Sol-Gel Synthesis of CdS/Glass & CdS/Si Thin Films for Optoelectronic Devices

I. Rathinamala (✉ rathinamala@vvvcollege.org)

V.V.Vanniaperumal College for Women

N. Prithivikumaran

V.H.N.Senthikumara Nadar College

Research Article

Keywords: CdS/Glass & CdS/Si thin films, XRD, SEM, EDAX, PL, FTIR, Four-probe

Posted Date: July 16th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-688129/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Sol-Gel Synthesis of CdS/Glass & CdS/Si Thin Films for Optoelectronic Devices

I. Rathinamala^{1}, and N. Prithivikumaran²*

¹Department of Physics, V.V.Vanniaperumal College for Women, Virudhunagar – 626001, Tamilnadu, India.

²Nanoscience Research Lab, Department of Physics, V.H.N.Senthikumara Nadar College,
Virudhunagar – 626001, Tamilnadu, India.

rathinamala@vvvcollege.org

Abstract

Cadmium chalcogenides have gained huge attention during the past few decades from investigators exploring various applications like optoelectronic, photovoltaic, thermoelectric devices etc. In the present work, CdS thin films had been deposited onto glass and silicon substrates using sol - gel spin coating technique. The structural, surface morphological, optical and electrical properties of the synthesized films were studied. The X-Ray diffraction analysis revealed that the prepared films have hexagonal structure with preferential orientation along (0 0 2) plane. The structural parameters such as crystallite size, strain and dislocation density of the prepared films were estimated and reported. The SEM image of the CdS thin films showed a uniform, homogeneous and granular morphology over the entire surface of the substrate. The PL spectrum showed three emission peaks; dominant peak occurs at 575 nm and the other two peaks occur at 525 nm and 480 nm. The FTIR study gave the bonding present in the CdS thin film samples. The Four-probe results showed that the electrical conductivity increases with increase in temperature. The present study suggested that CdS thin films on Si wafer could be a good promising candidate for the fabrication of optoelectronic devices.

Keywords: CdS/Glass & CdS/Si thin films, XRD, SEM, EDAX, PL, FTIR, Four-probe

1. Introduction

CdS, belonging to the II – VI group is one of the promising materials for optoelectronic applications. The deposition of CdS films has become increasingly important in recent years due to the widened industrial application with a large number of uses [1 – 3]. For example the heterojunctions, based on CdS thin films are very promising structures for solar cells because of suitable band gap, optical absorption, and good stability of the used materials [4 – 6]. CdS does not play a direct role in photovoltaic conversion of solar radiation, however, it is adequate as an optical window and preferred over other materials of

wide band gap due to its compact crystallographic cell and electronic affinity with CuInSe₂, InP, CdTe and other p-type semiconductors [7].

The modern electronics world greatly depends on silicon dioxide for the manufacture of semiconductors, wire insulation, and fiber optic cables. Crystalline Silicon's physical and chemical properties make it as a versatile material in accomplishing physical, structural and electrical tasks in the fabrication of electronic devices. In view of fabricating optoelectronic device, we choose p-type (1 0 0) silicon wafer as a substrate (Boron doped with 0 -100 Ωcm resistivity) on which n-type CdS was coated and studied.

In the present work, the spin coating technique has been employed for the deposition of CdS films on glass and silicon substrates, which is simple, relatively easier method and ideal for large area thin film preparation. The effect of substrates on the structural, surface morphological and optical properties of the prepared CdS nanocrystalline films has been studied. The results obtained are discussed and compared.

2. Materials and Methods

2.1. Materials

In this process, CdS was embedded in polyethylene glycol (PEG) based solution. The PEG sol was prepared by mixing 0.6 ml of PEG, with 8.9 ml of ethanol and 0.5 ml of acetic acid under stirring, which was continued for 1 hour. Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and thiourea ($\text{CH}(\text{NH}_2)_2$) of 0.3 M were used as precursors for the incorporation of Cd and S respectively. These precursors were dissolved in ethanol with stirring. The as prepared solution was slowly added to the PEG sol with vigorous stirring and was stirred for 5 - 6 hour to obtain the final sol ready for depositing thin films. The coating was made one day after the precursor was prepared, so that the prepared sol had 24 hour aging time.

