



Structural, Surface Morphology and Elemental Composition Analysis on CdS Thin Films Prepared By Vacuum Evaporation Deposition

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Abstract: Cadmium Sulphide thin films have been deposited on to well cleaned glass substrate in a vacuum of 10^{-6} Torr. The thickness of the films has been determined by quartz crystal monitor method. CdS thin film of lower thicknesses has amorphous structure and higher thickness has polycrystalline nature with cubic structure. The structural parameters such as interplanar distance (d), lattice constant (a), grain size (D), dislocation density and microstrain have been evaluated. The grain size is calculated for all films of different thicknesses. The SEM micrographs of different thickness are analysed at a resolution of $20\mu\text{m}$ with 5000x magnification. We clearly observe the small nanosized grains engaged in a fibrous-like structure, which clearly indicates the glassy nature along with amorphous phase of ZnS thin films. The AFM micrograph shows that the particle size and the surface roughness of ZnS thin films increases with increase in thickness. The Energy –dispersive X-ray spectroscopy (EDAX) expose that the presence of Zinc, Sulphur and Oxygen is confirmed in all the films.

Keywords: CdS, Structural Properties, X-ray diffraction, SEM, AFM, Vacuum Evaporation.

Introduction

The preparation of CdS thin films with controlled properties requires an operating environment which interfaces as little as possible with the process of film formation. Extensive work has been done on the attachment of very high vacuum to minimize the interaction between the residual gases and the surface of the growing films¹⁻². The film structural studies are made presently using a sophisticated Philips X-ray diffractometer proportional counter and signal channel pulse height analyzer³⁻⁵. The Scanning electron microscope micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. The AFM is one of the foremost tools for imaging, measuring, and manipulating matter at the nanoscale⁶⁻⁹. In some variations, electric potentials can also be scanned using conducting cantilevers. The Energy-dispersive X-ray spectroscopy (EDAX), as an x-ray detector to measure the relative abundance of emitted x-rays versus their energy¹⁰⁻¹². The energy as determined from the voltage measurement, for each incident x-ray is sent to a computer for display and further data evaluation¹³⁻¹⁵. The spectrum of x-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.

Materials and methods

Selection of substrates

Film has to be formed on a substrate to support itself. Hence the substrate is chosen based on their Physical and Chemical conditions. The substrates must be optically plane, transparent, electrically non-interfacing and amenable to fairly high temperature, chemically stable and comparatively cheaper¹⁶⁻¹⁷. A smooth surface facilitates the formation of a uniform thin film and is suitable for structure and optical condition studies. Glass substrates are used, since they are smooth, economical and can be easily cleaned.

Substrates cleaning

Cleanliness and preparation of substrates is essential for success in thin film work. Condensation rate and adhesion of the deposit are critically dependent on conditions of the surface. Even a thin layer of grease can have such a gross effect on a molecular scale as to alter completely the characteristics of the layer¹⁸⁻²⁰. A clean substrate is a prerequisite for the formation of any film for study or application. The glass substrate used in the present study is first rinsed with distilled water. Then they are treated with NaOH solution. This alkaline agent dissolves fatty material by saponification and renders them wet. After a rinse with distilled water, the substrates are kept in ultrasonic agitator for 30 minutes to remove organic impurities²¹⁻²². Finally substrates are cleaned with isopropyl alcohol vapours and hence enhance the removal of surface contaminants²³⁻²⁵. The substrates are then heated in an oven for about 45 minutes at a temperature of 100°C. Drying and dust removal finally makes them ready for the coating process.

Preparation Characterization of CdS thin films by Vacuum evaporation deposition.

CdS thin films have been prepared by vacuum evaporation deposition. The CdS powder of purity 99% is evaporated using Tungsten conical basket (200 amps) under the pressure of 2×10^{-5} Torr on to a pre cleaned glass substrate (3.25 x 2.75 x 0.1 cm dimension). The pressure is obtained by diffusion pump backed by rotary pump in the coating unit and is measured using Pirani and Penning gauge. A constant rate of evaporation of the order of 1 Å/sec is maintained throughout the film fabrication. A rotary device is employed to maintain uniformity in film thickness. The thickness of the film is controlled and measured by Quartz crystal monitor and the thickness monitor in a flat circular plate approximately 0.05 inch (1.4cm) in diameter and 0.011 inch (0.28 cm) thick. A substrate heater arrangement is employed to grow the thin film at different substrate temperatures. A Copper – constantan thermocouple is employed to measure the temperature inside the chamber.

