International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.5, pp 2171-2175, 2014-2015

X-ray photoelectron spectroscopic studies of CdS semiconductor thin films deposited by photochemical deposition

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Abstract: Cadmium sulphide (CdS) thin films were deposited on insulating glass substrates from an acidic solution using cadmium sulphate ($CdSO_4$) and sodium thiosulfate ($Na_2S_2O_3$) by photochemical deposition (PCD). Analysis by X-ray photoelectron spectroscopy (XPS) giving a greater insight into the chemical composition through peaks corresponding to excitation of different electronic energy levels and correlation of the calculated chemical shifts is presented in this paper.
Key words: Thin films; CdS; photochemical deposition; UV photons; XPS.

1. Introduction

Deposition and characterization of CdS semiconducting thin films are of very much interest due to their potential application in the area of electronic and opto-electronic device fabrications[1-3]. Polycrystalline CdS (II-VI compound semiconductor) thin films possess good optical transmittance[4], wide and direct band-gap (2.42 eV at 300 K) and good electrical properties which makes it as one of the ideal material for their application in solar cell fabrication. The thin-film CdTe solar cell (generally n-CdS/p-CdTe) is one of the leading candidates for terrestrial photovoltaic applications due to its low cost and high efficiency. Several techniques have been used to fabricate CdS thin films, such as electrodeposition[5,] chemical bath deposition[6] (CBD), sputtering[7], spray pyrolysis[8], successive ionic layer adsorption reaction[9] and molecular beam epitaxy[10]. One of the most common methods used for depositing II-VI semiconductor thin films from an aqueous medium mediated by thermal energy at elevated temperature (50° C to 90° C) is CBD. In the present study we used another technique called photochemical deposition[11] (PCD) in which we can deposit II-VI semiconductors from an aqueous medium mediated by light photon at room temperature. This method is cost effective and easy to scale up.

X-ray photoelectron spectroscopy[12] (XPS) also known as ESCA (Electron spectroscopy for chemical analysis) can be used as a best tool to characterize the surface layer of the films, to identify the elements present in the film and to reveal the energy state of the elements present in the films and composition of the films.

2. Experimental

The photochemical reaction mechanism[13] and details of experiment conducted to deposit CdS thin films by PCD[14] are reported in the previous articles. The conditions used to obtain PCD-CdS thin films are growth solution containing 0.2 M $CdSO_4$ and 0.2 M $Na_2S_2O_3$ in acidic medium (pH = 3.6) irradiated by UV light, stirring speed = 300 rpm and deposition for one hour at room temperature. The films are characterized by XRD, EDAX, UV-Visible spectrophotometer, Photoluminescence, Raman, SEM and AFM measurements. The results of these characterizations are reported and published[13,14].

3. Results

3.1 Structural studies

The X-ray diffraction (XRD) pattern (Fig. 1) of CdS thin films confirms hexagonal structure and EDAX spectrum (Fig. 2) of CdS thin films confirms the presence of cadmium (Cd), sulphur (S), oxygen (O) and carbon (C).

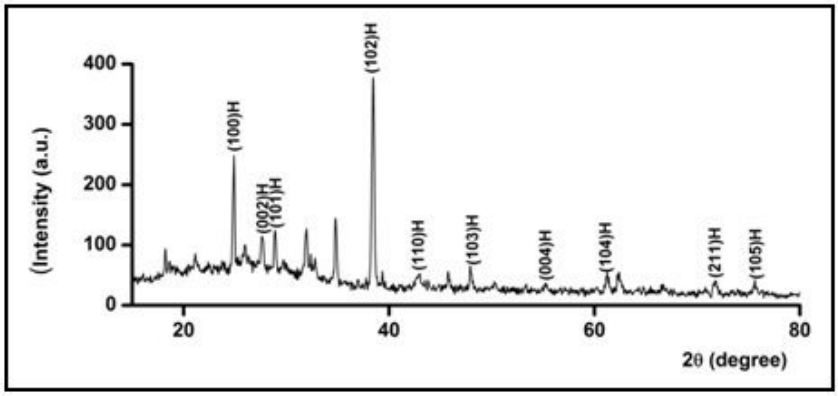


Fig. 1. XRD of the CdS thin films.