Fig. 1: Schematic of CdS Thin Film Formation

2.2 Preparation of CdS Thin films

Spin-coating technique was used to prepare thin films on substrates. The samples were prepared at rotation speeds of 1000 rpm with the spin time of 30 second. The films were subsequently annealed in air at 300°C for one hour in order to remove the solvent and residual organics. The schematic of CdS thin film formation was shown in Figure 1.

3. Results and Discussion

3.1. Structural Analysis

X-ray diffraction (XRD) analysis was performed on CdS films with a diffracting angle range of 20° to 80°, using a PANalytical XPERT- PRO X-ray diffractometer with Cu K α_1 radiation. The X-ray diffraction pattern for CdS thin film coated on glass and Si substrates are shown in Figure 2. The XRD pattern reveals the crystalline nature of deposited material, having preferential orientation along the c-axis. The crystallographic phases of samples are in good agreement with the typical hexagonal wurtzite structure. Zial Raza Khan et.al, [8] also reported that CdS films coated on (1 0 0) Si wafer prepared via thermal evaporation technique exhibited a hexagonal structure with (0 0 2) as the major plane.

Fig. 2: XRD Pattern of CdS Thin Films

In addition a much intense (4 0 0) peak in CdS/Si film was obtained at $2\theta = 69.2^\circ$ which is due to crystalline Si substrate. The crystallite sizes (D) were calculated using the Scherrer's formula from the full-width at half maximum (FWHM) β , by using the relation [9],

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \text{ (nm)} \quad (1)$$

where λ is the X – ray wavelength (CuK $\alpha_1 = 1.54060 \text{ \AA}$) and θ is the Bragg angle. The lattice constants 'a' and 'c' are obtained from the X-ray analysis using the following relationship for hexagonal crystal structure [10],

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

where h, k and l are the miller indices. The dislocation density (δ), defined as the number of dislocation lines per unit volume, was estimated using the formula [11],

$$\delta = \frac{1}{D^2} \quad \text{lines / m}^2 \quad (3)$$

The volume of the unit cell for the prepared films were evaluated using the relation,

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (4)$$

The various structural parameters for CdS thin films are calculated using the standard formulae and are systematically represented in Table 1.

Table 1: Structural Parameters of CdS Thin Films

Samples	Crystallite Size D (nm)	Dislocation Density δ (*10 ¹⁶) (lines/m ²)	Strain ϵ *10 ⁻³	Lattice Parameter		Unit cell Volume V (Å) ³
				a (Å)	c (Å)	
CdS/Glass	7.11	1.98*10 ¹⁶	5.09	4.14	6.94	103.12
CdS/Si	102.29	9.5580*10 ¹³	0.35	4.20	6.88	104.90
JCPDS Reference (06 - 0314)	-----	-----	-----	4.136	6.713	99.45

Thus, the film coated on Si substrate has a better crystalline quality, as indicated from its XRD pattern. The smaller values of dislocation density obtained in the present study confirmed the good crystallinity of the CdS films. It was also observed that the CdS/Si film has lesser strain and dislocation density. It is clear that the substrate plays an important role in determining the structure of the CdS films.

3.2. Surface Morphological Analysis

The Scanning electron microscopy (SEM) was used for topographic analysis of CdS thin film samples. Surface morphology of the CdS samples was recorded using TESCAN VEGA-3 LMU Scanning electron microscope. The SEM micrographs of CdS/Glass & CdS/Si thin films post annealed in air at 300°C are shown in Figure 3.

Fig. 3: SEM Micrographs of CdS Thin Films

The deposited film has been found to exhibit a uniform, homogeneous and granular morphology covering entire substrate surface. The grains, like small spheres on plane sheet, are clearly observed in the CdS/Si SEM micrograph.