The vacuum evaporated ZnS thin films of thickness 550 Å, 1150 Å and 1850 Å are measured by quartz crystal digital thickness Monitor. X-ray diffraction measurements were carried out with using Rigaku Miniflex system equipped with Cu-K_α radiation of average wavelength 1.54059 Å. The Scanning electron microscope is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times to more than 500,000 times, about 250 times the magnification limit of the best light microscopes²⁰⁻²². Atomic Force Microscope instruments (N9410S-5500) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. Elemental Composition Analysis important technique to separate the characteristic x-rays of different elements into an energy spectrum, and EDAX system software is used to analyze the energy spectrum in order to determine the abundance of specific elements²³⁻²⁵.

Result and discussion

Thickness measurements

Thin-film thickness monitors, deposition rate controllers, and so on, are a family of instruments used in high and ultra-high vacuum systems. It can measure the thickness of a thin film, not only after it has been made, but while it is still being deposited, and some can control either the final thickness of the film, the rate at which it is deposited, or both. Not surprisingly, the devices which control some aspect of the process tend to be called controllers, and those that simply monitor the process tend to be called monitors. The vacuum evaporated CdS thin films of thickness 880 Å, 930 Å and 2550 Å are measured by quartz crystal digital thickness Monitor.

X-Ray Diffraction analysis.

X-ray diffractogram of CdS thin films, taken from diffractometer is used to analyse various crystalline aspects. According to Bragg's law,

$$n\lambda = 2d_{hkl} \sin Q_{hkl} \quad (1)$$

Where 'n' is the order of reflection, 'λ' is the wavelength of the incident x-rays. The direction of propagation of scattered beams (Q_{hkl}) is related to the interplanar distance (d_{hkl}) in the lattice (h k l) which represents the property of the material and is related with the lattice constant and miller indices. The XRD patterns of vacuum evaporated CdS thin films of thickness 880 Å, 930 Å and 2550 Å are shown in Fig. 1, Fig. 2 and Fig. 3 respectively.

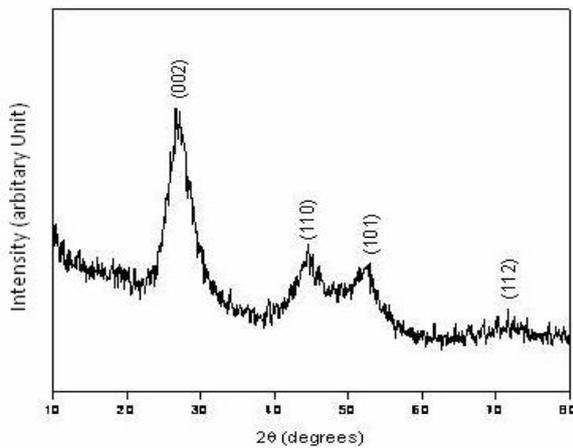


Figure 1. X-ray diffractogram of CdS thin film of thickness 880 Å

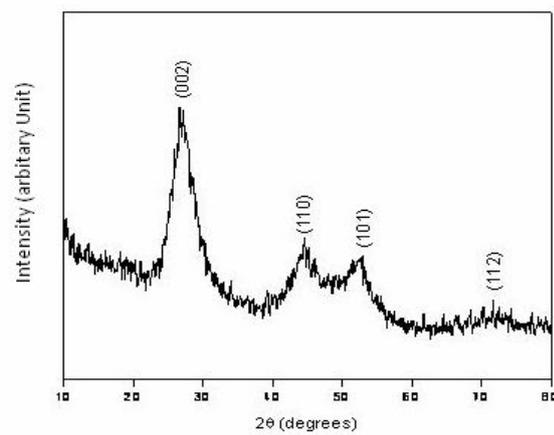


Figure 2. X-ray diffractogram of CdS thin film of thickness 930 Å

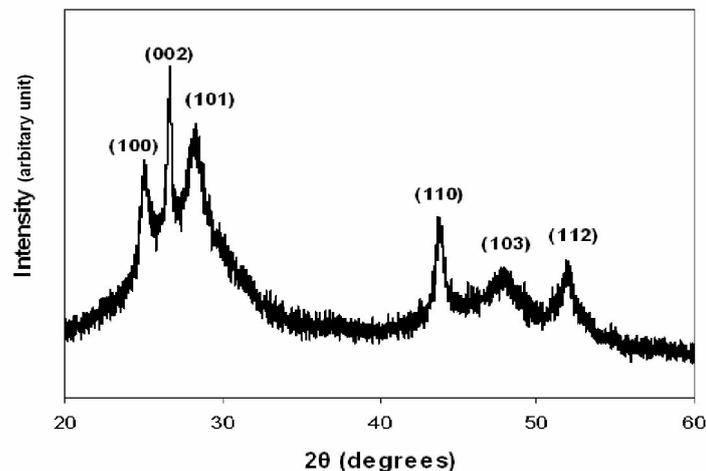


Figure 3. X-ray diffractogram of CdS thin film of thickness 2550 Å

From the diffraction patterns, it can be seen that the diffraction peaks are sharp and well defined indicating that the film is polycrystalline in nature. The XRD patterns exhibit prominent broad peaks at 2θ values of 24.94° , 26.56° , 28.41° , 36.66° , 43.82° , 47.85° , 51.92° and 53.04° . These results are in good agreement with (100), (002), (101), (110), (103) and (112) planes and show cubical structure. It is reported that CdS films prepared at room temperatures, normally show a cubic structure. From the figure, it can be seen that the intensity of diffraction peak increases as the thickness of the film increases. This is an indication of improvement in crystallinity with increasing films thickness. The intense peak along (002) plane in all the films indicates that the films are highly oriented along the 'c' axis.

