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Electrodeposition of CdS from acidic aqueous thiosulfate solution—Invesitigation of the mechanism by electrochemical quartz microbalance technique

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ABSTRACT

Electrochemical quartz crystal microbalance was used to study mechanism of cathodic electrodeposition of CdS from acidic aqueous solutions containing 0.01 M $Cd(ClO_4)_2$ and 0.1 M $Na_2S_2O_3$ as a source of sulfur. Experiments were performed by means of cyclic voltammetry and potentiostatic method. A comparison of gravimetric and current responses at pH 3 and 4 allowed for determination of the potential range in which side reactions of reduction of SO_3^{2-} and H^+ ions compete most strongly with formation of CdS. The film thickness was determined by means of two methods: from AFM profiles and EQCM measurements.

1. Introduction

Cadmium sulfide (CdS) is a direct n-type semiconductor with a band gap of about 2.4 eV and large absorption coefficient of 4×10^4 cm^{-1} [1]. Therefore, it is attractive material for application in thin-film photovoltaic cells [2,3] and references therein, photocatalysis [4,5] and solid state optics [6]. Thin layer of polycrystalline CdS may be prepared by chemical vacuum deposition [7], spray pyrolysis [8,9], chemical bath deposition [10,11], successive ionic layer adsorption and reaction (SILAR) [12], electrochemical atomic layer epitaxy (ECALE) [13,14] or electrodeposition [15–17]. The latter method has drawn a special attention because of low cost, easy procedure and good adhesion of the obtained films to the substrate. It is especially important in fabrication of thin-film pn-junction [18–22] and nanostructured solar cells [23–25].

Electrodeposition of CdS may be carried out from non-aqueous solutions [26–28], ionic liquids [29] and most often from aqueous solutions [30–41]. In the latter case, there are two main strategies: anodization of Cd substrate in strongly alkaline medium containing Na_2S [37–41] and cathodic deposition from alkaline [42] or acidic [30–36] solutions containing Cd^{2+} ions and a source of sulfur. According to the literature, anodization generally results in the formation of the films of limited thickness, containing defects and small crystallite size [17] and therefore, the cathodic method seems to be more relevant technique for fabrication of high quality CdS layers. Moreover, this technique is suitable for electrodeposition on substrates, which are not stable in the range of positive potentials used in anodic processes (stainless steel, Mo, Al, Ti, Cd) [43–46].

Morphology and quality of the CdS films and, in consequence, efficiency of resultant photovoltaic cells, are strongly dependent on several parameters which should be very carefully adjusted: composition of the solution, especially sources and concentration of sulfur and cadmium ions [22,27,33,34], pH [30,31,33,47] and temperature [27,32,43,47] of electrodeposition bath as well as value of applied potential [33,47] or current density [36], depending on the applied electrochemical method.

One of the most popular procedures is cathodic deposition from solution of pH 2–4, containing Cd^{2+} and $S_2O_3^{2-}$ ions [30–33,35]. Thiosulfate is a source of colloidal sulfur due to reaction of disproportionation:

$$S_2O_3^{2-} \xrightarrow{H^+} S + SO_3^{2-} \quad (1)$$

Although many schemes of consecutive electrochemical or electrochemical–chemical (EC) steps leading to deposition of CdS have been proposed, the exact mechanism of the process is still a matter of debate in the literature [17].

According to Denisson [32] two overall processes may be considered:

$$Cd^{2+} + S_2O_3^{2-} + 2e^- \rightarrow CdS + SO_3^{2-} \quad (2)$$

$$2Cd^{2+} + S_2O_3^{2-} + 6H^+ + 8e^- \rightarrow 2CdS + 3H_2O \quad (3)$$

Reaction (2), postulated for pH of about 4, was considered as EC-type process, in which an initial electrochemical step of reduction

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of Cd^{2+} to Cd^0 is followed by the rate determining reaction of Cd^0 with $S_2O_3^{2-}$. This second step of abstraction of sulfur from $S_2O_3^{2-}$, may be accelerated by increase of H^+ concentration. According to this scheme, the charge is only consumed in the reduction of Cd^{2+} ($2e^-$/CdS) and then deposition of CdS occurs via formation of complex of deposited cadmium with $S_2O_3^{2-}$ or other labile sulfur species.

The second scheme, reaction (3), occurring both via reduction of Cd^{2+} and $S_2O_3^{2-}$ ions with 4 electrons involved in formation of one molecule of CdS ($4e^-$/CdS), was postulated at lower pH [32]. However, no suggestion was given as to the exact mechanism of CdS electrodeposition.

Schemes (2) and (3) do not reflect all possible reactions which take place during cathodic polarization. Two products of disproportionation (1) may be reduced at the working electrode, according to the equations:

$$SO_3^{2-} + 4e^- + 6H^+ \rightarrow S + 3H_2O \quad (4)$$

(standard potential $E^0 = 0.243$ V vs Ag/AgCl,Cl^- (std.)) and

$$S + 2H^+ + 2e^- \rightarrow H_2S_{(aq)} \quad (5)$$

($E^0 = -0.08$ V vs Ag/AgCl,Cl^-).

Then, H_2S may react with Cd^{2+} ion to final product:

$$Cd^{2+} + H_2S \rightarrow CdS + 2H^+ \quad (6)$$

On the other hand, if amount of H_2S is not high enough, Cd^{2+} may be reduced to metallic cadmium:

$$Cd^{2+} + 2e^- \rightarrow Cd^0 \quad (7)$$

($E^0 = -0.62$ V vs Ag/AgCl,Cl^-).

