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Topological, Morphalogical, Structural and optical properties of CdS thin film with complex agents TEA /Ammonia mixer

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Abstract : This paper deals with the novel synthesis of CdS thin films with complexing agents TEA and Ammonia using the chemical bath deposition technique at room temperature UVis, FTIR, XRD, SEM and AFM characterisations were done. The influence of deposition and varying sulphur concentration on the optical absorption, transmittance, structural, surface morphological and topographical studies were examined. Band gap was observed for various sulphur concentrations structural studies revealed that, all the deposited films were nano-sized and crystalline in nature. Surface morphology showed that all the grains were spherical in nature and uniform. According to the properties observed it may be useful for solar cell and optoelectronics applications.
Keywords : CdS thin film, optical, structural, morphology, topography, complex agents, deposition duration and sulphur concentration.

1. 1 Introduction

EventhoughCdS is harmful to environment, its cost effectiveness, earth abundance and performance in semiconductor industry especially properties like optical window[1],wide band gap [2] made this material to employ. Also for their solar cell[3] and optoelectronic applications[4], CdS films have been prepared by various techniques such as chemical bath deposition[5],Chemical vapour deposition[6],Spray pyrolysis[7-8], vacuum evaporation[9], electron beam evaporation[10], sputtering [11] and SILAR[12-13]. CBD involves the controlled precipitation from solution of a compound on a suitable substrate [14]. This CBD technique offers many advantages to prepare semiconductor materials. It is the most convenient, reliable, simplest, inexpensive method and useful for large area of industrial applications. Thin film can be prepared at room temperature itself. Factors such as film thickness, deposition rate, pH value of the solution and reagent concentration can be varied and controlled. In this wok, CdS thin films have been deposited on a glass substrate by chemical bath deposition technique. Solution contains a novel mixture of soluble cadmium salt ($CdCl_2$), triethanolamine and aqueous ammonia. TEA and aqueous ammonia are used as complexing agents for both cadmium ions. Optical, structural and morphological properties of CdS films have been explained.

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1.2 Preparation and Characterization

CdS thin films are deposited on microscopic glass substates using CBD method. Before the deposition the substrates must be cleaned as follows.

Soap solution ⟶ tape water ⟶ HCl acid ⟶ tape water ⟶ distilled water ⟶

Acetone ⟶ dried in air.

The first beaker contains aquous solution of 0.8g of cadmium chloride, 5 ml of aquous ammonium solution and 4 ml of TEA as complexingagents[12-15]. TEA is added for smooth, unifom coating and to control free metal ion strength. Ammonia is added to regulate pH of the solution. The solution was continuously stirred. Thiourea $(NH_2)_2CS$ solution in second beaker was mixed by a magnetic stirrercontinuosly. After obtaining a clear homogenized bath, the stirrer was tuned off and the glass slides were placed vertically in the bath. The bath temperature was kept constant at 70°C to 74 °C for two different times of deposition 1.30 and 2 hrs. After deposition, the glass plates were washed with hot distilled water and dried in air. The CdS films were deposited for different concentrations of thiourea$(NH_2)_2CS$ as 0.7g or 0.6g [16]. The deposited CdS thin films were uniform, light pale yellow in color and highly adhesive. As prepared films were subjected to optical, structural, morphological and topographical analysis.

1.3 Result and Discussion

1.3.1 Optical Analysis

1.3.1(a) Absorbance

Figures 1 and 2 show the UV-Vis Absorption spectra of CdS thin films of different thiourea concentration as 0.7g and 0.6g and constant Cd concentration as 0.8g at two deposition durations as 1.30 and 2.00 hrs.Figure 1 shows that, CdS films with sulphur content of 0.7g and 0.6g exhibit the absorption in the wavelength range fom 330 to 530 nm. Precisely saying, thiourea of 0.6g shows 0.6223 absorption in 491 nm and 0.7g shows 1.2861 absorption in 522 nm. Less amount of sulphur exhibits lesser absorption and high amount of sulphur exhibits higher absorption comparatively. The main absorption edge is observed at 470 nm. Calculated band gaps of the CdS films are 2.37 and 2.52 eV for the sulphur contents 0.7g and 0.6g respectively.Figure 2 shows that, CdS films with sulphur content of 0.7g and 0.6g exhibit the absorption 0.9833 & 1.210 in the wavelengths 497 & 514 nm for the thiourea 0.6 &0.7g respectively. Photon energy absorption edge is observed at 470 nm. Table 1 Calculated band gaps of the CdS films are 2.41 & 2.49 eV for the sulphur contents 0.7g and 0.6g respectively.

