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Studies of stoichiometry of electrochemically grown CdSe deposits

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ABSTRACT

The proper deposition bath composition for electrochemical synthesis of the CdSe deposit in the hexagonal structure of the right elemental stoichiometry, and photoreacting as an n-type semiconductor which can be used as a stable photoanode is investigated. The deposits were prepared by a cyclic potentiodynamic technique and the concentration of Cd^{2+} and $SeO_3{}^{2-}$ in the deposition baths varied from 10^{-4} M to 0.1 M, and from 10^{-5} M to 10^{-3} M, respectively. The electrochemical, the X-ray diffraction (EDS and XRD), and the photoactivity studies of a number of deposits have shown that application of the solution composition following Cd:Se = 5:1 results in deposition of the stoichiometric CdSe. The detected ratio of reagents is explained on the base of reaction mechanism and necessary excess of cadmium ions preventing CdSe deposit dissolution. The procedure of CdSe electrosynthesis was developed to yield of a direct semiconductor in the hexagonal structure. The necessity for cadmium cations excess is explained on the basis of the mixed electrochemical/chemical deposition mechanism.

1. Introduction

Photoelectrochemistry started with Becquerel's studies on the photoeffects of solar illumination on metal electrodes in 1839 [1]. Much later it was understood that the most pronounced photoeffects were to be expected for semiconductive materials, while Brattain and Garrett observed large photocurrents during exposing a semiconductor electrode to the action of light of energy exceeding the electrode material band gap [2]. In the next years, photoelectrochemistry advanced rapidly [3–7]. The possibility of practical application of semiconductor electrodes was discussed by Williams as early as in 1960 [8]. A spark that ignited rapid research in electrochemistry of semiconductors was the observation of Fujishima and Honda [9,10]. These authors discovered a water photosplitting process at the irradiated TiO_2 electrode. The expectation for inexpensive production of hydrogen fuel resulted in an enormous increase in research effort in photoelectrochemistry field, which was additionally emphasised by the world oil crises (*e.g.* Refs. [11–17]). With time, because of some difficulties (*e.g.* low efficiency of photogalvanic cells) the interest in electrochemistry of semiconductors dropped significantly. A new attempt to develop these fields (electrochemistry of semiconductors and photoelectrochemistry) started with Brus's [18] demonstration that a quantum confinement of photocreated electron–hole pairs led to size dependent optical properties of semiconductor materials [19,20]. It drove the quest for the ways of preparation of nanostructured semiconductive materials, which exhibit new electronic and optical properties. But most attention was drawn to the synthesis of II–VI semiconductive nanocrystals and nanofilms, and among them cadmium selenide (CdSe) still remains one of the most thoroughly studied nanocrystal systems.

The CdSe band gap for bulk material is 1.7 eV, a threshold wavelength 729 nm [21], and depending on nanostructure radius, it might be tuned toward higher energy values (blue shift) up to 2.8 eV, a threshold wavelength 420 nm, for 1.2 nm nanocrystal [22]. Additionally, CdSe is a direct type of semiconductor and its electron affinity is in the range of 3.8–4.7 eV depending on nanostructure radius [23]. CdSe, because of its photoelectrochemical and photophysical properties is well known as a compound semiconductor suitable for solar energy conversion, optoelectronic devices, and for the preparation of antivirial drugs. It may also have a positive impact on the environment, as it was shown that it might be used to sequester CO_2 [24].

Methods for CdSe preparation can be divided into two major groups: dry methods carried out in the gas phase (vacuum evaporation and chemical vapor deposition) and wet methods (liquid phase synthesis and electrochemical deposition). While the gas phase techniques offer a high controllability of the growth of the structures and the feasibility to obtain a pure material, they, without exceptions, require an expensive high vacuum and high temperature equipment, and additionally, the gaseous waste material is another serious problem of these techniques.

The wet methods of CdSe nanostructures production are relatively inexpensive and simple to be carried out. Among a variety of the wet techniques, the electrochemical ones are the only

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techniques which can be used for a deposition of films on large and irregular surfaces. In comparison with other wet methods during electrodeposition, a strict control of an oxidation state of selenium is not required, the deposition occurs closer to an equilibrium state, and because the process is electrical in nature, it can be controlled precisely.

On the other hand, the electrochemical methods require a precise definition of experimental conditions such as potentials, reactant concentration, supporting electrolyte, deposition time, and the material of the working electrode is of great importance as well. The discussion on the theoretical thermodynamic conditions to be met to achieve cathodic deposition of stable binary semiconductor II–VI compounds have been developed by Kröger [25]. He distinguished two classes of deposition taking into account the difference in the deposition potential, the differences in the rate constants and exchange currents of the individual components. On this basis he tried to predict the stability of the deposits in dependence of the ions concentration in the bulk of the solution, and has found it to be proportional. Finally, he formulated the relations for the rest potentials in dependence on a discharge rate constant and ionic concentration. The deposition of CdSe he ascribed to class I, which means that this deposition is determined by a less noble selenium.

