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Electron spectroscopic investigations of CdS and CdTe electrochemically coated on glass

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Abstract. The electrodeposition of CdS and CdTe is investigated to improve the stoichiometric properties of CdS/CdTe layers on ITO-glass substrates for solar cell applications. X-ray photoelectron spectroscopy is utilized for the characterization of the CdS and CdTe layers. The influence of the electrodeposition potential, the pH and the thiosulfate concentration on the stoichiometry of CdS and CdTe layers are discussed.

Introduction

Thin films of CdS/CdTe can be used in solar cells with acceptable efficiency and costs because of their optimal band-gap of 1.45 eV [1.2]. Methods of preparation of such thin films include vacuum evaporation, sublimation, spray pyrolysis, molecular beam epitaxy, as well as, electrodeposition. However, for thin film applications large area production methods are needed to achieve significant saving in fabrication costs. Electrodeposition is such a technique and some properties of electrodeposited CdTe based solar cells have been published [3–5]. Influence of the electrodeposition potential on the optical, photoelectrochemical and structural properties of deposited CdTe has been described [6]. The aim of the present study is to investigate the stoichiometry of the electrodeposited CdS and CdTe on an ITO glass electrode using X-ray photoelectron spectroscopy (XPS).

Experimental

Electrochemical measurements were done using a double wall thermostated cell at 90° C. The working electrode was a rotating ITO-glass electrode, the counter electrode was a gold layer and for reference a saturated calomel electrode (SCE) was used. Cyclic and programmed potential voltammetry were used throughout this study. CdS is cathodically deposited from a solution containing 0.2 mol/l $CdCl_2$ and $S_2O_3^{2-}$, the concentration of which is varied from 0.01 to 0.05 mol/l. Deposition potentials of –0.6 and –0.7 V/SCE and pH values of 2 and 4 were used. CdTe films were deposited at –0.5 and –0.65 V/SCE using aqueous 0.001 mol/l $CdSO_4$ and 0.0003 mol/l TeO_2 electrolytes at pH = 2 for 30 min. In some cases CdTe is deposited after initial deposition of CdS on ITO. XPS measurements were performed on a KRATOS ES 300 spectrometer using AlKα excitation (hν = 1486.3 eV). The C1s line (binding energy (B.E.) = 285.0 eV) from the residual hydrocarbons deposited on the surface of the sample was used as reference with an overall accuracy of 0.1 eV in binding energies. The samples were investigated after heat treatment at 400° C for 10 min.

Results

Figure 1 displays part of the photoelectron spectra of the indium-tin-oxide (ITO) glass before and after electro-

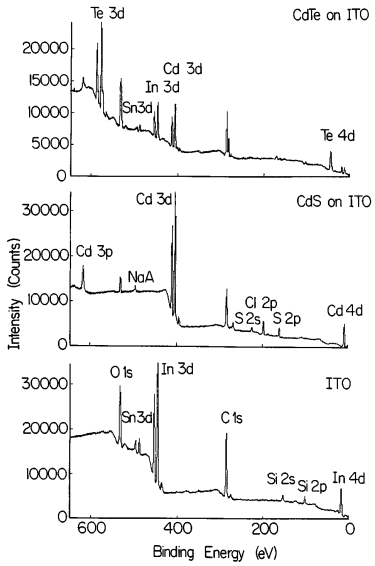

Fig. 1 AlKα X-ray photoelectron spectra of ITO glass before and after coating with CdS and CdTe

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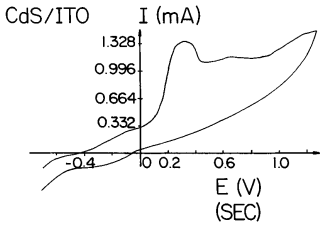

Fig. 2 Voltammetric curve of CdS coated on ITO glass electrode at pH = 4 and E = –0.7 V/MSE