3.3. EDAX Analysis

Quantitative analysis of the film was carried out using the EDAX technique to study the stoichiometry of the film. The elemental analysis of the CdS/Glass & CdS/Si thin films post annealed at 300°C was made by energy dispersive X-ray spectroscopy and it was shown in Figure 4.

Fig 4: EDAX Spectra of CdS Thin Films

The EDAX spectra (Figure 4) reveals that the films deposited using spin coating technique contain Cd and S as expected. It was significant to note that films deposited at optimized preparative parameters are nearly stoichiometric. The extra peaks arise due to the presence of the elements in amorphous glass substrate.

3.4. Optical Analysis

The Photoluminescence (PL) study was carried out with a Xenon lamp as light source and the used excitation wavelength was 380 nm. It shows the emission spectrum, since the most common radioactive transition in the semiconductor occurs between states at the bottom of the conduction band and the top of the valence band. Room temperature PL spectra of the CdS thin film deposited on glass & silicon substrates post annealed for the temperature of 300°C are shown in Figure 5.

Fig. 5: PL Spectra of CdS Thin Films

The role of surface and native defects has been invoked to explain the observed PL behaviour. The PL emission spectra are found to exhibit emission peaks centered at 480 nm, 525 nm and 575 nm. The band at 480 nm is related to the confinement effects and the direct inversion of the fundamental absorption edge for the nanometric dimensions of the crystallite [12]. The other green band composed of a peak centered at around 525 nm, originated from radiative recombination [13], which was related to the grain size distribution.

3.5. Fourier Transform Infra Red (FTIR) Spectral Analysis

Fig. 6: FTIR Spectra of CdS Thin Films

The Fourier Transform Infra Red (FTIR) spectrum of the samples was plotted using the Shimadzu FTIR - 8400S spectrometer in the wave number range of 4000 – 400 cm⁻¹ with

a resolution of 4 cm⁻¹. The resulting spectra represent the molecular absorption and transmission, creating a molecular fingerprint of the sample. The FTIR spectra of CdS thin films deposited on glass & Si substrates annealed at a temperature of 300°C are shown in Figure 6. The IR frequencies along with the vibrational assignments for CdS/Glass & CdS/Si thin films are given in Table 2.

Table 2: Observed Surface Bondings in CdS/Glass & CdS/Si Thin films

Sample	Wave number (cm ⁻¹)	Bonds	Vibration mode
CdS/Glass	3500	O - H	Stretching, H ₂ O
	2900	Cd - O	Stretching
CdS/Si	3520	O - H	Stretching, H ₂ O
	3000	Cd - O	Stretching
	1650	H ₂ O	Bending
	1080	Si-O	Stretching
	665	Cd - S	Stretching

The O–H stretching vibrations of water molecules were observed at 3500 cm⁻¹. The vibration absorption peak at 665 cm⁻¹ is due to Cd–S stretching. The two medium strong bands at 685 and 714 cm⁻¹ in FTIR spectra of CdS can be assigned to Cd–S stretching and were also reported by earlier workers [14].

3.6. Resistivity Measurement using Four Probe Method

The four point probe method (PID – 200 Model) was used to measure the resistivity of the CdS layers coated on Si substrate. The electrical properties of the thin films are strongly dependent on their structural characteristics. A constant current is passed through the two probes and the potential drop V across the middle two probes is measured. Heat treatment of thin films can modify the structural characteristics and hence the electrical conductivity of such films may change too. An oven is provided with a heater to heat the substrate so that behaviour of the sample is studied with increase in temperature such as 50°C, 75°C and 100°C. Figure 7 presents the voltage – current characteristics of CdS thin films deposited on Si wafer annealed at 300°C.

The resistivity of the deposited chalcogenide material was calculated using the formula,

$$\rho = \frac{\rho_0}{G_7 \left(\frac{w}{s} \right)} \quad (5)$$

$$\rho_0 = \frac{V}{I} 2\pi s \quad (6)$$

where, ρ - resistivity, $G_7(W/S)$ - divisor for computing resistivity, W - thickness of the film and S - distance between the probes. The function $G_7(W/S)$ is a divisor for computing resistivity which depends on the value of W and S .

