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Influence of electrodeposition conditions on the properties of CdTe films

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Abstract The results of the influence of electrodeposition conditions on the structural, compositional, optical, and photoelectrochemical properties of CdTe thin films deposited in one-step electrochemical method are presented. The CdTe films were prepared electrochemically from aqueous acidic solution with low ratios of Cd²⁺ ions to Te(IV) ions concentration. Instead of commonly used TeO₂, watersoluble Na₂TeO₃ was used as a source of tellurium ions. The cathodic deposition of CdTe was performed at different constant potentials from solutions containing different cadmium and tellurium ions concentration. As-deposited CdTe thin films were studied by different analytical techniques. The X-ray photoelectron spectroscopy spectra exhibited CdTe formation on the electrode with some amount of tellurium oxides and cadmium oxides. The best quality CdTe deposits, free of TeO₂, were formed in bath containing excess of Cd^{2+} ions and at the potential of -0.65 V vs. saturated calomel electrode, slightly more positive than E_{eq} of Cd/Cd²⁺ system. Structural X-ray diffraction studies revealed polycrystallinity of deposits with the highest content of the (111)-oriented cubic (111) form. Optical band gap energy values were found in the range from 1.36 to 1.6 eV for CdTe films prepared at various synthesis conditions. The preliminary photoelectrochemical studies have shown that the variation of the deposition potential as well as bath

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Department of Chemistry, Adelphi University, 1 South Avenue, Garden City, NY 11530, USA e-mail: widera@adelphi.edu composition leads to the formation of p- or n-type CdTe films. As-deposited CdTe films were not stable in polysul-fide solution under illumination.

Keywords CdTe thin films \cdot One-step electrochemical method \cdot Electrodeposition conditions \cdot Bath composition \cdot Deposition potential \cdot Na₂TeO₃ as a source of tellurium ions

Introduction

Of the emerging materials for solar cell applications, cadmium telluride is one candidate that has received much attention in recent years. Cadmium telluride optical characteristic is particularly very attractive for photovoltaic conversion of sunlight. Its energy bandgap of 1.45 eV provides an optimal match with the solar spectrum and thus permits its efficient conversion. Its high optical absorption coefficient (>10⁴ cm⁻¹) enables the use of thin films of CdTe in optical devices.

Various growth techniques have been applied for CdTe films formation. Among them, the electrochemical deposition is recognized as a simple, inexpensive, and reliable technique for preparing high-quality CdTe thin films for photovoltaic devices. The rich literature review on the electrodeposition and photoelectrochemical properties of CdTe can be found in "Electrochemistry of metal chalcogenides" published by Springer [1]. In principle, both anodic and cathodic deposition can be applied for CdTe formation. Lack of control of the deposit stoichiometry is a major disadvantage of the anodic deposition mode [2]. The cathodic electrodeposition of CdTe thin films has been reported to be successfully processed in both: acidic (pH 1-3) [2-17] and alkali aqueous solutions [18, 19]. Tellurium dioxide has been used as the main source of tellurium ions for CdTe formation. Based on Purbaix diagram and acid-base equilibrium constants [1, 20], it is generally accepted that in acidic solutions (pH \leq 3) the stable HTeO₂⁺ ions take part in CdTe formation. The present understanding of the CdTe electrodeposition process is based on some earlier publications, where thermodynamic and kinetic aspects of the process were discussed.

From the thermodynamic point of view, the conditions to be met to achieve the stoichiometric binary compounds have been described by Kröger [21]. Based on his model, there are two classes of binary compounds distinguished. Class I has a larger difference, while class II of binary compounds has a smaller difference of the individual components electrode deposition potential than the shift in deposition potential of either component resulting from compound or alloy formation. As for CdTe components, since the difference ΔE^0 is high (0.954 V, see below), CdTe belongs to class I, and then the deposition potential is determined by the less noble component (Cd).

$$Cd^{2+} + 2e \rightarrow Cd; \quad E^0 = -0.403 V (SHE)$$

 $\text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e} \rightarrow \text{Te} + \text{H}_2\text{O}; \quad E^0 = +0.551\text{V} \text{ (SHE)}$

