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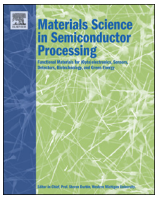

Electrodeposition of cadmium selenide

Remigiusz Kowalik[a,*], Honorata Kazimierczak[b], Piotr Żabiński[a]

[a] AGH University of Science and Technology, Faculty of Non-Ferrous Metals, al. A. Mickiewicza 30, 30-059 Krakow, Poland
[b] Institute of Metallurgy and Material Science, Polish Academy of Sciences, Reymonta 25, 30-059 Krakow, Poland

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ABSTRACT

In the present work the process of electrochemical synthesis of cadmium selenide from sulphate solutions has been examined. Electrode reactions taking place at co-deposition of cadmium and selenium were tested with the use of cyclic voltammetry. Two mechanisms of co-deposition of cadmium and selenium were suggested. Within the range of more positive potentials, the following two reactions take place: reduction of selenious acid to selenium, and then underpotential deposition of cadmium on selenium. The second mechanism proceeds within the potentials range below -0.4 V vs. SCE and relies on simultaneous reduction of ions of cadmium and selenious acid in a six-electron process. Next, the influence of selenious acid concentration and potential on the Cd–Se coatings deposition process on copper sheets was examined. The coatings were analysed with X-ray spectrofluorometry, electron scanning microscopy and X-ray diffraction. It was demonstrated that it is possible to obtain coatings stoichiometry corresponding to CdSe compound of hexagonal structure from sulphate electrolyte.

1. Introduction

Broadband semiconductors of II–VI types enjoy a lot of interest due to their application in electronics. They can be used as materials for constructing light-emitting diodes, semiconductor lasers or light detectors. Elements containing such semiconductors are used to produce devices for recording information, displays and flat television screens as well as heterojunction photovoltaic cells. So large possible applications of the materials result in a necessity to work out new methods of manufacturing semiconductor systems, and particularly, thin coatings of required parameters.

Currently, many research centres are conducting tests to get to know the mechanisms and kinetics of semiconductor compounds synthesis with electrochemical methods, which should lead to elaborating a technology to obtain such coatings electrochemically. It should be emphasized that electrochemical methods of deposition of coatings are commonly used in case of metallic layers [1]. Their greatest strengths are: a possibility to cover large surfaces, also porous ones, high uniformity of the obtained coatings, a possibility to obtain coatings of desired thickness, high purity of the spread coatings, good adhesion of the coatings, high velocity of spreading the coatings, a possibility of precise control of the deposition process and, the most important, no need of considerable financial outlays. The wide possibilities of the electrochemical method are confirmed by several publications concerning synthesis of CdSe of different structures: 3D structures onto the silica arrays [2–4] or a polystyrene template [5], "Mulberry-like" Nanoclusters [6], self-assembled nanowires [7], nanowires in a polycarbonate template [8], micro and nanowires in alumina membrane [9,10], 2D CdSe nanopillar arrays [11], core–shell nanowire arrays [12], nanofiber film [13], tubular end-capped nanofibers [14], two-dimensional photonic crystals in a polymer template [15]. Modification of both the structure and surface of the obtained coatings allows a precise tuning in of optoelectronic properties of cadmium selenide.

In case of CdSe electrodeposition the influence of different parameters of the electrolysis process on the possibility to obtain a stoichiometric compound was examined. The applied electrolytes were aqueous solutions, organic ones [16–18], ion liquids [19] and molten salts [20,21]. The substrate was gold [22–26], silver [26,27], nickel [28–30], titanium [28–31], InP [32], HOPG [33] or ITO [34].

In the present work cadmium selenide was obtained on a copper electrode. Sulphate solution was applied as the electrolyte. The influence of the electrolyte components concentration and its pH on a possibility of a stoichiometric compound synthesis were examined. Preliminary tests were performed on a gold electrode. The quality of the coatings was tested with the use of scanning electron microscopy. The elemental and phase composition got confirmed by X-ray spectrofluorometry and X-ray diffraction.

2. Experimental

Aqueous solutions containing proper salts or acids originating from elements being components of the coatings were applied as

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[*] Corresponding author.
E-mail address: rkowalik@agh.edu.pl (R. Kowalik).

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the electrolyte. Acids or bases of ions common with the basic solution were used in order to assess pH of the solutions. Distilled water was applied to make the electrolyte.

Voltammetric tests and potentiostatic deposition were conducted applying a classical three – electrode electrochemical vessel. It included a reference electrode – saturated calomel electrode, while the counter electrode was a platinum sheet of 12 cm^2 surface.

Gold or copper got used as the working electrode. Gold disks placed in a Teflon holder were applied for voltammetric tests. The electrodes were ground mechanically with sand paper of 320 gradation and then polished with diamond paste of 9 μm and 3 μm. The finishing polish was performed with a suspension of SiO_2 0.04 μm. Before the measurement, the electrodes were flushed with distilled water and acetone. The electrodes surface was 0.196 cm^2.

The deposition of coatings were carried out only on copper sheets placed in a Teflon casing. Each sheet was mechanically prepared as well as gold disks, and then chemically polished in a mixture of HNO_3 (analytical grade POCh), CH_3COOH (analytical grade POCh) and H_3PO_4 (analytical grade POCh) of components proportions 1:1:1. Concentrated acids were used to make the solution. Before the measurement, the electrodes were flushed with distilled water and acetone. The electrode surface was 2.8 cm^2. The time of deposition was 2 h for all experiments.