The inter planar distance (d) and the lattice parameter (a) are calculated in this case by means of the plane-spacing equation for cubic crystal, which is given by,

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

and the grain size is calculated using Scherer's formula,

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (3)$$

Where ' β ' is the full width half maximum of the peaks. The diffraction direction is solely determined by the structure and size of the unit cell. The calculated ' d ' values for CdS sample coincides fairly with those of bulk material reported in ASTM tables on cubic CdS. All these data showed a clear evidence for a cubic CdS. The interplanar distance (d), lattice parameter (a), grain size (D), dislocation density (ρ) and microstrain (ϵ) are shown in table 1.

Table 1. Structural parameters for CdS thin films

Thickness	(h k l)	d (Å) Exp	d (Å) ASTM	2 θ	a (Å)	Grain size (D) Å	Dislocation density (ρ)cm ²	Strain (ϵ) 10 ⁻³
880 Å	002	1.57	1.68	32	5.4682	5.0179	3.6347	6.4682
	110	3.24	3.42	16	5.0631	5.1884	3.5792	6.4789
	101	1.92	1.97	28	5.3598	2.5684	14.5793	13.5724
	112	3.34	3.36	14	5.3684	4.2434	8.6835	7.6379
930 Å	002	1.68	1.58	32	5.5679	5.0494	3.4646	6.3679
	110	3.46	3.56	18	5.6893	5.2484	3.4682	6.2893
	101	1.46	1.85	34	5.8734	2.5891	14.3518	13.4839
	112	3.73	3.68	15	5.4792	4.3389	8.3894	7.5793
2550 Å	100	1.59	1.57	29	5.5079	3.5752	7.3903	9.7021
	002	1.64	1.64	28	5.4392	5.0631	3.2315	6.2512
	101	1.89	1.93	24	5.3598	2.6192	14.1167	13.2406
	110	3.18	3.16	14	5.5079	5.2884	3.3730	6.1516
	103	1.93	2.04	22	5.5739	3.5684	9.7835	5.6972
	112	3.24	3.18	12	5.5234	4.5635	8.8149	7.3945

From the table 1, it is found that, the grain size of the film increases with film thickness and the dislocation density and microstrain is found to decrease. It can be attributed to the decrease in the imperfections and dislocations of the films with increasing film thickness.

Scanning Electron Microscope (SEM).