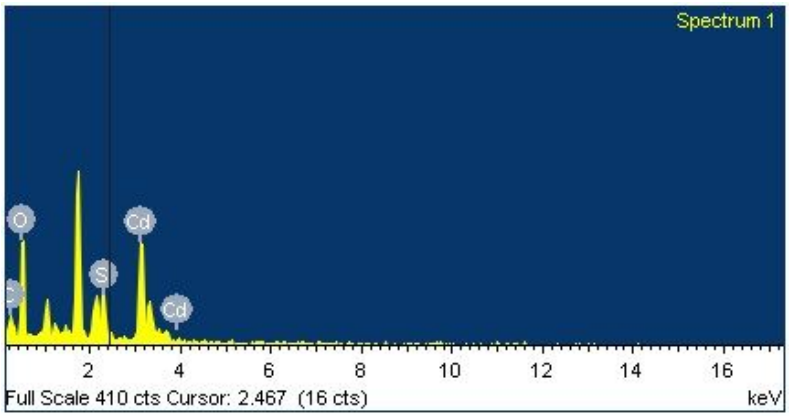


Fig. 2. EDAX spectrum of the CdS thin films.

3.2 XPS analysis

The PCD-CdS thin films are subjected to the surface analysis using XPS technique. XPS measurements were performed in the ultra high vacuum chamber (base pressure = 10^{-9} torr) of Kratos Axis Ultra XPS instrument using AlKα excitation source energy 1486.6 eV (analyser pass energy of 160 eV for survey and 20 eV for high resolution scans) operating at 150 W (15 kV, 10 mA) power. The energy scale was calibrated using C 1s at 284.8 eV as reference. All the reported binding energies are referenced to C 1s at 284.8 eV.

Fig. 3 is the typical survey spectrum of CdS thin film, showing the presence of Cd and S. In addition, it also shows the presence of C peak as well as O peak at 284.8 eV and 532.2 eV respectively as impurities. These contaminants have also been identified in CdS thin films deposited by CBD method by other workers[12,15,16]. High resolution spectra for C, O, S and Cd were also taken and are shown in Fig. 4, Fig. 5, Fig. 6 and Fig. 7 respectively. For quantitative study, the relative sensitivity factor (RSF) for Cd 3d is 6.623 and for S 2p is 0.668. The atomic concentration % of Cd is 58.38 and S is 41.62 and the Cd-to-S ratio is 1.40. The Cd/S ratio which is greater than unity in our case may be due to the partial oxidation of CdS film[12].

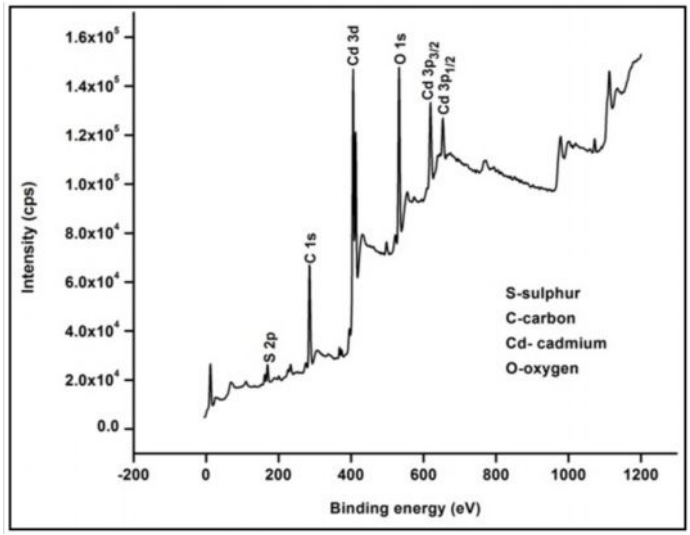
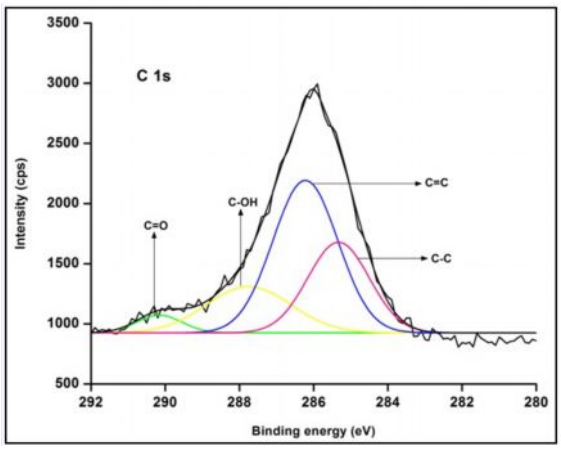


