Journal of Chemical, Biological and Physical Sciences



An International Peer Review E-3 Journal of Sciences Available online atwww.jcbsc.org Section C: Physical Sciences

CODEN (USA): JCBPAT

Research Article

Chemically deposited CdS thin film and its photoelectric performance

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Received: 31 December 2016; Revised: 11 January 2017; Accepted: 16 January 2017

Abstract: Cadmium sulfide (CdS) thin films are deposited on fluorine doped tin oxide (FTO) glass substrates at 80°C, 11pH by simple chemical bath deposition (CBD). The deposited thin films are characterized by X-ray diffraction (XRD), UV-VIS spectroscopy, scanning electron microscopy (SEM) surface wettability test, photo electrochemical study (PEC) and electrochemical impedance spectroscopy (EIS). The XRD study reveals the single phase cubic structure of CdS thin film. The optical study showed the direct band gap of 2.44 eV from the transmission data of UV-Vis spectroscopy. The surface morphology exhibits spongy agglomerated flakes- like morphology. The hydrophilic nature of the CdS thin film was observed from surface wettability test. The PEC study confirms the photo activity of the deposited film and EIS study gives the interpretation of carrier transportation through the interface in the fabricated PEC cell in light and dark.

Keywords: Cadmium sulfide, Chemical bath deposition, Contact angle, electrochemical impedance spectroscopy, Photoelectrochemical study.

INTRODUCTION

II-VI chalcogenide semiconductors¹ are widely used because of their significant potential applications in optoelectronic devices. Among the chalcogenides of II-VI group, CdS thin films are most popular due to their wide band gap, n-type semiconducting nature, good optical transmittance, relatively high conductivity and ease of deposition on conducting and non-conducting substrates etc. It is the most commonly used as window material in cadmium telluride² (CdTe), copper indium disulfide³ (CuInS₂), copper Indium gallium sulfide⁴ (CuInGaS₄) based solar cells, photo diodes⁵, photo transistors⁶, gas sensors⁷, water splitting photo electrochemical cells⁸ etc.

CdS thin films are obtained by different methods, such as thermal evoparation⁹, molecular beam epitaxy (MBE)¹⁰, chemical bath deposition (CBD)¹¹⁻¹², close space sublimation (CSS)¹³, spray pyrolysis¹⁴, sol-gel¹⁵ etc. Among all these methods, chemical bath deposition is simple, inexpensive and scalable to large area deposition and can be operated at low temperature. CdS exists in cubic, hexagonal or mixed form¹⁶⁻¹⁸. The properties of CdS thin films obtained by CBD depend on the preparative parameters such as pH of the solution, concentration of the solution, deposition temperature, deposition time etc. By optimising these parameters it is possible to tune the optical, electrical, morphological properties of CdS films so that CdS thin film becomes the suitable candidate in the fabrication of optoelectronic and other devices.

In the present work the growth and characterization of CdS thin films by CBD on transparent conducting fluorine doped tin oxide (FTO) glass substrates (FTO: FSnO₂) have been carried out. The structural, optical, morphological, photoelectrochemical, surface wettability properties are investigated. The actual carrier transportation through the interface is interpreted by means of electrochemical impedance spectroscopy (EIS).

MATERIALS AND METHODS

In the experimental work cadmium sulphate $(3CdSO_4.8H_2O)$ was taken as cadmium source, thiourea $(CS(NH_2)_2)$ was taken as sulfur source. Liquid ammonia was used as complexing agent¹⁹. CdS thin films were deposited on well cleaned FTO substrates of dimension 5cmX1cm X 0.3cm. All chemicals used are of analytical reagents (AR) grade and are used without further purification. The chemical bath comprises of 20mL, 0.05M cadmium sulfate in a clean 50 mL beaker. 30% liquid ammonia was added to it slowly drop by drop with constant stirring till pH 11 was obtained. Initially white precipitate was formed due to the formation of Cd (OH)₂. The white precipitate disappears on addition of excess of ammonia. To this 20 mL of 0.05M thiourea was added.

The contents of the chemical bath were stirred well. Pre-cleaned FTO substrates were introduced into the chemical bath in vertical position. The chemical bath then placed in a water-bath maintained at constant temperature 80°C under constant stirring for 1hour. The substrates were removed from the chemical bath, washed with double distilled water (DDW) and dried in air naturally for half an hour. Yellow-orange colored, well adherent, uniformly deposited CdS thin films were obtained and preserved in an air tight container. The deposited CdS thin film at pH 11 (**Figure 1**) is identified as CdS-11.