This concept was further developed and confirmed experimentally by Panicker et al. [2]. It was shown that, for stoichiometric CdTe deposition, it is necessary to use electrolyte with high concentration of the less noble component (Cd) and with low concentration of tellurium source. Since during the deposition, the concentration of $HTeO_2^+$ is very low at electrode interface, the rate of Te deposition is diffusion controlled. CdTe deposition occurs at potentials more positive than deposition potential of Cd. The formation of CdTe takes place only after Te deposition as a result of free energy gain in CdTe formation : Cd+Te \rightarrow CdTe ; $\Delta G=$ -106.7 kJ/mol. Engelken and Van Doren [6] developed a simple theoretical kinetic model for CdTe electrodeposition by applying Butler-Volmer equation that includes cathodic diffusion-limiting current. Based on the computer simulations for the Cd-Te system, they suggested the existence on voltammograms of an underpotential cadmium current density plateau in the potential range of which Cd should be deposited with Te in stoichiometry 1:1. This concept of underpotential deposition of Cd is currently accepted and is being developed further [22, 23]. Sella et al. [7] found out that formation of CdTe cannot be only controlled by diffusion but also by adsorption of HTeO₂⁺ ions. They suggested that the process of CdTe formation may be described by displacement of the adsorbed $HTeO_2^+$ ions by Cd^{2+} and further reduction of those ions in the reaction: $HTeO_2^+$ + Cd^{2+} (ads)+4e+3H⁺ \rightarrow Te (surf)+Cd ²⁺+2H₂O. The reaction of CdTe formation may be then following: $Cd^{2+}+Te$ $(surf)+2e \rightarrow CdTe$. In contrary to Panicker et al. [2], Sella et al. carried out the investigations of CdTe electrodeposition in the solutions containing low and similar concentration of noble (Te) and less noble (Cd) components and determined the influence of Cd²⁺ ion concentration on the CdTe deposition mechanism. The results suggested that, for an ion concentration ratio Cd²⁺/Te(IV)<10 in the bath, formation of CdTe occurs by a two-step reduction mechanism. Another model for CdTe deposition was developed by Saraby-Rentjes, Saraby-Rentjes et al. [8] for the substrate completely covered with CdTe. It is based on the assumption of a solid-state reaction occurring between Cd and Te, i.e. incorporation of Cd atoms at Te sites and Te atoms at Cd sites. Due to this fact, the surface coverage is important in determining the deposition rates. There are few factors, which influence the properties of the deposited CdTe: substrate, deposition potential, and concentration of Cd²⁺ ions [more accurately, the ratio of Cd²⁺/Te(IV) ions]. Many different substrates were applied for CdTe cathodic deposition such as titanium, fluorine-doped tin oxide-coated glass or stainless steel, molybdenum, titanium nitride, nickel, or cadmium sulfide on indium-tin oxide (ITO) [3, 9, 11, 13, 15, 16]. It was found that the optical properties, crystallinity and quantum efficiency of electrodeposited CdTe were improved when CdTe was deposited on CdS [9]. The influence of the electrodeposition potential on the properties of CdTe has been shown by Panicker et al. [2]. They found out that the deposition potential influences the type of CdTe conductivity. Based on Kröger [21] work, they reported a critical value of quasi-rest potential of +340 mV vs. Cd/Cd²⁺ system, below which n-type of CdTe is deposited, while at more positive potential p-type CdTe should be formed. The influence of deposition potential on the doping type of CdTe was demonstrated by Kampmann et al. [9]. A potential of + 5 mV vs. deposition potential of Cd leads to the formation of n-type CdTe, while at the relative potential of +250 mV ptype of CdTe is formed. The decrease in the deposition potential improved the crystallinity of as-deposited films. The choice of the electrodeposition potential is very crucial. Theoretically, there is only very narrow potential range, where pure CdTe deposits can be formed with Cd/Te ratio equal to unity. At the positive end of the deposition range, Te deposition is favored and gives rise to Te-rich CdTe deposits, while application of potentials at the negative end of the deposition range should give rise to Cd-rich CdTe films. The type of conductivity can be changed by the incorporation of interstitials atoms of Te or Cd and the formation of defects in the so-called stoichiometric CdTe. However, in practice, it is very difficult to obtain p-type CdTe from acid baths. A special procedure needs to be used such as thermal treatment of n-type of CdTe that converts it into a p-type semiconductor.