Fig. 3. XPS survey scan of CdS thin films.

C 1s peak (Fig. 4) is deconvoluted in to four components corresponding to species such as C-C/C-H, C-OH and C=O[12,17] which would correspond to adsorbed organic species from the solution (acetate and hydrolysis products) and also to CO_2 from the air. The O 1s peak is deconvoluted in to four components such as cadmium oxide (CdO), cadmium carbonate ($CdCO_3$), cadmium hydroxide [$Cd(OH)_2$] and water (H_2O) [12,17]. This confirms the presence of CdO, $CdCO_3$, $Cd(OH)_2$ and water in the films. The reported binding energies (E_B) of C 1s peaks and O 1s peaks and their experimentally obtained binding energies are tabulated (Table-1).

Fig. 5 shows the Cd $3d_{5/2}$ and Cd $3d_{3/2}$ core level spectrum of PCD-CdS thin films. It shows two core levels. No chemical-shift was observed in Cd in the system (Table-2). This confirms that there is no change in the chemical environment of Cd in CdS. The spin-orbit doublet of the Cd $3d_{5/2}$ and Cd $3d_{3/2}$ core levels is well separated by a binding energy interval of about 6.7 eV.



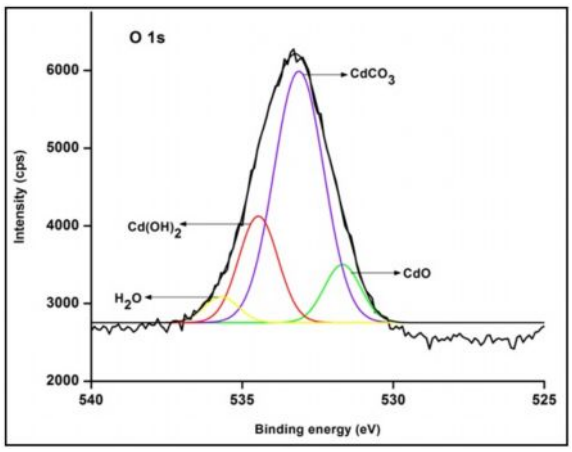


Fig. 3. XPS spectrum of C 1s level. **Fig. 4. XPS spectrum of O 1s level.**

Table 1: E_B values of deconvoluted C 1s and O 1s XPS lines

XPS lines C 1s	E_B standard (eV)	E_B experimental (eV)	XPS lines O 1s	E_B Standard (eV)	E_B experimental (eV)
C-C	284.8	284.4	CdO	530.5	530.3
C=C		284.8	$CdCO_3$	531.4	531.3
C=O	286	286.3	$Cd(OH)_2$	532.5	532.2
C-OH	287	286.7	H_2O	533.3	533.6

Table 2: E_B values of Cd 3d XPS lines

XPS lines	E_B standard (eV)	E_B experimental (eV)	Chemical Shift (eV)	Separation of $3d_{5/2}$ & $3d_{3/2}$ (eV)
Cd $3d_{5/2}$	405.2	405.2	zero	6.7
Cd $3d_{3/2}$	411.9	411.9	zero	