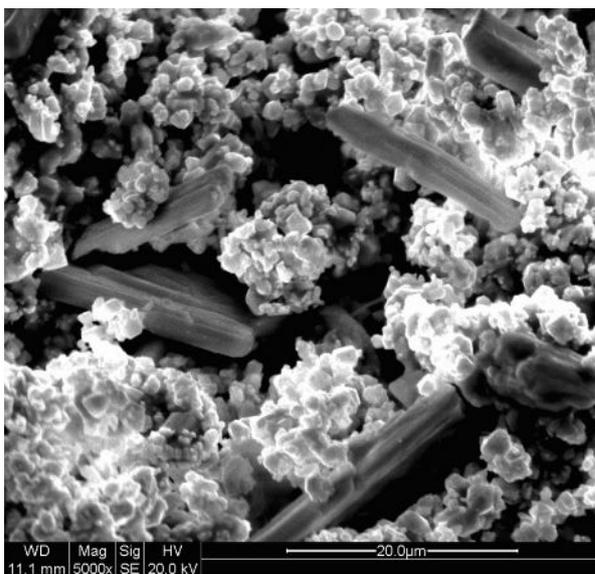


Figure 4. SEM micrographs of CdS thin film of thickness 880 Å

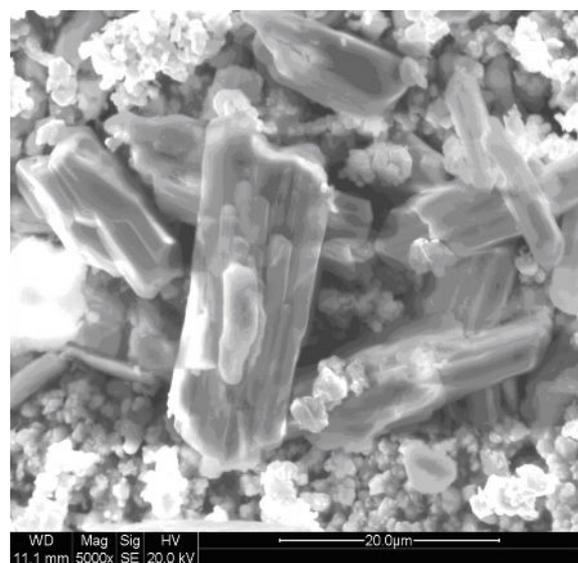


Figure 5. SEM micrographs of CdS thin film of thickness 930 Å

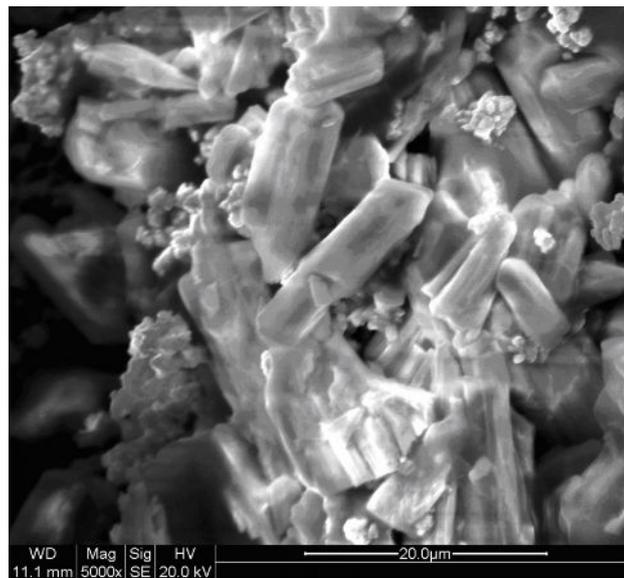


Figure 6. SEM micrographs of CdS thin film of thickness 2550 Å

Scanning electron microscopy is a convenient technique to study the microstructure of thin films. Fig. 4, Fig. 5 and Fig. 6 show SEM images of CdS thin films of different thickness. The SEM micrographs of different thickness are analyzed at a resolution of 20 μm with 5000x magnification. The SEM micrographs of 880 Å thickness shows that the distributions of grains are not uniform throughout all the regions. But the films are without any void, pinhole or cracks and that they cover the entire substrate well. We clearly observe the small nanosized grains engaged in a fibrous-like structure, which clearly indicates the glassy nature along with amorphous phase of CdS thin films. The grains are found to be thickly packed and inter grain spacing is reduced in the case of film thickness 930 Å shown in Fig. 5.

From the Fig. 6, for the films of higher thickness (2500 Å) the crystals grow in size and such a size difference might be due to the presence of some amorphous phase in the films along with their predominant crystalline phase. The surface morphological study also indicates that the decrease in the Cd content improves the surface smoothness.

Atomic Force Microscope (AFM).