Figure1: CdS-11 thin film on FTO substrate

Growth mechanism of CdS thin film: The chemical bath contains cadmium salt and thiourea in ammonical bath. The liquid ammonia in the reaction mixture provides OH^- ions required for the hydrolysis of thiourea which gives S^{2-} ions and also controls the amount of Cd^{2+} ion in the bath through the formation of $[Cd(NH_3)]^{2+}$ (tetra-amine-cadmium (II) complex). The decomposition of $[Cd(NH_3)]^{2+}$ and hydrolysis of thiourea gives the slow release of Cd^{2+} and S^{-2} which results in CdS formation²⁰⁻²¹.

The formation mechanism of CdS thin film is proposed by the following equations,

(I) Reactions in the solution:

$\mathrm{CdSO}_4 \to \mathrm{Cd}^{2+} + \mathrm{SO}_4^{2-}$	(dissociation of cadmium Sulfate)	[1]		
$\rm NH_4OH \rightarrow \rm NH_3 + H_2O$	(dissociation of ammonia)	[2]		
$Cd^{2+} + 4NH_3 \rightarrow [Cd(NH_3)]_4^{2+}$ (formation of tetra – amine – cadmium II complex)				
$\mathrm{CS} (\mathrm{NH}_2)_2 + 2\mathrm{OH}^- \rightarrow \mathrm{S}^{2-} + \mathrm{CH}$	$_2N_2 + 2H_2O$ (decomposition of thiourea)	[4]		

(II) **Reaction at the surface :**There are 2 types of mechanism involved in the CdS film formation at the surface of the substrate, the first one corresponds to the growth from individual atoms called ion by ion process and the other one is cluster by cluster process.

a) ion by ion process	
$Cd^{2+} + S^{2-} \rightarrow CdS$	[5]
b) Cluster by cluster process	
$[Cd(NH_3)]_4^{2+} \rightarrow Cd^{2+} + 4NH_3$ Release of Cd^{2+} ions	[6]
c) Cluster formation	
$nCd^{2+} + 2n(OH)^{-} \rightarrow [Cd(OH_2)]_n$	[7]
$[Cd (OH)_2]_n + nS^{2-} \rightarrow nCdS + 2nOH^-$	[8]

Characterization of CdS thin films: The structural evaluation of CdS-11 thin film is performed by obtaining XRD pattern using the X-ray diffractometer Bruker made D2 phaser of XAS Analytical instruments (p) Ltd. Germany. The thickness of the CdS thin film was measured using XP stylus profiler XP-1, Ambios technology USA. The optical properties of the film were carried out by using UV-VIS spectrophotometer UV 1800, Shimadzu, Japan. The surface morphology of thin film was examined by using scanning electron microscope (SEM) JSM 6360A, JEOL USA. The surface wettability of the CdS thin film was studied by measuring the water contact angle to the CdS thin film using contact angle goniameter rame-hart instrument USA. The photo electrochemical study of the film was performed by using photo electrochemical set up Auto lab 302N, Metrohm, Switzer land. The electrochemical impedance study of the film was performed by electrochemical impedance spectrophotometer Zive SP5, WonAtech, South Korea.

RESULTS AND DISCUSSION

Structural properties: The structural and phase identification of CdS-11 thin film were carried out by X-Ray diffractometer using Cu-K α radiation 1.542Å. Figure 2 shows the XRD pattern of CBD grown CdS thin films for pH 11. The pattern exhibits well defined peaks (200), (220), (311), (222) and (400) at $2\theta = 30.80^{\circ}$, 43.91°, 51.91°, 54.58° and 63.68° respectively. The observed XRD data compared with the standard JCPDS data (JCPDS Data Sheet No. 00-001-0647) and it was found that the obtained film showed the cubic structure²²⁻²³.



Figure 2: X-ray diffraction pattern of the CdS-11

The crystallite size (D) of the film was calculated from Sherrer's formula²⁴,

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$
[9]

Where, λ is wave length of X-ray used, β is full width at half maximum of the peak and θ is Bragg's angle.

The interplanar spacing (d) is calculated using the equation

$$d = \frac{\lambda}{2\sin\theta}$$
[10]

The average dislocation density (ρ) of CdS thin film can be calculated by

$$\rho = \frac{1}{D^2} \tag{11}$$

Number of crystallites/unit surface area (N) can be calculated by $N = \frac{t}{D^3}$ [12]

Where *t* is thickness of the film.

The induced strain (ε) in the sample can be calculated by

$$\varepsilon = \frac{\beta}{4\tan\theta}$$
[13]

The experimental (exp) values of 2θ , d, lattice constant (a) are compared with standard (std) values of JCPDS data sheet No. 00-001-064 and are tabulated in Table 1.