According to Nishino et al. [33] the mechanism of CdS electrodeposition is strongly influenced by the processes occurring in a double layer. In the range of low potentials the positively charged ions (Cd^{2+} and H^+) are attracted to the inner layer, whereas negatively charged thiosulfate ions remain at the outer Helmholtz plane. A local decrease of pH leads to release of sulfur via Eq. (1) followed by its reduction in the cathodic reaction (5). Since H_2S reacts with Cd^{2+}, the process of CdS deposition is controlled by the mass transfer of Cd^{2+} to the electrode.

Takahashi et al. [34] proposed another mechanism in which small sulfur particles stabilized by gelatin (in the form of S_8), specifically adsorbed on the electrode give rise to adsorption of Cd^{2+} ion on colloidal sulfur. In the second, rate determining step, CdS is formed in effect of electrochemical reaction between both adsorbed species:

$$Cd^{2+}_{ads} + S_{8(ads)} + 2e^- \rightarrow CdS + S_{7(ads)} \quad (8)$$

All studies on CdS electrodeposition reported above were performed by means of classical electrochemical methods (potentiodynamic, potentiostatic or galvanostatic), which are very useful in investigation of simple electrode reactions. However, these methods are often not sufficient in determination of the most probable mechanism of complex processes, which occur with adsorption of the substrates or products or/and when intermediate products are formed. Therefore, in this work we applied electrochemical quartz crystal microbalance (EQCM) method to verify the mechanisms of CdS electrodeposition discussed above.

2. Experimental

All electrochemical experiments were carried out in a conventional, single compartment cell with a platinum wire counter electrode (CE) and Ag/AgCl,Cl^- reference electrode (RE). Measurements were done on a Pt disc electrode of the surface area of 0.5 cm^2 or Au thin film electrodes deposited on 10 MHz AT-cut quartz crystals (International Crystal Manufacturing Co. Ltd., Oklahoma City, OK), with piezoelectrically and electrochemically active areas of 0.21 cm^2 and 0.23 cm^2, respectively. Cyclic voltammograms were obtained by means of potentiostat AUTOLAB PGSTAT 30 (Ecochemie, The Netherlands), whereas EQCM studies were carried out using a QCM unit (Type M3, UELKO, Poland) combined with AUTOLAB. All measurements were made at room temperature (23 ± 2 °C).

Deposition of CdS was performed by cyclic voltammetry or chronoamperometry from aqueous solutions containing 0.01 M $Cd(ClO_4)_2$ and 0.1 M $Na_2S_2O_3$ at pH 3 and 4 maintained by citrate buffer. The buffer of pH 3 contained 0.08 M citric acid and 0.04 M Na_2HPO_4, whereas that of pH 4 was composed of 0.063 M citric acid and 0.074 M Na_2HPO_4. All solutions in these studies were carefully deoxygenated prior experiments by bubbling of Ar.

The change of the resonant frequency (Δf) recorded in EQCM experiments was recalculated into the change of mass of the surface layer (Δm) by means of Sauerbrey equation [48], which for 10 MHz AT-cut quartz crystals used in this work may be expressed in the form:

$$\Delta m(g) = -1.1 \times 10^{-9} \Delta f(Hz) \quad (9)$$

The coefficient 1.1 in this relation (within ±2%) was found by calibration for silver deposition from aqueous solution. Repeatability of the EQCM measurements was very good: dispersion of the slope of Δm–Q plots obtained from three independent experiments was within ±(3–5)%. The quartz crystals were mounted in the vessel in vertical position to avoid sedimentation of colloidal sulfur on the electrode surface.

Composition of the deposited films was determined by means of energy-dispersive full range X-ray microanalysis (EDS INCA Energy TEM, Oxford Instruments, Great Britain).

Morphology of the CdS films was characterized by AFM (Nanoscope III A and Nanoscope V, Digital Instrument, USA) and TEM (JEM 1400, JEOL Co., Japan) techniques. The silicon cantilevers with a spring constant ca. 40 N m^{-1}, 125 μm long, and a resonant frequency range 277–306 kHz were applied for imaging in Tapping Mode Atomic Force Microscopy (TM-AFM). AFM was also used for determination of the film thickness, according to the procedure described in the literature [49,50]. After imaging of the surface of an area 10×10 μm^2, the mode was changed to contact (CM-AFM) and the surface of the chosen area of 2×2 μm^2 was scratched by scanning. Then, the mode was changed back to tapping and again the large surface area was imaging. The thickness of the film was determined from the section analysis of the image.

3. Results and discussion

3.1. EQCM studies of CdS electrodeposition

Electrodeposition of CdS was performed from acidic aqueous solutions of 0.01 M $Cd(ClO_4)_2$ containing 0.1 M $Na_2S_2O_3$ as a source of sulfur at pH 3 and 4. Constant pH was maintained by citrate buffer to avoid local changes of H^+ concentration and in consequence changes of amount of sulfur formed in reaction (1) [31]. In order to specify more carefully the optimum conditions for electrodeposition of CdS, the EQCM studies were carried out separately in the background solution (citrate buffer), in the buffered solution of thiosulfate, in the buffered solution of Cd^{2+} (without thiosulfate) and in the solution containing all components, in a broad potential range, from 0.2 V to −1.1 V vs Ag/AgCl,Cl^-. In the background solution H^+ ion is reduced at the electrode, giving rise to