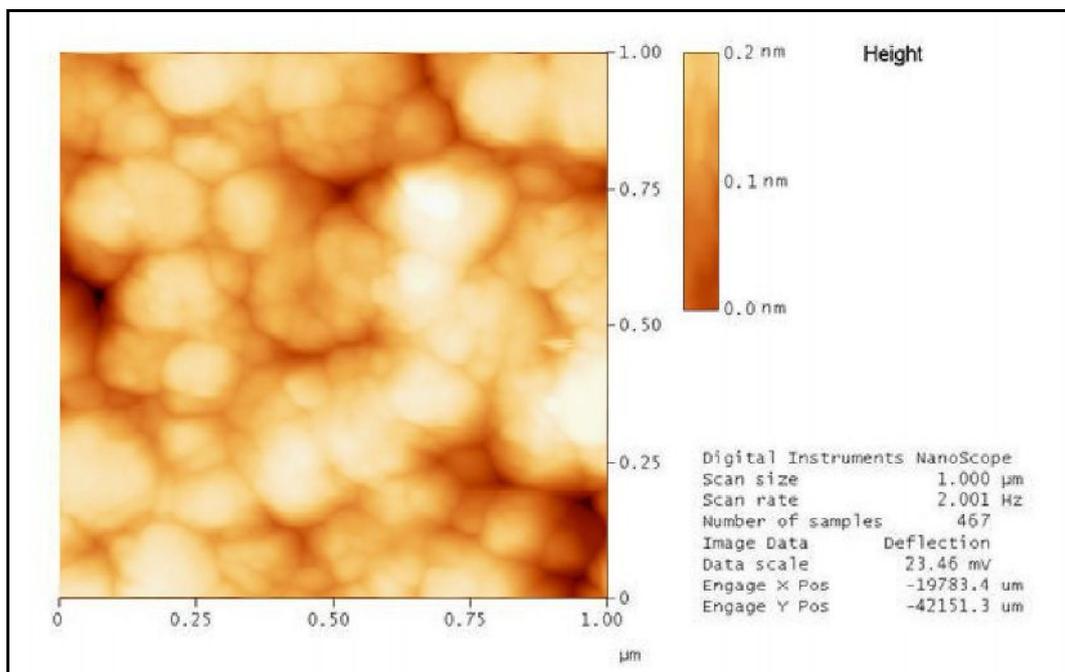


Figure 7. Two dimensional AFM micrograph of the CdS thin film of thickness 880 Å

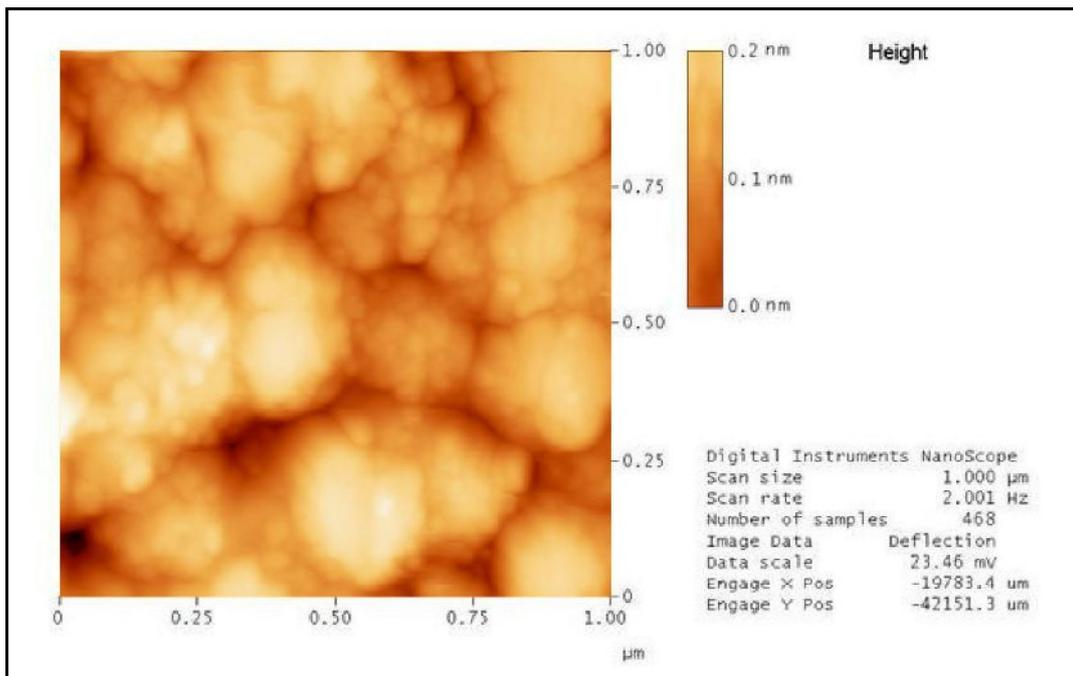


Figure 8. Two dimensional AFM micrograph of the CdS thin film of thickness 930 Å

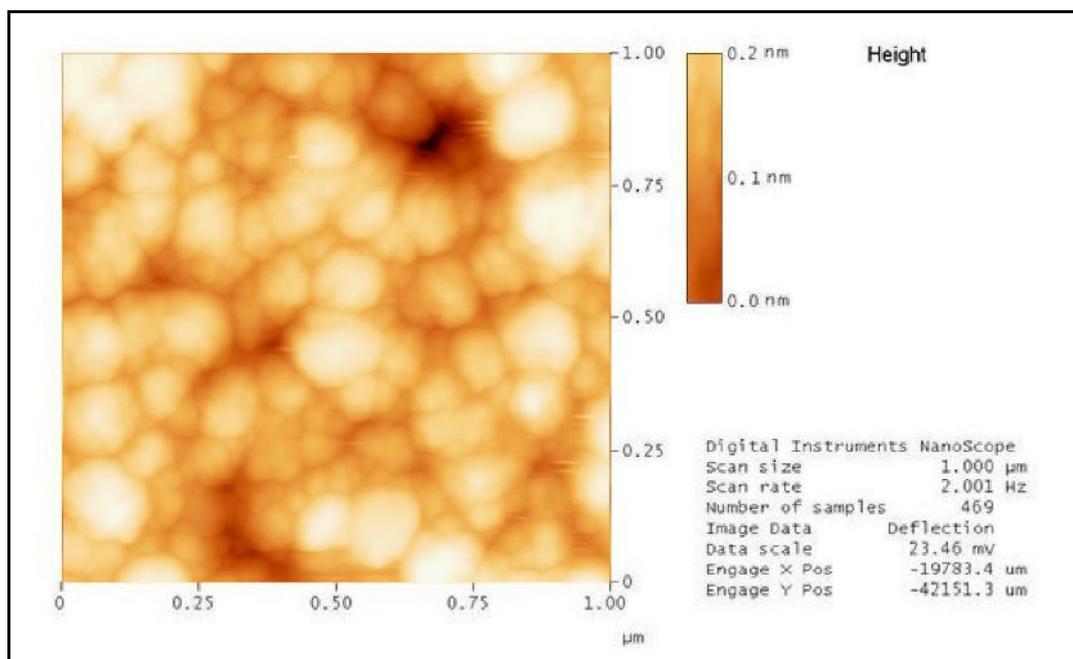


Figure 9. Two dimensional AFM micrograph of the CdS thin film of thickness 2550 Å