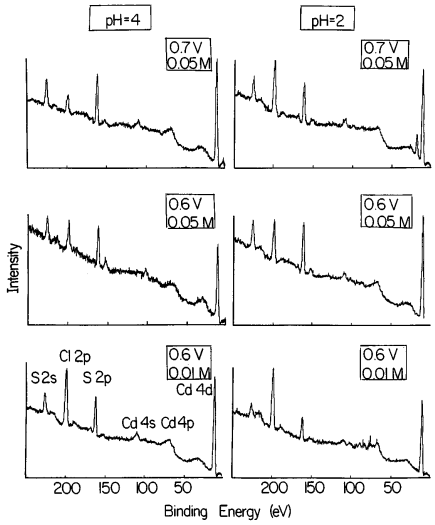

Fig. 3 0–250 eV region of the photoelectron spectra of CdS coated on ITO at various pH, deposition potential and thiosulfate concentrations

chemical coating with CdS and CdTe. The most prominent features belong to the strong 3d and 4d photolines of Cd, In, Sn and Te as well as others like the O1s, C1s, Cl, S and Si 2s and 2p photo and Na Auger lines. Binding energies of Cd in all cases are close to that of the +2 and those of Cl to the –1 oxidation states. For both S and Te, however, two peaks with varying intensity are observed. The lower binding energies at 162.2 and 573.2 eV can be assigned to S^{2-} and Te^{2-}, respectively, but the higher ones at 169.0 and 577.0 correspond to SO_x^{2-} and TeO_x^{2-} (x = 3 or 4), respectively. As can be inferred from the figure, in the case of CdS coated glass no feature (except maybe for the Na Auger line) belonging to the ITO glass surface can be observed. In the CdTe case, however, features of ITO are still observable. Quantitative information can be obtained from the observed intensities using the formula [7]: $[A]/[B] = (I_A/I_B) \times (\sigma_B/\sigma_A) \times ((E_k(B)/E_k(A))^{3/2}$ where I represents the observed intensity as calculated from the area of the peak, σ is the tabulated photoelectron cross section [8] and E_k is the kinetic energy (1486.3 – B.E.). Although any line corresponding to an element can be used for this calculation, large uncertainties may result if the photoelectron lines are very far apart (large kinetic energy differences) and/or if their cross-sections are widely different.

Thiosulfate ions disproportionate in acidic solutions affecting the deposition of CdS according to: $Cd^{2+} + S_2O_3^{2-} + 2e^- \rightarrow CdS + SO_3^{2-}$. A voltammetric curve of CdS coated on ITO at –0.7 V and pH = 4 is shown in Fig. 2. The anodic peak at 0.3 V (which does not depend on pH and/or deposition potential) corresponds to the oxidation reaction: $CdS + 4H_2O \rightarrow Cd^{2+} + SO_4^{2-} + 8H^+ + 8e^-$. Figure 3 shows the region of the photoelectron spectra where Cl, S 2s and 2p peaks and Cd and In 4d peaks are present for the various CdS coated glasses obtained under different pH, deposition potential, and concentration of $S_2O_3^{2-}$. Other preparation parameter as concentrations, deposition times etc. are the same for all these samples. Table 1 gives the data obtained from the spectra of these and other samples as well as the calculated atomic ratios using Cl 2p, S 2p and Cd 4d lines. As it can be inferred from the figures and Table 1 the surface composition is never free of Cl^- but nearly a stoichiometric CdS surface is obtained at pH = 4 and –0.6 V. Figure 4 shows the Te, Sn, In, and Te 3d and S 2p regions of the CdTe and CdS + CdTe coated glasses. Since the photoelectron cross section as well as the binding energies are close to each other, the 3d photolines of Te, Sn, In and Cd are used for the calculation of the atomic ratios in Table 2. For S again the 2p lines are used.

Table 1 XPS data of CdS coated on ITO glass under different pH, deposition potential and thiosulfate concentrations