(hkl)	2θ (std)	20 (exp)	Interplanar spacing d (std) Å	Interplanar spacing d (exp) Å
(200)	30.80°	31.41°	2.90	2.845
(220)	43.91°	44.99°	2.06	2.013
(311)	51.91°	52.39°	1.76	1.745
(222)	54.58°	55.36°	1.68	1.658
(400)	63.68°	62.50°	1.46	1.484

Table 1: Comparison of Interplanar distance (d)

The calculated values of structural parameters of the CdS film are tabulated in Table 2.

Table 2: Calculated values of structural parameters

D (nm)	ρ (lines/m ²)	N m ⁻²	N m ⁻²	ρ N ϵ	3	Lattice constant(a) (Å)	
(inn) (innes/in)	111		(std)	(exp)			
3.22	9.65 X 10 ¹⁷	2.44 X 10 ¹⁸	0.64	5.82	5.77		

Optical study of CdS thin film: The UV-VIS spectroscopy is used to study the optical properties of CdS-11 thin films prepared by CBD method. The absorption spectrum of the CdS thin film recorded at room temperature within the wavelength range 300 to 900 nm is shown in the Figure 3a.

The optical band gap of thin film is calculated using the following equation for near edge optical absorption in semiconductor²⁵,

$$\alpha h v = k(h v - E_g)^{\frac{1}{2}}$$
 [14]

Where, α is the absorption coefficient, ν is the frequency of radiation, k is a constant, h is the planck's constant, E_s is the band gap.

The optical band gap of the CdS thin film is determined from the intercept made by the straight line portion of the plot of $(\alpha hv)^2$ as a function of photon energy hv (**Figure 3b**). This plot is linear in high energy region; this indicates CdS-11 is a direct band gap semiconductor²³ with a band gap 2.44 eV. Figure 3c gives the optical transmittance spectra obtained for the film and its transmittance²⁶ is found to be nearly 65% in the wavelength range 500-600 nm.



Figure 3a: Optical absorption spectra of CdS-11

Figure 3b: $(\alpha hv)^2$ vs hv plot of CdS-11



Figure 3c: Optical transmission spectrum of CdS-11

Surface morphological study: Figure 4a and 4b shows the surface micrographs of the thin film at X 5,000 and X 10,000 magnifications. The SEM result reveals the presence of spongy agglomerated flakes-like morphology^{27, 35}. The thin film formed is homogeneous, well adherent, free from cracks and pin holes. For the film the flakes are agglomerated and connected to each other. These interconnected flakes like morphology would enhance the conduction mechanism and suitable for solar cell applications.



Figure 4: SEM images of CdS-11 a. at x5,000 and b. at x10,000 magnifications

Surface Wettability Study: The wetting studies refers to the fact that, how a liquid spreads on a deposited solid substrate. The contact angle measurement quantifies the wettability of a solid surface by a liquid surface. The wetting nature of the surface is characterized by the water contact angle measurement (θ). If the wettability is good, the contact angle will be small ($\theta < 90^\circ$) then the surface is hydrophilic and if the wettability is poor, the contact angle will be high ($\theta > 90^\circ$) then the surface is hydrophobic.

The important application of the contact angle measurement is the assessment of the surface free energy of the solid. The surface free energy is equivalent to the surface tension of the liquid. The contact angle (θ) can be measured using Young-Dupre equation²⁸ given by

$$\cos\theta = \frac{\gamma_{\rm sv} - \gamma_{\rm sl}}{\gamma_{\rm lv}}$$
[15]

Where γ_{sv} is the interfacial tension between solid and vapour, γ_{sl} is the interfacial tension between solid and liquid, γ_{lv} the interfacial tension between liquid and vapour.

Surface wettability of the CdS-11 thin film has been studied by means of measuring the water contact angle to the thin film. Figure 5 shows the captured water drop image on the CdS-11 sample. The contact angle of CdS-11 sample is $67^{\circ}_{\pm} 1^{\circ} (\theta < 90^{\circ})$. This shows the obtained thin film exhibits the hydrophilic²⁹ surface nature due to good wetting. As a result there is a formation of better interface in the PEC cell³⁰. The observed value of the contact angle is in the range of transition region of hydration repulsion to hydrophobic attraction.



Figure 5: Image of water drop on CdS-11

Photoelectrochemical analysis: The PEC performance of the CdS-11 thin film electrode was examined by measuring the current density (J) versus Voltage (V) characteristic on FTO substrate in 1M polysulfide electrolyte³¹. 1M Poly sulfide is an aqueous redox electrolyte of 1M sodium hydroxide (NaOH) + 1M anhydrous sodium sulfite (Na₂S) + 1M sulfur (S) powder used to fabricate the PEC cell along with two electrodes.