Fig. 7, Fig. 8 & Fig. 9 show two dimensional AFM micrograph of the CdS thin films having thickness 880 Å, 930 Å and 2550 Å respectively. The scanning is done over an area of 1μm x 1μm. The AFM images expose the high uniformity of the films with spherical shape particles and also show the beta phase films which consists of grain size 40-180 nm.

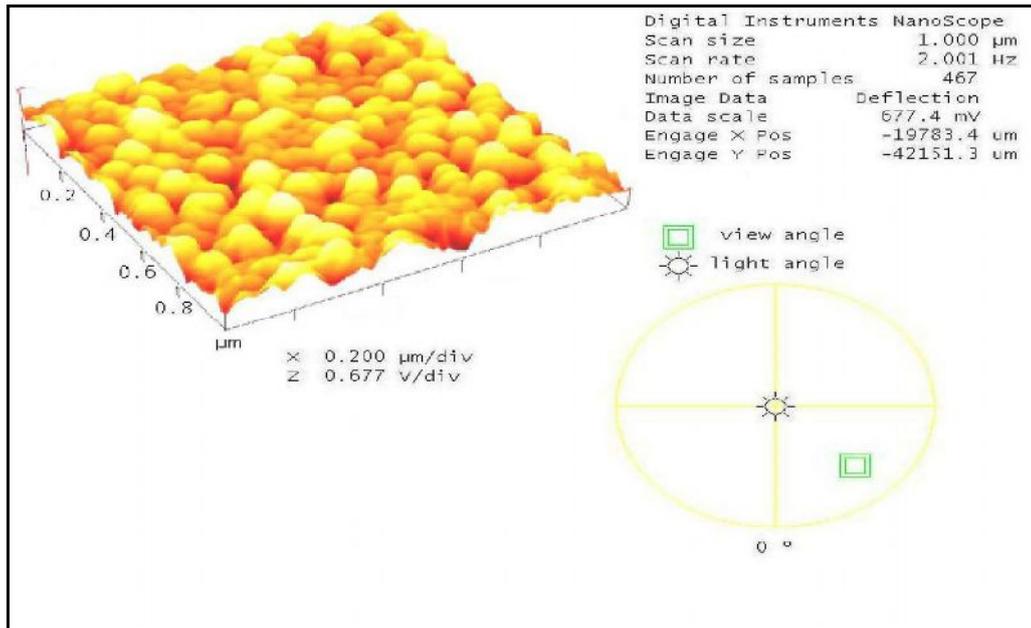


Figure 10.Three dimensional AFM micrograph of the CdS thin film of thickness 880 Å

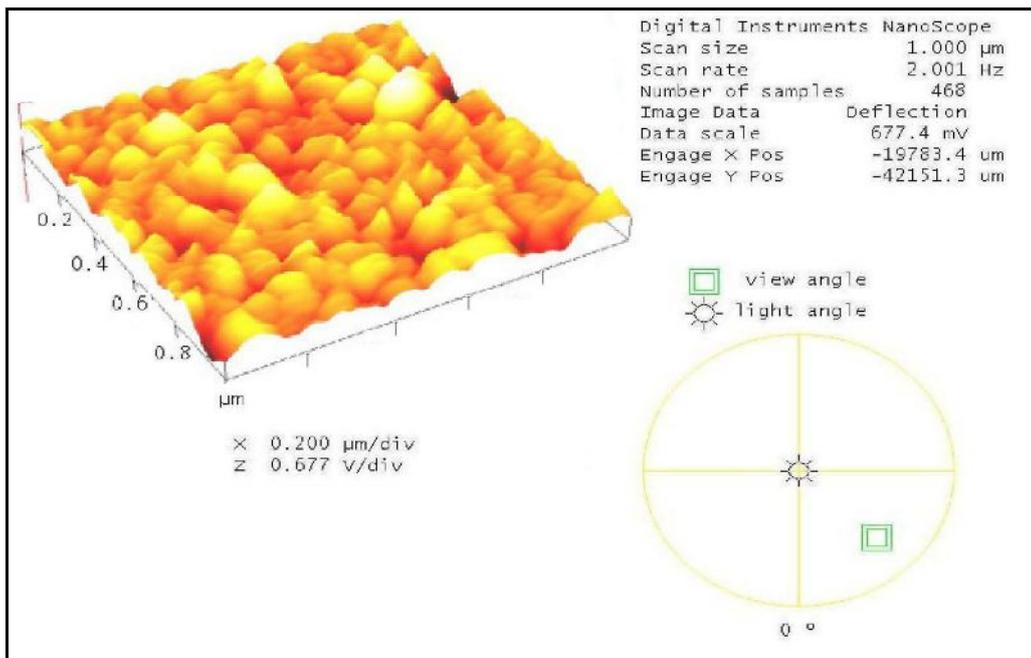


Figure 11.Three dimensional AFM micrograph of the CdS thin film of thickness 930 Å

