phase layers) [37]. In addition



**Figure 1.** Cyclic voltammograms registered for rather perfect CdSe single crystal with smooth, chemically polished surface {face  $(10\bar{1}0)$ } without any visible defects (to an unaided eye) in darkness [34]. 1, 2 – in aqueous solution of  $\text{Na}_2\text{SO}_4$  (0.5 M); 3, 4 – in the electrolyte obtained after adding of  $\text{CdSO}_4$  ( $4.3 \cdot 10^{-5}$  M) to the aqueous solution of  $\text{Na}_2\text{SO}_4$  (0.5 M). Resistivity of the electrode material was equal to 0.7 Ohm-cm. Cathodic sweep rate: 0.05 V/s (1, 2, 3, 4). Anodic sweep rate (V/s): 0.05 (1, 3, 4), 0.10 (2). The sweep was stopped for 20 seconds at the limiting potential of cathodic polarization only during registration of curves 1 and 2.

to the well-known Gibbs-Thomson effect [38], there is also another specific and very substantial factor decreasing the rate of the initial phase of electrodeposition of metals on semiconducting electrodes, namely, small values of exchange current densities on them as compared to those on metallic electrodes [34].

3D-nucleation occurs mainly on ‘active’ sites of the electrode surface such as areas where dislocations and other crystallographic defects exit or where scratches exist [38]. Their role in this process can be



**Figure 2.** Anodic stripping voltammograms registered after cathodic polarization of a CdSe single crystal, not having very smooth surface, with visible macroscopic defect (scratch) in darkness {face  $(10\bar{1}0)$ } [15]: 1 – in the aqueous solution of  $\text{Na}_2\text{SO}_4$  (0.5 M); 2, 3, 4 – in the electrolyte obtained after addition of  $\text{CdSO}_4$  ( $4.3 \cdot 10^{-4}$  M) to the aqueous solution of  $\text{Na}_2\text{SO}_4$  (0.5 M). Sweep rate was equal to 0.02 V/s everywhere. The cathodic stage was performed within 50 seconds (curve 1) and 10 seconds (curves 2, 3, 4) at the following potential values (V vs. SHE): -0.91 (curves 1 and 2), -0.78 (curve 3), -0.75 (curve 4). Resistivity of the electrode material was equal to 0.7 Ohm-cm.

readily understood from the below-referred experiments. If we scratch the surface of a semiconductor single crystal cathode with a firm sharp tool at moderate pressure, creating some additional defects, then nucleation and electrodeposition of any metal from solution will occur mainly at the damaged (scratched) site of the electrode surface [39]\*. If we do not perform such damage, there is a lack of such ‘active’ sites on the smooth surfaces of the perfect semiconductor single-crystal electrodes. It should be expected that this factor may slow down the rate of initial electrodeposition of metals on such cathodes [34]. But this situation is entirely changed after the cathodic reduction (decomposition) of

\*However, excessive pressure of the sharp tool may result in local amorphization of the surface layer of *n*-Si single crystal wafers, reducing electrical conductivity of the scratched regions and preventing electrodeposition of the metal on them [40].

the surface layers of the semiconducting substrate due to the formation of either pure metal microcrystals or the layer of non-stoichiometric products of this process rich in the metal (even if its thickness is as small as some nanometers). It results in the following changes of the electrode surface properties:

1) Significant increase of the exchange current density on it which leads to the acceleration of reduction of metal cations from the solution to the metal adatoms on the electrode surface as compared to bare semiconducting electrodes in the same conditions [34].

2) Appearance of a great number of small hollows and micropores on the surface of the layer of the product of cathodic decomposition of the semiconducting material. For example, Chen Y. *et al.* [20] reported that after ZnO cathodic reduction, the surface becomes much rougher and particles of height 60 nm are formed. Wan Y. *et al.* [18] revealed that cracks and holes were formed in the layer of silver which had been produced by reduction of its oxides. These hollows are the sites where formation of metallic nuclei requires less energy than that on flat electrode surface.

3) The existence of the freshly formed and non-oxidized metal-like product of cathodic decomposition of the semiconducting material can be favourable for the subsequent epitaxial electrodeposition of the metal from the solution, which eliminates the necessity of three-dimensional nucleation and Gibbs-Thomson effect.

Hence, the appearance of metal microcrystals or the layer of metal-like products of cathodic decomposition can eliminate many factors hindering the initial phase of electrodeposition of metals on semiconductors. This must influence greatly the rate of this process and the properties of the electrodeposited metal. This theoretical conclusion is confirmed by the following experimental evidences.