CdS thin film electrode of area 1 cm^2 was used as working electrode or photoelectrode and graphite as counter electrode. The counter electrode and photoelectrode are separated by 1 cm. Figure 6 shows the PEC performance of CdS thin film under 50 mWcm⁻²illumination and dark conditions. The solar cell parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), are obtained from the graph.

The power conversion efficiency of cell (η) is calculated using the following equation³²,

$$\eta = \frac{J_{sc} \times V_{oc}}{P_{in}} \times FF$$
 [16]

Here, P_{in} is the power of input radiation, FF is the fill factor. Fill factor can be calculated by using following equation,

$$FF = \frac{J_{m} \times V_{m}}{J_{sc} \times V_{oc}}$$
[17]

Where J_m and V_m is the maximum current density and maximum voltage respectively chosen in such a way that the power become maximum. From the water contact angle measurement it is observed that the obtained CdS film has shown good wetting and resulted in the formation of better interfacial region in the PEC cell .



Figure 6: PEC performance of CdS-11

From the calculation it has been observed that for the deposited CdS thin film J_{sc} value0.28mAcm⁻², the V_{oc} value 0.16V, the fill factor 0.354 and the efficiency of the PEC cell was found to be 0.07%²². The J-V characteristics of Figure 6 indicates that under illumination the magnitude of the voltage increase with negative polarity towards working electrode showing the cathodic behavior of the film³³. This indicates that CdS-11 thin film is an n-type semiconductor.

Electrochemical impedance spectroscopy (EIS) study: The electrochemical mechanism at the interface of the CdS thin film such as electron recombination resistance, kinetics of the charge carriers etc. can be understood by electrochemical impedance spectroscopic studies (EIS). The EIS of CdS-11 thin film was conducted in dark as well as light using 1M polysulfide electrolyte. The measurements are conducted with an applied forward bias voltage -0.5 V and the measuring AC frequency in the range 1-10kHz.

Figure 7a shows the impedance spectroscopy of CdS-11 thin film under dark and illumination. The impedance spectra of the film was fitted into the corresponding semicircle of CdS sample using Nova 9.1 software in terms of the geometrically appropriate equivalent circuit shown in Figure 7b. The equivalent circuit is composed by resistors (R) and constant phase elements (Q)³⁴⁻³⁵. The first semi arc in the spectrum is appeared due to the graphite electrode/electrolyte interface in the high frequency region. The second semi arc is due to the electron transfer at the CdS/electrolyte interface at high frequency region. In CdS-11 sample the first semi arc at higher frequency split up into two parts indicate that the charge transfer is occurring between the graphite/electrolyte interface and FTO/electrolyte interface.



Figure 7a: Impedance spectroscopy of CdS-11



Here, R_s is the sheet resistance of the substrate, R_1 is the charge transfer resistance of the graphite/electrolyte interface. R_2 is the charge transfer resistance of the FTO/electrolyte and R_3 is the recombination resistance of the photo generated electrons at the CdS/electrolyte interface. The extra semi arc appeared in the CdS sample was due to the spongy agglomerated nature of film which cause the diffusion of Cd²⁺ ions hence the FTO gives the contribution in the charge transfer resistance³⁶⁻³⁷. By EIS studies the sheet resistance for the CdS-11 film was found to be 25 Ω .

CONCLUSION

Thin film of CdS at pH 11 was deposited on FTO glass substrate from the aqueous alkaline reaction bath by CBD. The XRD results revealed cubic phase of the film. The UV-Visible spectroscopic study indicated that film has the direct band gap of 2.44eV. The surface morphology of the CdS film examined by SEM found to be uniform with spongy agglomerated interconnected flakes-like structure. The flake-like morphology is suitable for solar cell applications. The water contact angle with the film revealed that the surface of the film exhibited hydrophilic nature due to good wetting. This would give rise to a better interfacial region in the PEC cell which in turn may account for its performance. The power conversion efficiency of the PEC cell is found to be 0.07%. This confirms the photo activity of the CdS thin film and the film showed n-type semiconducting nature. The sheet resistance of the deposited CdS thin film was found to be 25Ω by EIS studies.

ACKNOWLEDGEMENT

The authors are grateful to Prof. C D Lokhande, former HOD of Physics, Instrumentation Facility Center (PIFC), staff and research students in the Department of Physics, Shivaji University, Kolhapur for the valuable discussion and guidance to carry over the present work.

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On line publication Date: 16.01.2017