Table 1 Optical properties of TEA and Ammonia added CdS thin film

S. No	$CdCl_2$	Thiourea	Complexing agent	Dipping time	Absorption edge	Absorbance (a.u)	Band Gap Eg (eV)
1	0.8 g	0.7 g	TEA 4 ml &Ammoniu m5 ml	1.30 Hrs	522 nm	1.2861	2.37
2		0.6 g			491 nm	0.6223	2.52
3		0.7 g		2.00 Hrs	514 nm	1.210	2.41
4		0.6 g			497 nm	0.983	2.49

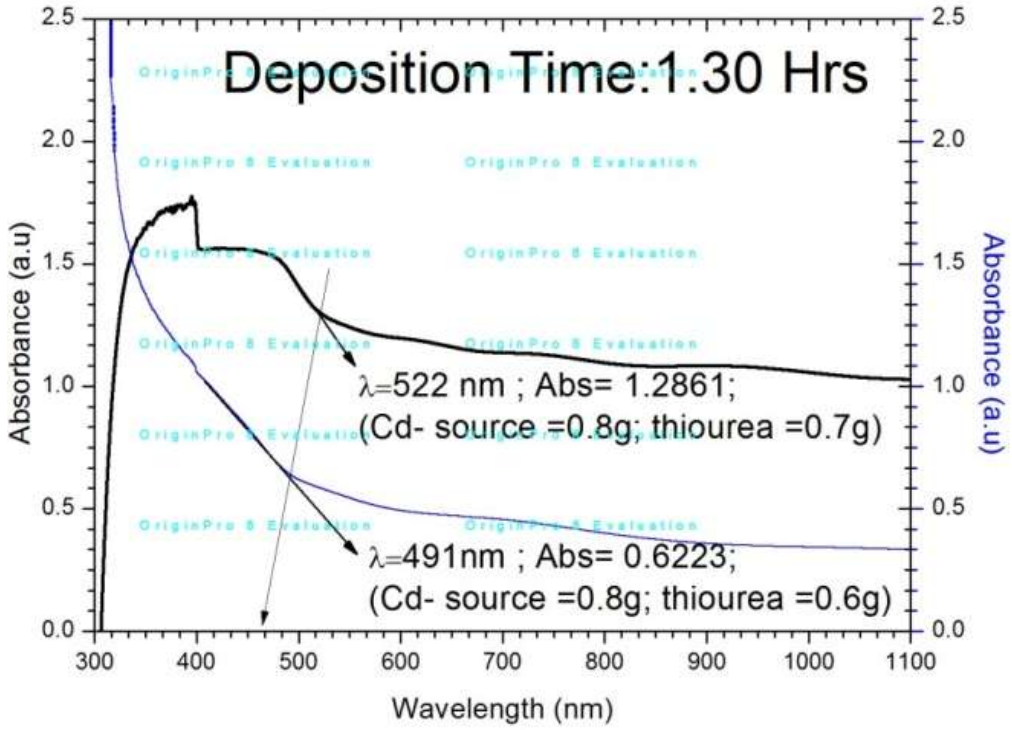

Fig.1 Absorbance spectrum of CdS thin films at 1.30 Hrs

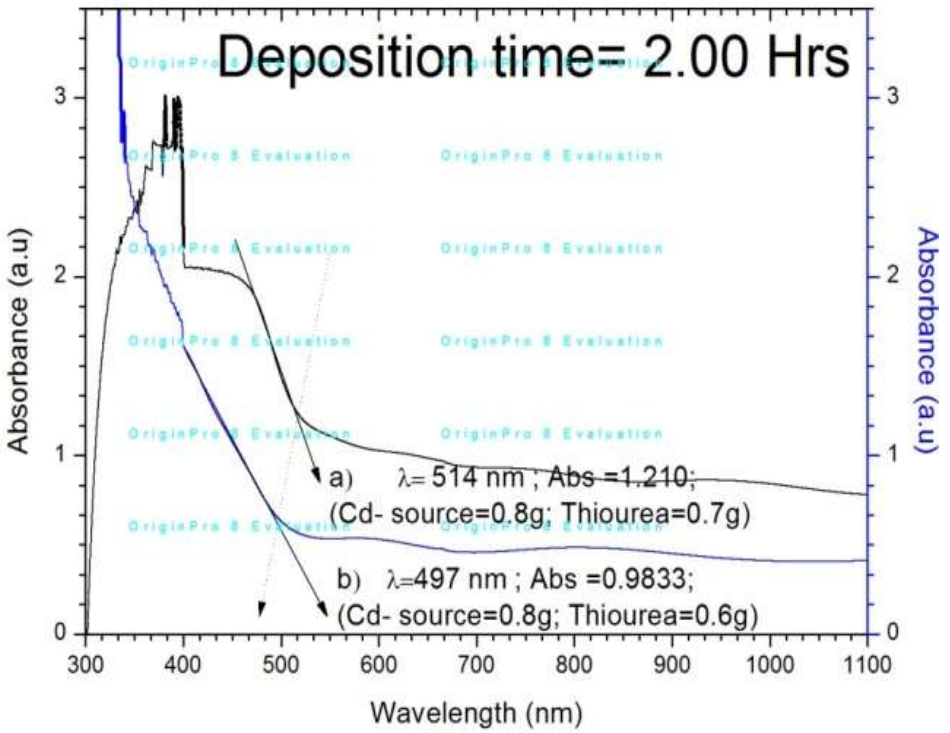

Fig.2 Absorbance spectrum of CdS thin films at 2.00 Hrs

The Band gaps were calculated using the fomula [17],

$$E = \frac{hc}{\lambda} = \frac{(6.624\times10^{-34}\,J.S)\times(3\times10^{8}\,m/s)}{514\times10^{-9}\,m}$$

$$E = \frac{19.872\times10^{-26}\,J}{514\times10^{-9}\,m} = \left[0.038661478\times10^{-17}\,J\right] = [(0.038661478\times10^{-17})\times(6.24\times10^{18}\,eV)]$$

$$E = 2.41eV$$

1.3.1 (b) Transmittance

Transmittance of the title compound is shown in Figures 3 and 4 for two different deposition time as 1.30 and 2.00 hrs. For increasing sulphur concentration, transmittance increases fom 1 % to 9 % in the UV –Vis to NIR regions . The transmittance of the film increases with increase in wavelength from UV-VIS regions (300 nm to 1100 nm). The transmittance increases rapidly in the UV region, but increases slowly and constantly towards NIR regions. For the CdS film, the average transmittance is greater than the above wavelength 468 nm throughout UV-Vis- NIR regions.This property of high transmittance makes it a good material for optical coatings. From the spectra, it is revealed that the CdS films have high absorbance in the visible region, which is the characteristic of the transmittance edge. In Figures 3 and 4,peakes are attributed to the formation of excitons of CdS thin films, which increases with increase in concentration of thiourea.Band gap decreases for the increasing concentration of thiourea. Absorption edge and absorbance increases for the increasing concentration of thiourea. It is observed for both the coating durations 1.30 and 2.00 hrs.Band gap increases for 2 hours of dipping duration for the higher concentration (0.7g) of thiourea and decreases for 1.30 hours of dipping duration for the lower concentration (0.6g) of thiourea.Band gap decreases for 2 hours of dipping duration for the lower concentration (0.6g) of thiourea and increases for 1.30 hours of dipping duration for the higher concentration (0.7g) of thiourea. $CdCl_2$ and complexing agents TEA (4 ml) and Ammonium (5 ml) are maintained constant for all the four cases.