There are not many experimental facts available in the literature, showing the influence of concentration or ratio of concentration of $Cd^{2+}/Te(IV)$ ions on the properties and composition of as-deposited CdTe films. Most of the data were obtained for the solution containing high Cd^{2+} ion concentration (>0.05 M) or very high ratio of $Cd^{2+}/Te(IV)$ ions concentration [2–6, 8–17, 22, 23]. There are few

publications on the application of other source of tellurium(IV) ions-tellurite ions ($\text{TeO}_3^2^-$) in both alkaline solution and acidic solutions [24–27] for the formation of CdTe nanocrystals [25], nanowires [24], and organic /CdTe junctions [26]. However, in these cases, the influence of the deposition potential and bath composition was not investigated, and CdTe chemical composition was not determined.

In this paper, we report the application of cathodic electrodeposition method for synthesis of nanostructured CdTe films of different conductivity type. Instead of commonly used TeO₂, we use water-soluble Na₂TeO₃ as a source of tellurium ions. We present the studies of the effect of electrodeposition potential as well as concentration ratio of cadmium ions and the source of tellurium ions on the composition, morphology, and crystallographic structure of the CdTe films. We also present some preliminary results bearing on the photoelectrochemical applications. Up to our knowledge, there are no data concerning the composition and properties of CdTe films obtained at low concentrations of Cd²⁺ and Te(IV) ions. We also show that CdTe films are not stable in polysulfide solutions.

Experimental

Electrochemical measurements and procedure

As a substrate for CdTe deposition, the Pt electrode (geometric surface area, 0.5 cm^2) was used. Glassy carbon (GC) electrode (geometric surface area, 0.03 cm²) was applied for cyclic voltammetry. For optical absorption studies, ITOcoated glass was used. The Pt and GC electrodes were polished with aluminum paste and washed using ethanol, acetone, and Milli-Q grade water. ITO was treated with organic solvents and then cleaned ultrasonically. All electrochemical experiments were performed in conventional three-electrode cell with Pt counter electrode and saturated calomel electrode (SCE) reference electrode using Autolab (Ecochemie) and recorded on PC equipped with the GPES 4.5 software. Before electrodeposition, argon was purged through the bath for 15 min to remove oxygen from the solution. The solutions were prepared from Millipore Milli-Q grade water and analytical-grade reagents (Sigma-Aldrich). The pH of solution was adjusted with HClO₄.

The values of the deposition potentials E_{dep} were chosen based on the information collected from cyclic voltammetry measurements carried out in the blank solutions containing only Cd²⁺ ions or TeO₃²⁻ ions and in bath solutions containing 1 mM Cd(ClO₄)₂, 1 mM Na₂TeO₃, 0.1 M LiClO₄ [bath A, 1:1 concentration ratio of Cd(II)/Te(IV) ions sources] or 5 mM Cd(ClO₄)₂, 1 mM Na₂TeO₃, 0.1 M LiClO₄ [bath B, 5:1 concentration ratio of Cd(II)/Te(IV) ions sources] at pH 2 and temperatures 22 and 70 °C.

In the initial deposition experiments, the cadmium telluride films were deposited at the temperature of 22 °C from the both baths A and B; however, in that case, we obtained amorphous films showing very small photoactivity. Since the increase in the deposition bath temperature improved the crystallinity of the deposits, the further experiments were carried out at the temperature of 70 °C. Deposition was performed at potentiostatic conditions, mainly at -0.45 and -0.65 V vs. SCE; however, some samples were obtained also at: -0.5 V, -0.55 V and -0.6 V vs. SCE. Comparing E_{dep} values with the equilibrium potential values of Cd/Cd²⁻ system equal to -0.698 V (1 mM Cd²⁺) and -0.677 V (5 mM Cd²⁺) vs. SCE (SCE potential equals +0.207 V vs. normal hydrogen electrode at 70 °C), the CdTe films were deposited at +48 and +248 mV (bath A) and +27 and + 227 mV (bath B) with respect to Cd/Cd²⁺ electrode. The other applied deposition potentials matched the range between +27 and +248 mV. The time of CdTe electrodeposition was 3,600 s. The average charge, which passed during the electrodeposition, was equal to 0.57 and 0.75 C/cm² (bath A, at -0.45 and -0.65 V, respectively) and to 0.73 and 0.96 C/cm^2 (bath B, at -0.45 and -0.65 V, respectively).