## B. Experimental results

Typical cyclic and anodic stripping voltammograms registered for CdSe single-crystal electrodes both in indifferent aqueous electrolyte (curves 1 in Figures 1 and 2; curve 2 in Figure 1) and in similar electrolytes containing cadmium salt (all other curves therein) are shown in the above Figures (they had been registered in full darkness in order

to prevent the possibility of photoanodic oxidation of the electrode material). It should be noted that the calculated equilibrium potential values of the redox pair  $\text{Cd}^{2+}/\text{Cd}$  ( $E_{\text{eq}}$ ) are equal approximately to  $-0.53 \div -0.56$  V vs. SHE in the conditions of those experiments performed with the electrolytes containing  $\text{CdSO}_4$  (it relates to the curves 3 and 4 in Figure 1 and to the curves 2 – 4 in Figure 2) [34].

Comparison of the cyclic voltammograms (Figure 1) registered in both types of these electrolytes reveals clearly that a cathodic peak **K** (or **K'**) caused by the reduction of  $\text{Cd}^{2+}$  ions from the solution and a high, explicit anodic peak **A2** caused by subsequent anodic ionization of cadmium metal arise on them after addition of cadmium salt to the indifferent electrolyte. The peak **A2** exists also in each anodic stripping voltammogram if the potential of the cathodic deposition of cadmium metal is more negative than  $-0.78$  V vs. SHE (curve 2 in Figure 2). Its potential (about  $-0.5$  V vs. SHE)\* is close to that of the above-described peak **A0** registered in indifferent electrolyte but the height of the peak **A2** is much greater than that of the peak **A0** (Figures 1 and 2). The amounts of cadmium deposited on these electrodes from electrolytes containing  $\text{CdSO}_4$  (which are estimated by the charge spent for its ionization) are also much greater than those in indifferent electrolyte at the same conditions. This can be readily revealed by comparing the areas of the figures bounded by the curves 1 under the anodic peaks **A0**, on the one hand, and those under peaks **A2** in other anodic voltammograms shown in the Figures 1 and 2, on the other.

If the cathodic polarization of the CdSe electrode is performed in electrolytes containing  $\text{CdSO}_4$  at potential values of  $-0.58 \div -0.75$  V vs. SHE where the cadmium metal in the 2-nd (equilibrium) energy state can be deposited [15], then anodic ionization of this metal results in the formation of another peak **A1** at the potential value near  $-0.4$  V vs. SHE (curve 4 in Figure 2).

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\*Potentials of all the anodic peaks shift to somewhat more positive values when their height increases because of increasing amount of the ionizing metal and concentration of the  $\text{Cd}^{2+}$  ions formed after ionization of Cd in the layer of solution near the electrode [15].

The anodic peak **A1** disappears on the anodic stripping voltammograms if the potential of the cathodic stage is more negative than  $-0.8$  V vs. SHE but the peak **A2** is formed instead of it in these conditions (curve 2 in the Figure 2). This is the evidence of the fact that electrodeposition of cadmium metal at potentials more negative than  $-0.75$  V vs. SHE (when cathodic decomposition of CdSe substrate becomes possible) results in the specific form of the metal which has higher value of molar Gibbs energy as compared to the stable modification of cadmium metal. This can be explained as the influence of the product of cathodic decomposition of CdSe on the structure of the metal deposited from the solution due to the epitaxial mechanism.

This results also in considerable acceleration of the electrodeposition process and substantial increase in the amount of the deposited metal as was indicated above.

Detailed analysis of the above-mentioned cyclic voltammograms (curves 3, 4 in Figure 1 and other CVA presented in [34]) reveals that two waves of cathodic current may exist in them:

- 1) The first cathodic wave appears in the potential interval from  $-0.58$  V up to  $-0.70$  V vs. SHE where cathodic decomposition of CdSe is impossible.
- 2) The second cathodic wave appears at potentials which are more negative than  $-0.71$  V where cathodic decomposition of CdSe becomes possible [2].