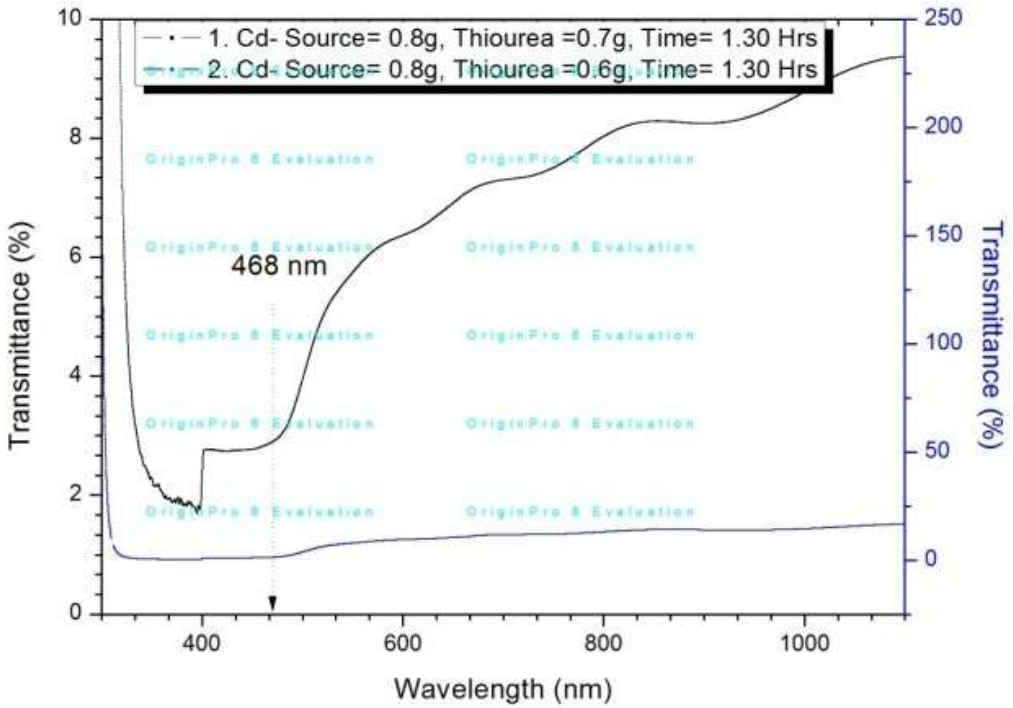

Fig.3 Transmittance spectrum of CdS thin films at 1.30 Hrs

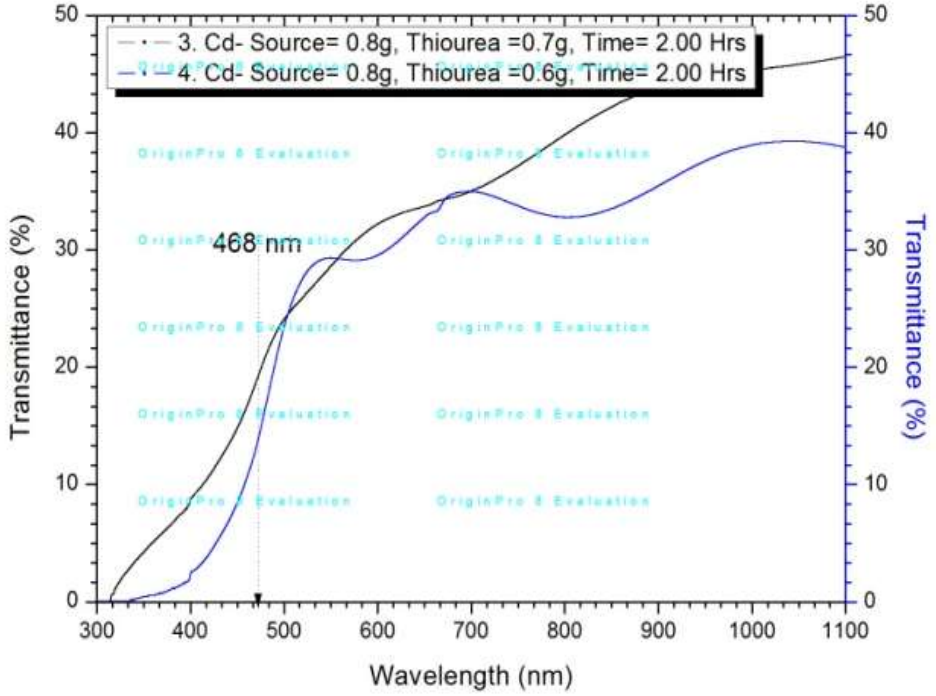

Fig4 Transmittance spectrum of CdS thin films at 2.00 Hrs

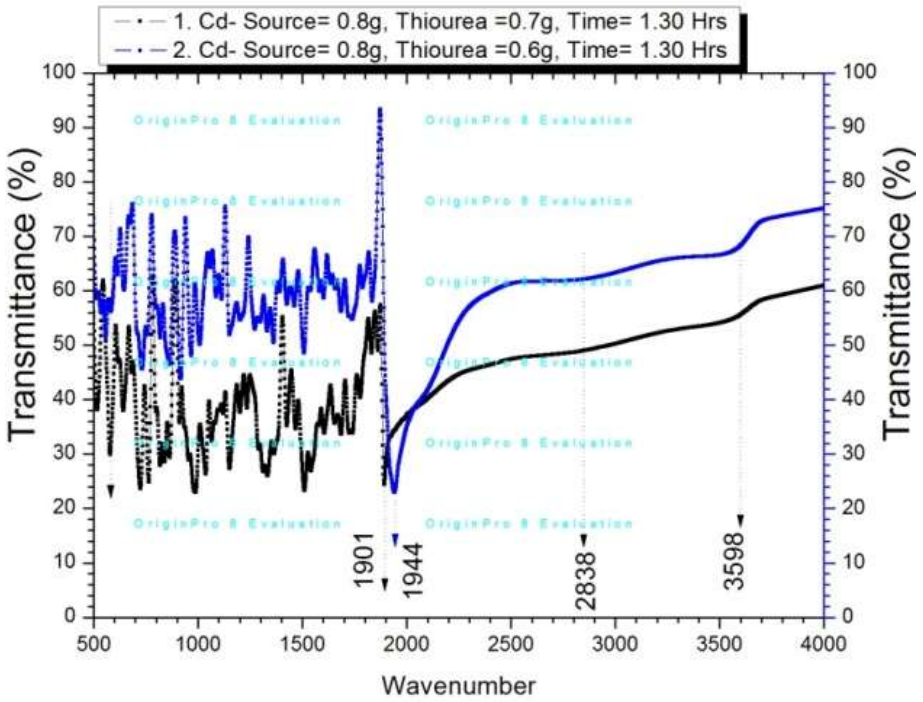