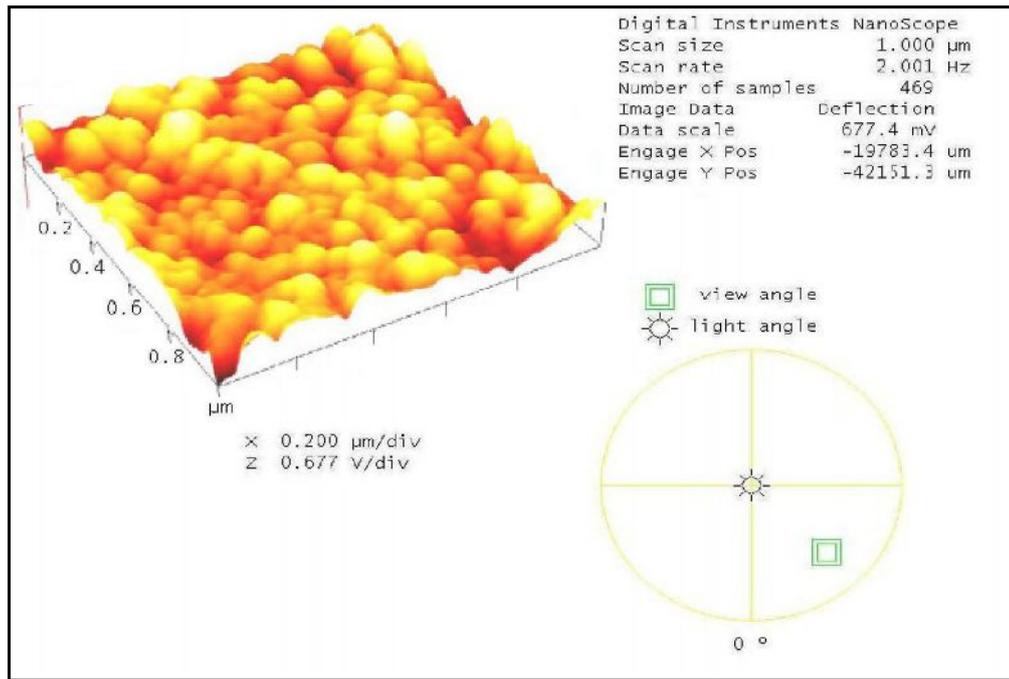


Figure 12. Three dimensional AFM micrograph of the CdS thin film of thickness 2550 Å

Fig. 10, Fig. 11 & Fig. 12 show the three dimensional AFM micrograph of the CdS thin films having thickness of 880 Å, 930 Å and 2550 Å respectively. The average size of the particle is calculated by Debye-Scherrer equation. The average size and the root mean square of the roughness (rms) of the surface of CdS films of thickness 880 Å, 930 Å and 2550 Å are tabulated in Table 2. The Table 2. reveals that, the particle size and the surface roughness of CdS thin films increases with increase in thickness.

Table 2. Variation of particle size with thickness

Sl. No.	Film thickness (Å)	Particle size (nm)	Roughness of the surface (nm)
1	880	57.20	12.50
2	930	60.45	13.12
3	2550	165.75	23.78

Energy Dispersive X-ray Spectrometer (EDAX).

Fig. 13, Fig. 14, & Fig. 15, show the energy dispersive X-ray spectra of CdS thin films having thickness 880 Å, 930 Å & 2550 Å respectively.

From the table 3, the presence of Cadmium, Sulphur and Oxygen is confirmed in all the films. The oxygen due to the using of octylamine. The concentrations of Cd, S & O are observed to be varying with film thickness, but no systematic variation is noticed.