In previous years the CdSe was electrodeposited from the solutions of pH = 0 to pH = 14 [26–31]. The use of the reagent concentrations and their ratios varied widely, the Cd:Se ratio varied from 200:1 to 1:200 [26,29,31,32]. The potentials studied ranged from −1.5 V to 2.0 V [26,30]. The substrates used were Au, Pt, Ag, Cu, amalgamated Au [26,33], Ti [34], ITO [35] and HOPG [31]. A wide range of studied experimental conditions was examined in order to determine the best way of electrosynthesis of the material with the proper elemental stoichiometric ratio and of the suitable dimensions. Recently an excellent review on electrodeposition of semiconductive materials has been published by Lincot [36]. In this paper the two steps synthesis of semiconductive films is discussed, as well as the method of obtaining the precursor layer and after deposition annealing treatment. The influence of the deposition conditions on the free energy of the deposit formation is shown as an essential factor for the quality of the deposits.

The aim of the present studies was to investigate the influence of deposition solution composition on the elemental stoichiometry and photoreactivity of the CdSe surface structures. The deposits were prepared by a potentiodynamic technique, the concentration of Cd^{2+} varied from 0.1 M to 0.2 M, and the concentration of $SeO_3{}^{2-}$ varied from 10^{-5} M to 10^{-3} M. The elemental stoichiometry, compound formation and crystal structures were analyzed by X-ray energy dispersive spectroscopy (EDS) and X-ray diffraction spectroscopy (XRD), respectively. The photoelectrochemical activity of the CdSe structures was determined and the magnitude and direction of photocurrents were correlated with a structure and elemental stoichiometry.

2. Experimental

2.1. Electrodes and experimental procedures

A three-electrode and a three-compartment electrochemical cell with a quartz window were used. Working electrodes were made of a polycrystalline platinum disk. The working area was circular in shape, ca. 9 mm in diameter. The surface of the electrode was polished with alumina, down to 0.05 μm, and then it was cleaned with Millipore-Q water in an ultrasonic bath.

Counter electrodes were made of Pt/Pt gauze or wire, and an electrode potential was measured against an Hg|$HgSO_4$ reference electrode placed in saturated Na_2SO_4 solution. The potential values were recalculated to a normal hydrogen electrode scale (NHE) through this paper. Both counter and reference electrodes were placed in the compartments separated by a glass frit.

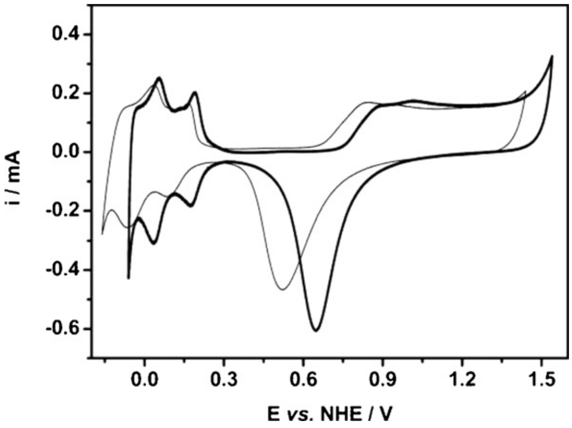

Fig. 1. The CV dependencies of the Pt electrode placed in 0.5 M H_2SO_4 solution (thick line) and 0.1 M Na_2SO_4 solution, (thin line). Sweep rate 50 mV s^{-1}.

Electrochemical activity of the working electrode surface and the purity of the solutions were checked by a cyclic voltammetry (CV), at first in an acidic solution (Fig. 1, thick line), and then in the solution of pH = 3 (Fig. 1, thin line). Obtaining of well defined CV dependencies for the Pt electrode attesting a measure of solution high quality was a desirable condition to start deposition experiments. CdSe deposition was carried out by a CV technique. The deposition time was determined by a number of CV cycles registered at 50 mV s^{-1}. A synthesized CdSe deposit was examined for its photoactivity by registering a CV dependence in the basic electrolyte solution free of Cd^{2+} and $SeO_3{}^{2-}$ ions. For the study of stoichiometry of the deposits the electrode was taken out of the cell, carefully washed out with Millipore-Q water, then dried and placed in a chamber of a secondary electron microscope (SEM) equipped with EDS device. The confirmation of the CdSe compound formation and detection of its crystallographic structure was done by an X-ray diffraction technique. In order to keep the electrode material constant, the XRD experiments were carried out for the CdSe deposits electrosynthesized on platinum substrate, which introduced a high background due to much higher absorption of X-ray energy by platinum than by graphite, which is usually employed as a substrate in such studies.

During the experiment, solutions were deoxygenated by bubbling Ar through an electrochemical cell and all experiments were carried out at an ambient temperature of 22 ± 2 °C.

2.2. Solutions

All solutions were prepared from Millipore-Q water and reagent grade $3CdSO_4{\cdot}8H_2O$, SeO_2, Na_2SO_4, and 98% H_2SO_4. The supporting electrolyte solution, pH = 3, was prepared from 0.5 M Na_2SO_4 solution, and pH was adjusted with 0.5 M sulfuric acid. The deposition baths (B) of five different Cd:Se ratios, 200:1 (BA), 5:1 (BB), 2:1 (BC), 1:1 (BD), and 1:5 (BE) were prepared by mixing $CdSO_4$ solution with SeO_2 solution. The Cd^{2+} concentration range varied from 10^{-4} M to 0.1 M, while $SeO_3{}^{2-}$ concentration varied from 10^{-5} M to 10^{-3} M. The composition of the deposition baths is given in Table 1.

2.3. Equipment

A three-electrode cell with a quartz window was used in all experiments. The current–voltage behavior was monitored with a programmed potentiostat (EG&G 263A, U.S.A.).