Fig. 7: IV Characteristics of CdS Thin Film coated on Silicon Substrate

The decrease in resistivity of the films (shown in inset of Figure 7) with increase in temperature indicates the semiconducting nature of the film as it tends to increase the density of the charge carriers.

4. Conclusion

The CdS thin films had been deposited successfully onto glass and silicon substrates using sol - gel spin coating technique. The X-Ray diffraction analysis revealed that the prepared films have hexagonal structure with preferential orientation along (0 0 2) plane. It also observed that the CdS/Si film has lesser strain and dislocation density. The SEM image of the CdS thin films showed that the grains are spherically shaped and also the surface composition of the film was identified by EDAX analysis. The FTIR study gave the vibrational assignments along with the bonding present in the CdS thin film samples. The electrical study revealed that the conductivity increases with increase in temperature due to the increase of grain size and carrier density of the chalcogenide material. The present study

showed that CdS thin films coated on Si substrates proves to be a promising candidate for the fabrication of optoelectronic devices.

Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the author.

Consent to participate

There are no human subjects in this experimental work and hence informed consent is not applicable.

Consent to publish

Open access: This article is distributed under the terms of Creative Commons Attribution 4.0 International License which permits unrestricted use, distribution and reproduction in any medium provided appropriate credit is given to the original authors and the source.

Authors Contribution

Both authors made substantial contributions to conception of design, analysis and critical review of manuscript.

Funding

This research work was not financially supported by any agency or organization.

Competing Interest

The authors declare that they have no competing interest.

Availability of data and materials

All information regarding the synthesis and characterization are available with the authors. If necessary, the complete data will be shared with the journal review team.

Reference

1. R. Hill, in: T.J. Coutts (Ed.), Thin Film Active and Passive Devices, Academic Press, New York (1987) 487.
2. M. Ueno, H. Minoura, T. Nishikawa, M. Tsuiki, J. Electrochem. Soc., 140 (1983) 43.
3. Xiaoyan Yang, Bo Liu, Bing Li, Jingquan Zhang, Wei Li, Lili Wu, Lianghuan Feng, Applied Surface Science, Volume 367, 30 (2016) 480.
4. Wenzhi Chen, Xuan Huang, Qijin Cheng, Chao Chen, Daqin Yun, Fengyan Zhang, Optik - International Journal for Light and Electron Optics, Vol. 127, Issue 1 (2016) 182.

5. J. Escorcia-García, D. Becerra, M.T.S. Nair, P.K. Nair, Thin Solid Films, Vol. 569 (2014) 28.
6. Khagendra P. Bhandari, Paul J. Roland, Hasitha Mahabaduge, Neale O. Haugen, Corey R. Grice, Sohee Jeong, Tienneke Dykstra, Jianbo Gao, Randy J. Ellingson, Solar Energy Materials and Solar Cells, Vol. 117 (2013) 476.
7. S. Durand, Thin Solid Films 44 (1977) 43.
8. Ziaul Raza Khan, M. Zulfequar, Mohd. Shahid Khan, Materials Science and Engineering B 174 (2010) 145.
9. M.D.Uplane, S.H.Paward, solid State commun. 46 (1983) 847.
10. A. Goswami, Thin Film Fundamentals, New Age International (P) Ltd. Publishers, New Delhi (2005) 69.
11. Alah Abdul-Jabbar Jassim, Abubaker A. Rashid Ali Zumaila, Gassan Abdella Ali Al Waly, Results in Physics 3 (2013) 173.
12. B.Ullrich, D.M.Bagnall, H.Sakai and Y.Segawa, J.Luminesc. 1162 (2000) 87.
13. A.Giardini, M.Ambrico, D.Smaldone, R.Martino, V.Capozzi, G.Perna and G.F.Lorusso, Mater. Sci. Eng. B 43 (1997) 102.
14. T.P. Martin, Helmut Schaber, Spectrochem. Acta A. 38 (1982) 655.