The solutions were prepared from Millipore Milli-Q grade water and analytical-grade reagents (Sigma-Aldrich). The pH of solution was adjusted with HClO₄.

Characterization of CdTe films

Crystal structure of CdTe was characterized by an X-ray diffraction technique using Rigaku Ultima III diffractometer with Cu K_{α} radiation. The morphology of CdTe films was studied using a scanning electron microscope (Merlin, ZEISS). The atomic composition was determined by energy dispersive spectroscopy (EDS). Chemical composition of the electrochemically deposited thin films was determined by Raman and X-ray photoelectron spectroscopy (XPS). Raman spectra were obtained with Labram HR800 (Horiba Jobin–Yvon) confocal microscope system using Nd:YAG laser (532 nm) as the excitation source. XPS measurements were performed with nonmonochromator Al K_{α} excitation (1,486.6 eV) and SPECS Phoibos analyzer. Optical absorption study was carried out using Shimadzu (2401) ultraviolet–visible spectrometer.

Photoelectrochemical measurements

Photoactivity of as-deposited CdTe films was tested in polysulfide solution (0.5 M Na₂S, 0.5 M NaOH, and 0.5 M S). The measurements were carried in three-electrode photocell equipped with quartz window, containing Pt sheet (counter electrode) and Ag/AgCl, Cl⁻ (1 M) (reference electrode). The CdTe modified electrodes were illuminated with tungsten lamp (1,000 W). A water filter was used to avoid the direct heating of the cell. To prepare polysulfide solution, the 12 g of $Na_2S.9H_2O$, 2 g of NaOH, and 2 g of sublimed sulphur were added to 100 ml of Ar-purged Milli-Q water. The solution was heated to 50 °C for an hour and sonicated for 2 h. After that treatment, the solution was clear and had an orange color.

Results and discussion

Electrochemical studies

For understanding of the CdTe formation in acidic solution containing tellurite salt, the influence of pH on equilibrium established in $H_2O+TeO_3^{2-}$ should be considered [20]. At pH >9, the tellurite ions exist in the solution. When the pH decreases, the equilibrium is shifted towards the formation of $HTeO_3^-$ ions according to the reaction: $HTeO_3^-=TeO_3^{2-}+H^+$, pK=7.74. In acidic solutions, the equilibrium is further shifted towards the formation of $HTeO_2^+$ ions according to the reaction: $HTeO_2^++H_2O=HTeO_3^-+2H^+$, pK=10.9. In water solution of pH 2, which we used for dissolution of Na_2TeO_3 , like in the case of TeO_2 , the $HTeO_2^+$ is a source of tellurium. The main advantage of tellurite salt comparing to tellurite dioxide is its better solubility in water at room temperature (after sonication) and at higher temperature without any additional treatment.

In order to evaluate the deposition potentials of CdTe films, the cyclic voltammograms were recorded in the blank solutions containing sources of Cd²⁺ or Te(IV) ions and in the bath solutions (A and B) applied in CdTe deposition. The typical CV curves obtained in 1 mM Na₂TeO₃+0.1 M LiClO₄, pH 2 and in 5 mM Cd(ClO₄)₂+1 mM Na₂TeO₃+0.1 M LiClO₄, pH 2 solutions at 70 °C are presented in Fig. 1a and b, respectively. As may be seen in Fig. 1a, in the case of Na₂TeO₃ electrolyte presence, the initial cathodic current wave (at about E=-0.2 V) is followed by plateau from about -0.4 to -0.65 V. The observed current plateau appears due to the low concentration of HTeO₂⁺ ions, and it is a diffusion limited current region. According to many authors [2, 7, 8, 17], the Te deposition takes place in this potential range according to the reaction:

$$HTeO_2^+ + 3H^+ + 4e \rightarrow Te + 2H_2O$$

Further increase in the negative potential results in the increase of cathodic current due to the reduction of Te and H_2 Te formation. In anodic part of CV curve, the peak at + 0.4 V can be ascribed to the oxidation of Te to tellurium(IV) ions. The CV curves recorded in solution B (Fig. 1b) revealed the current plateau in the potential range from -0.4 to -0.8 V. In this potential range, the CdTe formation takes place according to the reaction:

 $Cd^{2+} + Te + 2e \rightarrow CdTe$



Fig. 1 CV curves recorded on GC electrode in solutions containing a 1 mM Na₂TeO₃, 0.1 M LiClO₄, pH 2; b 5 mM Cd(ClO₄)₂, 1 mM Na₂TeO₃, 0.1 M LiClO₄, pH 2. Scan rate 20 mV s⁻¹, temperature=70 °C

At the potentials more negative than -0.8 V, sharp current onset is observed due to Cd deposition and H₂Te or H₂ evolution. The reverse cathodic scan revealed a peak at -0.73 V, which can be assigned to stripping of electrodeposited cadmium. Based on these results, the potentials in the range from -0.45 to -0.65 V vs. SCE were chosen for CdTe electrodeposition. These potential values are in the range of cathodic current plateau and are more positive than the equilibrium potential E_{eq} of Cd/Cd²⁺ system (see "Experimental").

Properties of as-deposited CdTe films

Crystal structure

The structural characterization of as-deposited CdTe films, obtained in acidic aqueous solutions A and B at -0.45 and -0.65 V is shown in Fig. 2a–d, respectively. It is clearly seen



Fig. 2 XRD patterns of CdTe as-deposited films on Pt electrode from: bath A (patterns a, b) and bath B (patterns c, d) at potentials: -0.45 and -0.65 V, respectively

that the X-ray diffraction patterns recorded for the samples prepared in bath A are very rich. Except the peaks at 2Θ in the range of $23.84-23.89^{\circ}$, which correspond to (111) plane of cubic phase of the CdTe (ICDS 093942) and the peak at $2\Theta=33.4^{\circ}$, which probably corresponds to (101) plane of the tetragonal phase of CdTe or hexagonal phase (100) of Cd [28], the other peaks confirmed the existence of various phases of CdO and TeO₂. Based on the literature [28-32], we ascribed the peaks at $2\Theta=34.8$, 37.9, and 38.9° to CdO; however, the peak at 37.9° can also correspond to tetragonal phase (200) of TeO₂. The other peaks, which can be ascribed to TeO₂ exist at $2\Theta=30.6$ and 49.3° [28].

The X-ray patterns of CdTe films obtained in bath B are simpler and contain only three or four peaks, depending on the applied deposition potential E_{dep} . In both cases (E_{dep} =-0.45 V, -0.65 V), the peaks at 2 Θ equal to 23.8–23.9 ° correspond to the (111) plane of cubic CdTe phase, the peak at 2 Θ =34.9 ° can be ascribed to CdO. The sharp peaks recorded at 2 Θ = 39.5–40.06 ° and at 46.4–47.3 ° in all diffraction spectra, we ascribed to Pt substrate [33]. The X-ray patterns of CdTe films

obtained at -0.55 V in both baths A and B (results not shown here) confirmed the influence of bath composition on deposit crystallinity and its chemical composition. In the case of CdTe films obtained in bath B [5:1 ratio of $Cd^{2+}/Te(IV)$ ions], the Xray patterns were very simple, containing only three sharp peaks ascribed to CdTe (cubic phase), Pt and a small peak ascribed to CdO. The structure and the chemical composition of CdTe is not too much influenced by the deposition potentials [samples were prepared at +27, +73, and +227 mV vs. E (Cd/Cd²⁺), it means -0.65, -0.55, and -0.45 V vs. SCE, respectively]. When the amount of Cd^{2+} ions decreased (bath A), the X-ray patterns were much more complicated showing existence of not only CdTe but also TeO2 and CdO as well. The changes of the deposition potential in direction towards E (Cd/Cd^{2+}) value (+248, +148, and +48, which means -0.45, -0.55, and -0.65 V vs. SCE) did not influence the patterns very much. These results are in contrary to that of Kampman et al. [9]; however, it has to be noticed that they investigated the influence of the deposition potential in solution containing very high concentration of Cd^{2+} ions (1 M).