Gradual increase of the cathodic current density during the potential sweep is characteristic for the first wave and its rate depends both on the concentration of  $\text{Cd}^{2+}$  ions in the electrolyte and on the density of defects on the surface of the electrode (the latter acts as the 'active sites' for nucleation). If both of these values are relatively low, then the CVA shown as curves 3 and 4 in Figure 1 will be registered. These two voltammograms have been registered with slightly different values of the limiting potential of cathodic polarization which were either more positive than the onset potential of cathodic decomposition of CdSe (curve 3) or slightly more negative than that (curve 4). Relatively slow increase of the cathodic current during the cathodic sweep occurs in the first case (curve 3) and much more rapid growth of the cathodic current at

potential values near  $-0.71$  V vs. SHE (curve 4 in Figure 1) occurs in the latter, resulting in greater increase of the amount of cadmium metal deposited on CdSe electrode (curve 4). The analysis of these voltammograms reveals that the rate of nucleation is relatively low at potentials  $\geq -0.70$  V vs. SHE (curve 3) but it increases sharply at the potential values near  $-0.71$  V vs. SHE (curve 4) where cathodic decomposition of CdSe begins [34]. It means that the sites with the metal-like product of this decomposition act as nucleation centres for electrodeposition of cadmium metal from the solution [34]. This conclusion agrees well with the brief statement of Gorochov and Stoicoviciu that the islands of the product of cathodic reduction of InP (which consists mainly of indium) may behave as nucleation centres for foreign metal photodeposition [12].

A similar cyclic voltammogram has been registered for  $\text{SnO}_2$  film in aqueous  $\text{CdSO}_4$  solution [41]. A very rapid growth of current occurs during the cathodic sweep in this system at the potential values at which cathodic reduction of  $\text{SnO}_2$  becomes possible [10]. Subsequent anodic sweep produces two close anodic peaks of ionization of the deposited cadmium metal [41].

Liu, Laverty *et al.* [11] reported that the cathodic reduction of  $\text{SnO}_2$  film leading to extraction of a part of the oxygen atoms from its surface layer influences substantially the subsequent process of electrodeposition of copper on it. It improves the adhesion of the deposited copper film significantly due to the formation of Sn–Cu bonds which are stronger as compared to the bonds between copper atoms and the unreduced  $\text{SnO}_2$  surface [11].

Vinkyavichyus *et al.* [42] investigated the process of electrodeposition of nickel from Watts electrolyte onto  $\text{Cu}_{2-x}\text{S}$  films with the aid of methods of cathodic voltammetry and X-ray photoelectron spectroscopy. They revealed that cathodic reduction of the surface layer of  $\text{Cu}_{2-x}\text{S}$  film resulting in the formation of copper metal takes place before the stage of electrodeposition of nickel metal from the solution on it. This means that nickel is deposited on the copper layer formed by reduction of  $\text{Cu}_{2-x}\text{S}$  [42]. This conclusion is valid also for many other metals (such as cobalt, iron, etc.) which are deposited at more negative electrode potentials than the onset potential

for reduction of the substratum material. Thin films of other metals (with more positive values of standard electrode potentials) cannot be electrodeposited on this electrode with good results. For example, copper can be electrodeposited on  $\text{Cu}_{2-x}\text{S}$  films successively only from electrolytes containing cyanides like KCN but not from solutions containing only simple salts like  $\text{CuSO}_4$  because of higher overpotentials of the cathodic process in the former case [42].

Samoilenko *et al.* [43] revealed that solid-state reduction of the surface of CdS film precedes the electrodeposition of nickel from solution onto the cadmium sulphide substratum (this was proved by means of metallographic and X-ray structure analysis). It should also be noted that these investigators used the films which had been produced by the method of chemical deposition from solutions. It is known that such films consist not of pure CdS; they also contain appreciable amounts of some other cadmium compounds which can be reduced cathodically at more positive electrode potentials than that of the reduction onset of pure CdS. Nonetheless, this work is very important in its principle as one of the pioneer investigations in this field which had been performed with the use of modern experimental methods and instruments for analysis.

Electrodeposition of copper onto ruthenium electrode is complicated by the presence of ruthenium oxide on its surface. Therefore, several research groups have proposed cathodic treatments of this electrode in order to reduce the oxide of ruthenium before electrodeposition of copper or silver onto it, thereby enhancing nucleation and adhesion of these metals [44]. It should be pointed out that the structure of ruthenium formed by reduction of its oxide may differ from that of the native ruthenium metal and it may influence the structures of electrodeposited copper or silver (this follows from the general peculiarities of the products of solid-state reduction of slightly soluble compounds which were described above). This remark may be valid also for electrodeposition on many other metallic electrodes covered with oxide layers.

## CONCLUSION

It is evident from the above-mentioned results that although cathodic decomposition of binary

compounds may proceed relatively slowly in many cases, even very small amounts of the decomposition products can substantially influence the rate of the initial phase of the subsequent electrodeposition of metals from solutions and the properties of the deposited metal. This can be explained by the fact that these products act as the active sites (centres of nucleation) for the deposition of the metal from solutions.

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## CONFLICT OF INTEREST STATEMENT

There are no conflicts of financial interests related to this work.

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