Fig.5 (a) FTIR spectrum of CdS thin films 1.30 Hrs (frequency range 500 cm^{-1} to 4000 cm^{-1})

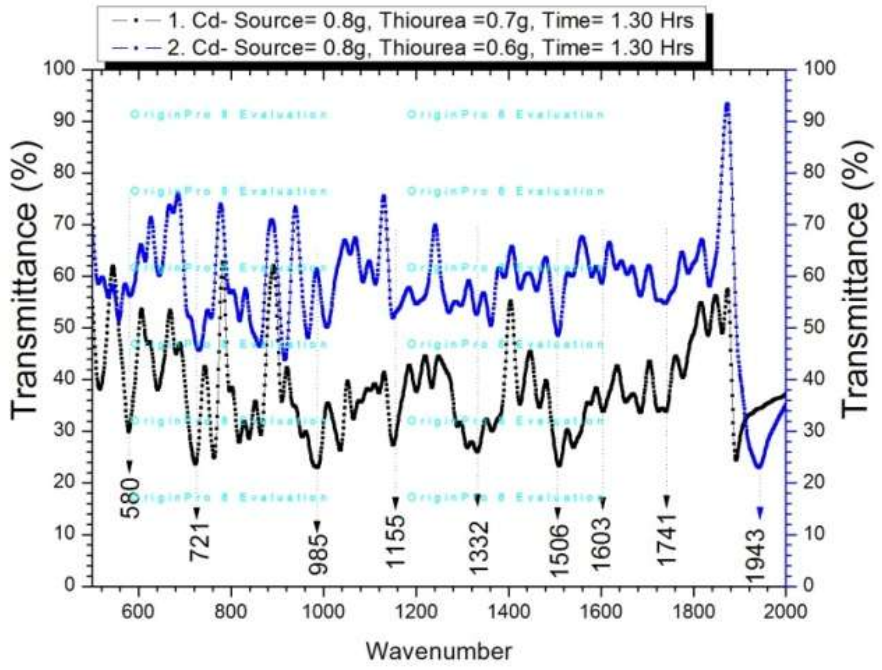

Fig.5 (b) FTIR spectrum of CdS thin films 1.30 Hrs (Frequency range 500 cm^{-1} to 2000 cm^{-1})