Table 3: E_B values of S 2p XPS lines

XPS lines	Compound	E_B standard (eV)	E_B experimental (eV)	Chemical Shift (eV)	Separation of $2p_{3/2}$ & $2p_{3/2}$ (eV)
S $2p_{3/2}$	CdS	161.6	161.5	0.1	7.3
S $2p_{3/2}$	$CdSO_4$	168.8	168.8	zero	

Fig. 6 shows two S 2p peaks. The first peak corresponds to CdS (161.5 eV) while the second peak is attributed to $CdSO_4$ (168.8 eV). The formation of a sulphate surface layer on sulphide materials when exposed to oxidizing environment (H_2O vapor, O_2) has already been observed by other authors[12]. Therefore, some $CdSO_4$ should be present at the surface of the films. The E_B and chemical shifts are tabulated (Table-3).

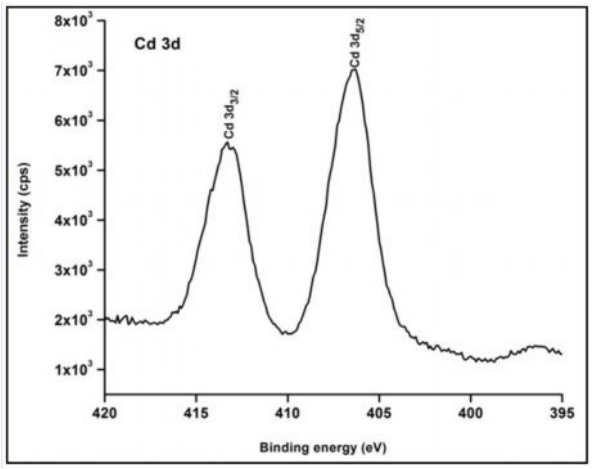


Fig. 5. XPS spectrum of Cd 3d level.

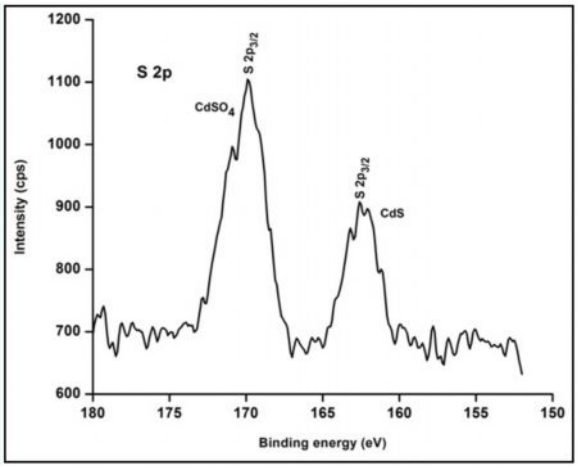


Fig. 6. XPS spectrum of S 2p level.

Discussion

XPS study shows oxygen as well as carbon contamination in the film along with Cd and S as confirmed by EDAX. With the presence of these elements the films are mainly composed of CdS with some CdO, $CdCO_3$, $Cd(OH)_2$ and water inclusion. The S deficiency of the films certifies the presence of CdO species absorption. The surface is also contaminated by some $CdSO_4$. From the atomic concentration percentage, the film is Cd rich as evidenced by EDAX[14].

Conclusion

The elements present in the films were identified and their chemical states were also studied by XPS. XPS spectra indicate composition of the films both qualitative and quantitatively.

Acknowledgements

The authors greatly acknowledge Dr. R Gopalakrishnan, Department of Physics, Crystal Research Laboratory, Anna University, Chennai, Tamilnadu for providing an opportunity to carryout PCD experiment. The authors are also thankful to Centre for Nano Science and Engineering (CeNSE), Indian Institute of Science

(IISc), Bangalore for providing XPS characterization facility.

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