Fig. 3 Raman spectra (a) and (b) of CdTe as-deposited films formed on Pt electrode at potential -0.65 V, from the solutions of baths A and B, respectively

Chemical composition of CdTe films

X-ray results confirmed that the deposited films are polycrystalline and contain CdTe with cubic structure. They also suggested that the composition of the formed films depends on the bath composition, and that besides CdTe, there are some other species formed on the electrode substrate. To look more closely at the chemical composition of the deposited films, we used Raman spectroscopy and XPS. The Raman spectra were recorded for the samples prepared in baths A and B at two potentials: -0.45 and -0.65 V vs. SCE. As the results did not differ very much, in Fig. 3, only the spectra of samples prepared in baths A and B at -0.65 V are shown. The spectra reveals four sharp bands at 92, 120, 140. and 163 cm⁻¹ and two broad bands centered at 265 and 330 cm^{-1} . The presence of the bands at 140, 163, and 330 cm⁻¹ [34, 35] proved the formation of CdTe. Other bands at 92 and 120 cm⁻¹ can be ascribed to elementary Te, which was not seen in X-ray pattern [36]. The broad band at 265 cm^{-1} can be ascribed to cadmium oxide [37]. We did not observed the week bands around 450 cm^{-1} in any samples, which have been related to the Te-O-Te

linkages [35]. The presence of the elementary Te band in CdTe spectra recorded with micro-Raman methods has been reported by Soares et al. [38]. It was shown that irradiation of CdTe with laser line of length lower than 840 nm resulted in decomposition of CdTe with formation of tellurium aggregates on the sample surface. This is probably the reason why the presence of Te signal is observed in Raman spectra but not in X-ray diffraction (XRD) patterns.

X-ray photoelectron spectroscopy was applied to confirm the formation of oxides during CdTe electrodeposition. For this purpose, the analysis of binding energy of Cd $3d_{5/2,3/2}$ and Te $3d_{5/2,3/2}$ regions was carried out. We obtained the values of binding energy of Cd $3d_{5/2}$ and Cd $3d_{3/2}$ in the range of 404.7– 405.5 eV and 411.6–412.6 eV, respectively. These values are in good agreement with published data for CdTe (NIST XPS data base) [39, 40]. However, the values of width at half maximum (2–3 eV) are higher than those for pure CdTe and may suggest the presence of other Cd compounds such as: Cd or CdO [40]. The representative Te 3d spectra for the CdTe samples prepared at different experimental conditions are shown in Fig. 4. The spectra reveals two sets of Te $3d_{5/2}$ $3d_{3/2}$ bands split by 3–4 eV for samples: a and b (bath A,



Fig. 4 XPS spectra of Te 3d core level revealed from CdTe spectra of as-deposited films. Deposits were obtained: from the solutions of bath A (spectra \mathbf{a} , \mathbf{b}) and bath B (spectra \mathbf{c} , \mathbf{d}) at potentials: -0.45 and -0.65 V, respectively

Fig. 5 SEM images of CdTe as-deposited films. Deposits were obtained: from the solutions of bath A (images **a**, **b**) and bath B (images **c**, **d**) at potentials: -0.45 and -0.65 V, respectively



-0.45 and -0.65 V, respectively), and c (bath B, -0.45 V). For sample d, electrodeposited in bath B at -0.65 V, only two bands appeared on XPS spectra. The Te 3d_{5/2} bands at a binding energy 572, 572.3, 573.3, and 571.7 eV (samples ad, respectively), and the Te $3d_{3/2}$ bands at binding energy 582.1, 583.2, 582.0, and 581.8 eV (samples a-d, respectively) can be ascribed to Te-Cd bonds in CdTe, while the bands at 574.8, 576.1, and 575.9 eV (samples a-c, respectively) and bands at 584.9, 587.6, and 584.5 eV can be ascribed to Te-O bonds in TeO₂ (NIST XPS database) [34, 39-41]. Comparing the ratio of the peak intensity of bands ascribed to Te-O and the bands ascribed to Te-Cd, equal to 1.37, 1.17, 0.48, and 0 for Te $3d_{5/2}$ and equal to 1.41, 1.28, 0.54, and 0 for Te $3d_{3/2}$, (samples a-d) one can clearly see the influence of bath composition and the value of electrodeposition potential on chemical composition of the deposited films. The general trends, which can be formulated on the basis of all XPS results obtained for the samples prepared in baths A and B at -0.45, -0.50, -0.55, -0.6 V, and -0.65 V, are as follows:

- − In the bath A [1:1 ratio of Cd^{2+} / Te (IV) ions], the amount of TeO₂ is high (Te–O/Te–Cd>1), the amount of tellurium oxide slightly decreases (Te–O/Te–Cd→1), when the value of the deposition potentials are shifted towards $E(Cd/Cd^{2+})=-0.698$ V.
- In the bath B (5:1 ratio of Cd²⁺/Te(IV) ions), the amount of TeO₂ is much lower (Te–O/Te–Cd<0.6) and decreases significantly when the value of the deposition potentials are shifted towards *E*(Cd/Cd²⁺)=-0.677 V.

It was shown that CdTe deposit, free of TeO_2 can be formed in bath containing some excess of Cd^{2+} ions, at the

potential -0.65 V vs. SCE (+27 mV against E_{eq} of Cd/Cd²⁺ system). While, when the deposition potential is much more positive than E_{eq} of Cd/Cd²⁺system or the concentration of Cd²⁺ is not sufficient, the amount of TeO₂ increases in the deposit as a result of oxidation of Te not involved in CdTe formation.

SEM microstructure of CdTe deposits

The influence of the electrodeposition conditions on morphology of as-deposited CdTe films was studied using scanning electron microscopy (SEM). The representative images are presented in Fig. 5a–d. In the case of sample a, obtained in bath A at lower deposition potential (-0.45 V), the granular surface layer is observed with spherical grains of dimension about 20–50 nm. The similar granular structure like in the case of sample a was observed for sample c obtained in bath B at -0.45 V. The morphology of the CdTe films changed significantly when the sample was prepared in bath A or B at -0.65 V (image b and d). Then, the CdTe consist of small, very sharp crystals deposited on the surface of the grains.

The EDS (spectra not shown here) revealed that the deposits prepared in baths A and B at potential -0.65 V and in bath B at -0.65 V exhibited a nearly stoichiometric Cd/Te ratio (ratio from 1.02 to 0.980), while the one prepared in bath A at -0.45 V has an excess of tellurium (ratio Te/Cd from 1.2 to 1.1). However, comparing these stoichiometry data with XRD and XPS results, there is no evidence that all Cd and Te are involved in CdTe formation.



Fig. 6 The $(\alpha h\nu)^2$ vs. $h\nu$ dependence obtained for as-deposited CdTe films. Deposits were obtained: from the solutions of bath A (curve **a**, **b**) and bath B (curve **c**, **d**) at potentials: -0.45 and -0.65 V, respectively

Optical properties

Optical absorption studies were carried out in the wavelength range of 300–900 nm for CdTe films deposited on ITO substrate. The variation of optical density with wavelength was analyzed in order to find the band gap energy of CdTe deposits, using the relation [42, 43]:

$$h\nu\alpha = A(h\nu - E_g)'$$

where $h\nu$ is an incident photon energy, A is a constant, α is absorption coefficient, and E_g is an optical band gap energy.

Fig. 7 Photoelectrochemical results for as-deposited CdTe films recorded in polysulfide solution. OCP changes vs. time obtained for CdTe deposited from bath A at potentials: -0.65 and -0.45 V and from bath B at potential -0.65 V represented by plots a-c, respectively. Plot c shows also changes in OCP after photocurrent measurements at -0.40 and -0.50 V. Plot d represents changes of current in time during illumination at -0.50 V for CdTe formed in bath A at -0.65 V

As CdTe is a direct bandgap material (for direct transition n=0.5), the E_g energy could be obtained from the intercept of $(h\nu\alpha)^2$ vs. $h\nu$ plot presented in Fig. 6. The estimated band gap energy values slightly differ depending on bath composition and they are as follow: 1.36 eV (bath A, E_{dep} –0.45 V), 1.45 eV (bath A, E_{dep} –0.65 V), 1.56 eV (bath B, E_{dep} –0.45 V), and 1.5 eV (bath B, E_{dep} –0.65 V). For the samples obtained at the other mentioned deposition potentials the E_g values are in the same range (1.4–1.6 eV). Such differences are in the range of error, which was estimated as 0.1 eV taking in account the measurements and extrapolations. The obtained E_g values are in good agreement with the literature data for CdTe films prepared by various methods [9, 15, 44–47].