Table 3. Elemental composition of CdS thin films

Element	Wt %			At %		
	880 Å	930 Å	2550 Å	880 Å	930 Å	2550 Å
Cd L	67.15	67.73	67.73	16.12	20.71	20.71
S K	07.64	15.57	15.57	04.85	12.61	12.61
O K	25.21	16.70	16.70	79.03	66.68	66.68

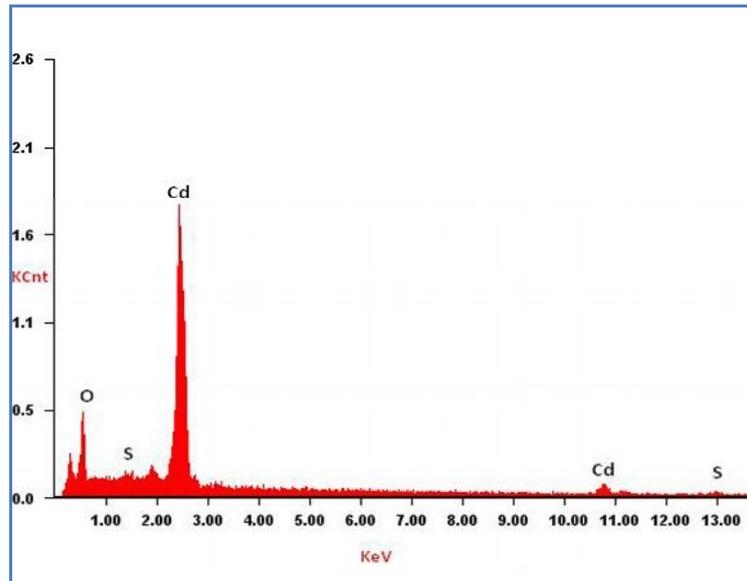


Figure 13. EDAX spectrum of CdS thin film of thickness 880 Å

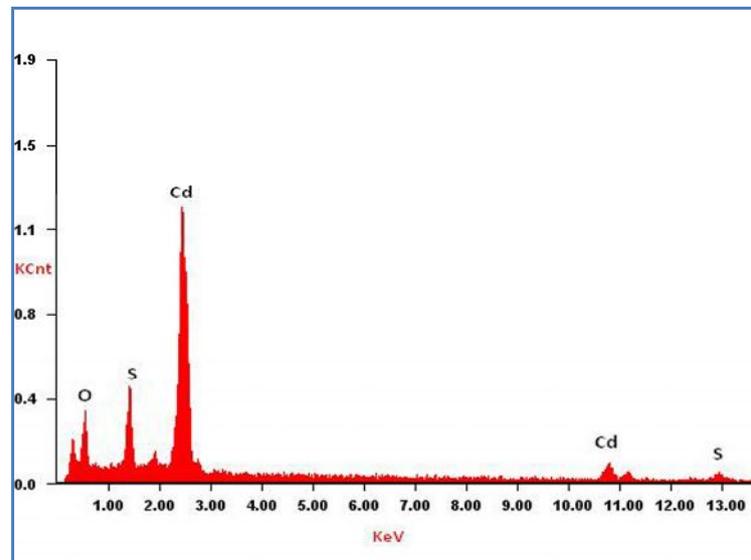


Figure 14. EDAX spectrum of CdS thin film of thickness 930 Å

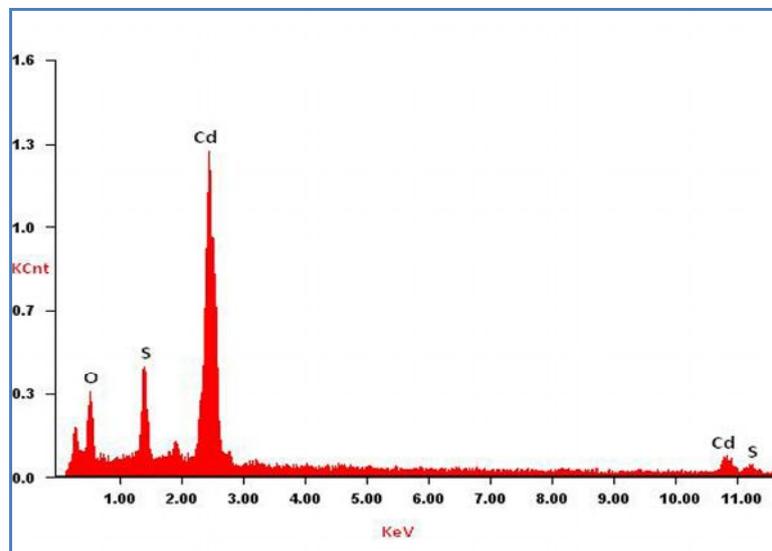


Figure 15. EDAX spectrum of CdS thin film of thickness 2550 Å

Conclusions

CdS thin films are prepared from Vacuum Evaporation deposition. From the diffraction patterns, it is concluded that the film is polycrystalline and exhibits cubic structure. The intensity of diffraction peaks increases as the thickness of the film increases. It is an indication of the crystallinity improvement with increasing films thicknesses. The SEM micrographs reveal that, the distributions of grains are not uniform throughout all the regions, which clearly indicates the glassy nature along with amorphous phase of CdS thin films. The AFM studies show that the size of the particles increases with increase of film thickness. Energy dispersive x-ray analysis confirms the compositions of constituents in the CdS thin films.

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