Conditions	Binding energy (eV) (Area)						Area ratio		Atomic ratio		Formula
	O1s	$Cd3d_{5/2}$	Cl2p	S2p	Si2p	Cd4d	Cl2p/ Cd4d	S2p/ Cd4d	Cl/Cd	S/Cd	
pH = 4, E = –0.6 V 0.01 mol/l $S_2O_3^{2-}$	532.8 (8337)	405.8 (80549)	199.3 (7841)	162.3 (3100)	99.4 (804)	11.9 (9951)	0.788	0.311	0.80	0.41	$CdS_{0.41}Cl_{0.80}$
pH = 4, E = –0.6 V 0.05 mol/l $S_2O_3^{2-}$	532.8 (11203)	405.6 (23039)	199.1 (1158)	162.2 (1628)	101.2 (526)	11.8 (2877)	0.403	0.566	0.41	0.75	$CdS_{0.75}Cl_{0.41}$
pH = 4, E = –0.7 V 0.05 mol/l $S_2O_3^{2-}$	532.7 (9679)	405.4 (63200)	199.0 (2382)	162.1 (4549)	100.3 (439)	11.8 (9023)	0.264	0.504	0.27	0.67	$CdS_{0.67}Cl_{0.27}$
pH = 2, E = –0.6 V 0.01 mol/l $S_2O_3^{2-}$	532.7 (6692)	405.9 (40427)	199.4 (5429)	162.4 (1496)	101.8 (447)	11.8 (4827)	1.125	0.310	1.14	0.41	$CdS_{0.41}Cl_{1.14}$
pH = 2, E = –0.6 V 0.05 mol/l $S_2O_3^{2-}$	532.7 (8934)	405.6 (65795)	198.7 (3905)	162.3 (4655)	102.4 (414)	11.9 (9167)	0.426	0.508	0.43	0.67	$CdS_{0.67}Cl_{0.43}$
pH = 2, E = –0.7 V 0.05 mol/l $S_2O_3^{2-}$	532.7 (11662)	405.8 (57898)	199.1 (5561)	162.2 (3350)	99.9 (128)	12.0 (7378)	0.754	0.454	0.76	0.60	$CdS_{0.60}Cl_{0.76}$

Table 2 XPS data of some CdTe coated ITO glasses

Conditions	Binding energy (eV) (Area)						Area ratio			Atomic ratio		
	O 1s	Te $3d_{5/2}$	Sn $3d_{5/2}$	In $3d_{5/2}$	Cd $3d_{5/2}$	S 2p	Te3d/ Cd3d	In3d/ Ed3d	S2p/ Cd3d	Te/Cd	In/Cd	S/Cd
pH = 1.6	531.9	576.9	488.1	445.8	405.6	162.0						
E = –0.65 V		573.9				169.0	2.371	0.865	0.082	2.027	0.820	0.728
(CdTe)	(22776)	(52666)	(3146)	(19218)	(22215)	(1822)						
pH = 1.6	532.6	576.9	–	445.9	405.6	162.3						
E = –0.50 V		573.2				169.5	0.225	0.304	0.033	0.192	0.288	0.293
(CdTe)	(15805)	(9104)		(12257)	(40375)	(1335)						
pH = 1.6	532.6	576.90	–	445.9	405.6	162.2						
E = –0.65 V		573.2				169.0	0.949	0.091	0.139	0.811	0.086	1.23
(CdS + CdTe)	(20127)	(27905)		(2680)	(29423)	(4077)						

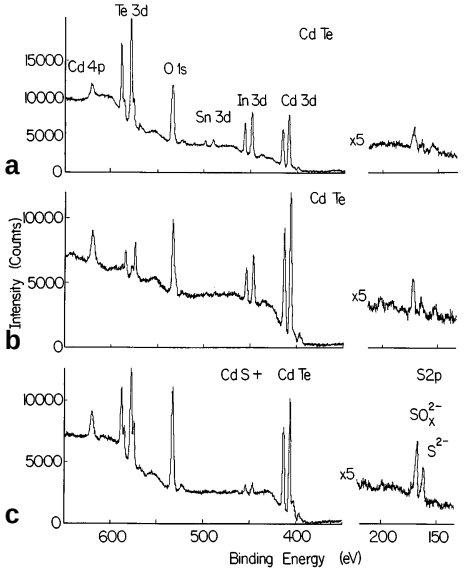

Fig. 4 a–c Parts of the photoelectron spectra of CdTe coated on ITO at pH = 1.6, deposition potential **a** –0.65 V, **b** –0.50 V, **c** –0.65 V after an initial deposition of CdS, the y-axis in the region between 0–250 eV is multiplied by 5 for better comparison

Electrodeposition of CdTe on CdS produces n-type semiconductors and only after heat treatment in air at 400° C p-CdTe can be obtained. According to these results a relatively stoichiometric CdTe film on the surface is obtained at pH = 1.6 only after an initial deposition of CdS and heat treatment. However, the surface also contains a significant amount of S both as S^{2-} and SO_x^{2-}.

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