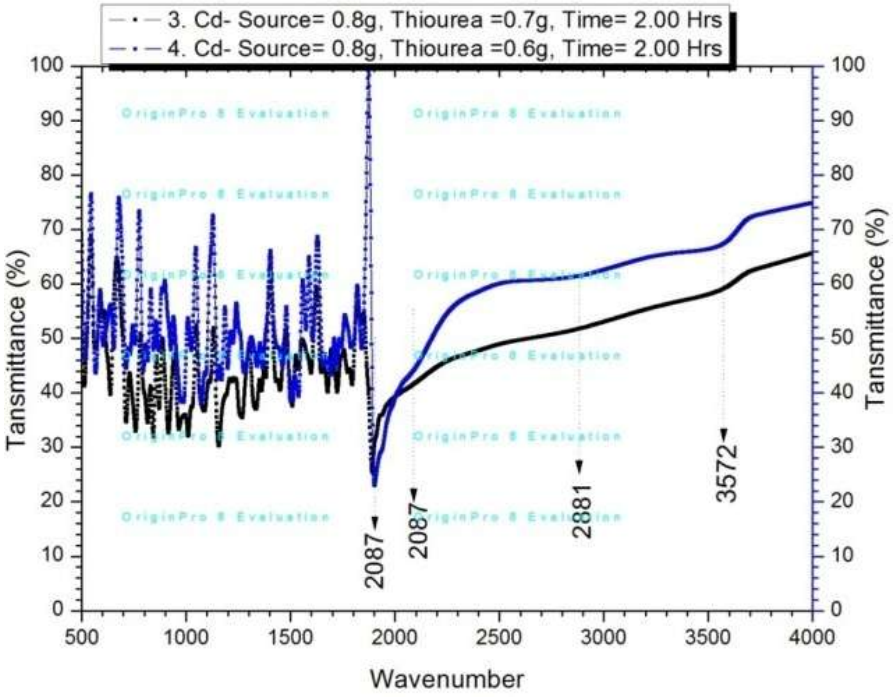

Fig.6 (a) FTIR spectrum of CdS thin films 2.00 Hrs (Frequency range 500 cm^{-1} to 4000 cm^{-1})

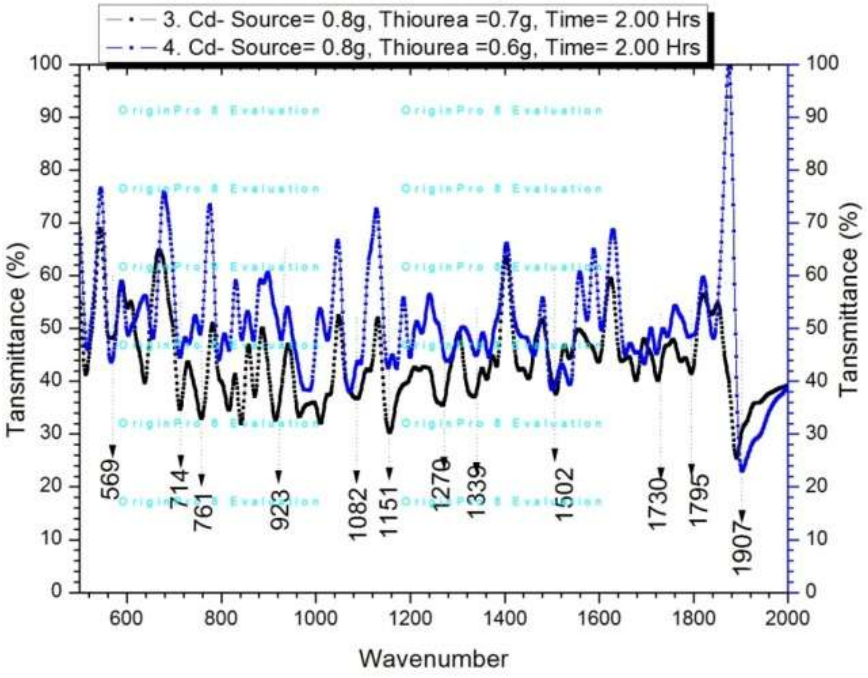

Fig.6 (b) FTIR spectrum of CdS thin films 2.00 Hrs (Frequency range 500 cm^{-1} to 2000 cm^{-1})

1.3.2 FTIR Analysis

The FT-IR spectrum is used to understand and analyze the structure and molecular arrangements of thin films more elegantly. Type of functional groups present in the substance is indicated by the absorption that occurs at various frequencies. Figures 5(a,b) and 6(a,b) shows the FT-IR spectra of CdS thin films in the range of 500 - 4000 cm^{-1} . The presence of broad band range of 2087 cm^{-1} to 3572 cm^{-1} is attributed to hydrated water and the hydoxyle group in the spectra results from the hydroscopic nature of CdS. The tansmission band of bending vibrations at 3572,2881 and 2087 cm^{-1} is due to O-H stretching vibrations of water molecules . The frequency bands at 500 to 2087 cm^{-1} are assigned to the C-N bond stretching vibration of C-N . Strong bands which have been assigned to cards stretching these results will be matched with the reported values.