Photoelectrochemical preliminary results

The photoactivity of as-deposited CdTe films was tested in polysulfide solution (S^{2-}/S_n^{2-}). For CdTe samples formed in bath B at two deposition potentials: E_{dep} of -0.45 and -0.65, and in bath A at E_{dep} of -0.65 V, we obtained the negative changes of V_{oc} (open circuit potential) during illumination, as it is expected for n-type semiconductors. In this case, the best values of photopotential (V_c^{ph}) are in the range of 150– 200 mV (see representative results in Fig. 7a). The positive changes of V_{oc} during illumination were observed for the CdTe films deposited in bath A at potential of -0.45 V (Fig. 7b). This evidence confirmed that p-type CdTe was formed. During the measurements under illumination, we observed the decrease in open circuit voltage and current



(Fig. 7c, d) resulting from photodecomposition of CdTe in the reactions:

n CdTe (photoanode) + $2h^+ \rightarrow Cd^{2+} + Te$

 $p \text{ CdTe (photocathode)} + 2e \rightarrow \text{Cd} + \text{Te}^{2-}$

The CdTe (narrow band semiconductor) is characterized by its extreme susceptibility to photocorrosion in aqueous electrolytes. The problem is even worse in thin film relative to the single crystal samples. For protection of Cd chalcogenides (CdS, CdSe, and CdTe), very often the polychalcogenide electrolytes are applied. It was shown by pioneering work of Wrighton (year 1977) [48] that n-type CdTe can be protected against photocorrosion by Te^{2–}/Te_n^{2–} system and that this system is the most efficient in CdTe protection.

Because of lack of $\text{Te}^{2-}/\text{Te}_n^{2-}$, we choose the polysulfide system to suppress the reaction of photoanodic or photocathodic dissolution of CdTe. The photodecomposition reactions should be quenched partially by oxidation of S_n^{2-} species at the photoanode and reduction of S_n^{2-} or $\text{Se}_n^{2-}/\text{Se}_n^{2-}$ (alkaline solutions), the reactions of cadmium hydroxides/ oxides and elemental Te formation are possible with further exchange reaction and formation of CdS or CdSe on a top of CdTe films.

Conclusions

Cathodic electrodeposition of CdTe thin films was carried out in acidic aqueous solution containing Na₂TeO₃ as a source of tellurium ions. We applied low ratios of Cd²⁺ ions to Te(IV) ions. Using XRD and XPS methods, it was shown that, when the ratio of $Cd^{2+}/Te(IV)$ ions is low (1:1, 5:1), the chemical composition of as-deposited CdTe films is influenced by two factors: bath composition and the value of deposition potential. Changes in bath composition ratio from 1:1 to 5:1 resulted in improvement of the crystallinity of the deposited films and in reduction of the TeO₂ amount on the CdTe surface. Structural XRD studies revealed polycrystallinity of CdTe deposits with the highest content of the (111)-oriented cubic form. Changes in the deposition potential values in the direction towards the equilibrium potential of Cd/Cd^{2+} at constant bath composition caused also the decrease in the TeO₂ amount on the CdTe surface. The best quality of CdTe deposits, free of TeO₂, was formed in bath containing excess of Cd²⁺ ions and at the potential of -0.65 V, slightly more positive than E_{eq} of Cd/Cd²⁺ system. When the deposition potential was much more positive than E_{eq} of Cd/Cd²⁺ system or the concentration of Cd²⁺ was not sufficient, the amount of TeO₂ increased as a result of oxidation of Te not involved in CdTe formation. The preliminary photoelectrochemical studies have shown that the variation of the deposition potential as well as bath composition leads to the formation of *p*-type or *n*-type CdTe films. *n*-type CdTe films were formed in bath B [5:1 concentration ratio of Cd(II)/Te(IV) ion sources] at both deposition potentials: E_{dep} of -0.45 V and -0.65 V, and in bath A (1:1 concentration ratio of Cd(II)/Te(IV) ion sources) at E_{dep} of -0.65 V, while *p*-type CdTe was formed in bath A [1:1 concentration ratio of Cd(II)/Te(IV) ion sources] at potential of -0.45 V.

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