Electrochemical tests were conducted with the use of PAR273A, Autolab PGSTAT30 and EDAQ EA 161 potentiostat/galvanostat. Voltammetric tests and potentiostatic deposition were carried out on them. The elemental composition of the obtained layers was examined and observation of the surface was performed in the Laboratory of Scanning Microscopy with Field Emission and Microanalysis in the Institute of Geological Sciences of the Jagiellonian University (HITACHI S-4700 and NORAN Vantage) and in the Laboratory of Electron Scanning Microscopy in the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences (SEM – PHILIPS XL30). Additionally, the samples were analysed with the method of X-ray fluorescence using a fluorescent spectrometer Rigaku Primini WDXRF. The elemental analysis carried out for the deposited coatings were concentrated on Cd and Se content in the coatings. Only percentage of cadmium is shown on graph for clarity. The phase analysis was examined by X-ray diffraction applying Rigaku Miniflex II diffractometer with Cu Kα radiation.

3. Results and discussion

Preliminary tests concerning a possibility of CdSe synthesis with an electrochemical method were conducted on a polycrystalline gold electrode. Fig. 1 presents cyclic voltammograms obtained in solutions containing, respectively, 0.1 M $CdSO_4$, 0.001 M H_2SeO_3 and 0.1 M $CdSO_4$+0.001 M H_2SeO_3. Additionally, for comparative purposes, examinations in the base solution (H_2SO_4 pH=2) were also performed. When the solution contained only ions of cadmium, cathodic current occurs already from potential −0.1 V. It is probably connected with reduction of oxygen or underpotential deposition of cadmium on gold[35]. Next, an intensive increase of cathodic current is observed from potential −0.7 V. At the same time, two processes can take place here. Processes of hydrogen evolution and overpotential cadmium deposition begin:

$$2H^{+}+2e^{-}=H_2 \tag{1}$$

$$Cd^{2+}+2e^{-}=Cd^{0} \tag{2}$$

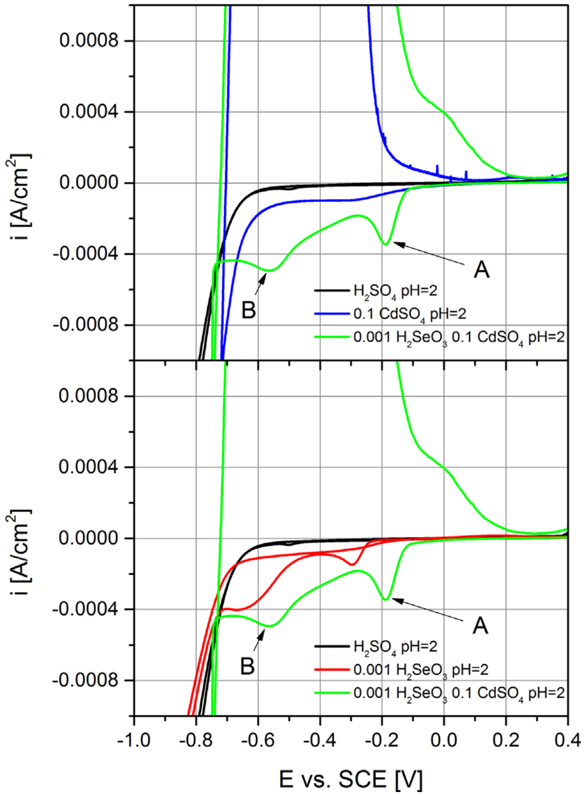

Fig. 1. Cyclic voltammograms on gold electrode in different solutions, pH=2 at 20 mV/s.

Next, when scanning is performed towards positive potentials, there occurs a characteristic anodic peak, connected with dissolution of previously deposited cadmium. When voltammetric tests were conducted in a solution containing only selenious acid (IV), slight cathodic current is registered already from potential 0.2 V. It is likely to be connected with underpotential deposition of selenium on gold. It should be noticed that in researches on voltammograms presented in literature there appear characteristic peaks, perfectly visible [36–43], connected with underpotential deposition of selenium on gold. In the voltammogram presented in Fig. 1 only a slight increase of cathodic current is seen. The above effect can be linked to the type of gold electrode used during the tests and the method of preparing the surface before the experiment. In case of the cited works, the tests were carried out on electrodes obtained by sputtering gold on sheets of different types. In the results presented here, the function of the electrode was fulfilled by a polycrystalline gold disk. It can be assumed that the sputtered gold electrode demonstrates higher reactivity in relation to selenium than a disk electrode that previously was only mechanically polished. That is why not all subtleties connected with surface phenomena taking place in the system Au–H_2SeO_3 are so intensive. When scanning is continued towards negative potentials, a cathodic peak occurs at potential −0.3 V. The peak corresponds to the process of overpotential deposition of selenium following the reaction [39]:

$$H_2SeO_3+4H^{+}+4e^{-}\rightarrow Se+3H_2O \tag{3}$$

From the potential −0.5 V another increase of cathodic current is observed that can be connected with the reactions[40,41]:

$$H_2SeO_3+6H^{+}+6e^{-}\rightarrow H_2Se+3H_2O \tag{4}$$

$$Se+2H^{+}+2e^{-}\rightarrow H_2Se \tag{5}$$