1.3.3 XRD Analysis

The X-ray diffraction pattern of the CdS thin film s is exhibited in Figuers 7 (a,b,c,d) . XRD analysis is carried out on CdS films and typical diffraction patterns of as grown CdS thin films prepared by CBD technique on glass substrates with different sulphur content. The Spectra are obtained by scanning 2θ in the ange 10 - 80°. The XRD pattern confirms the presence of CdS. The XRD pattern of a typical CdS sample exhibits prominent broad peakes at 2θ values of 22.34°, 29.22° and 43.33° which could be indicated as reflection from the (111), (220) ans (311) cubic phases of CdS planes respectively suggest that the nanoparticles are in cubic form and are in good agrement with the data on reported CdS [16]. High intensity peaks indicate that the significant increase in crystallite size with the cubic modification. The average crystallite size (D) was estimated using Scherrer formula [18];

$$D = k\lambda/\beta \cos\theta \qquad (1)$$

Where k is the shape factor that was taken equal to 0.9 , λ is the wavelength of X-ray source 1.5406, β is the full width at half maximum (FWHM) of (111) and (220) peakes corresponding to cubic phase of CdS and θ is the Bagg's diffraction angle in degrees. The average crystallite size is found to be 8 nm [19].

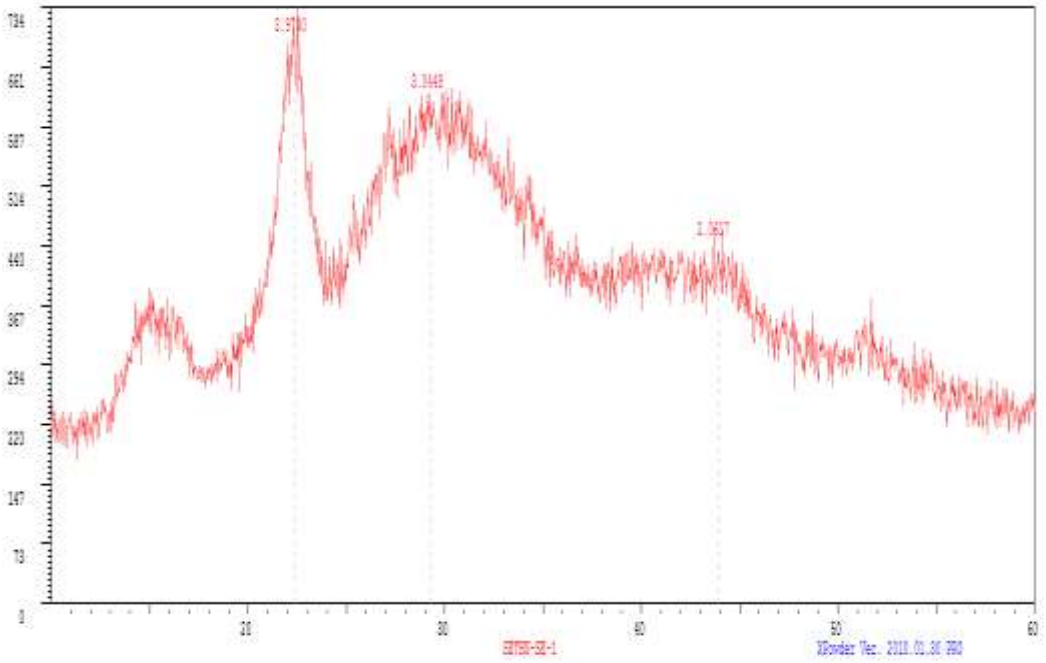

Fig. 7(a) X-ray diffraction (XRD) pattern of CdS thin film at 1.30 hrs (Thiourea = 0.7g; Cadmium =0.8 g)

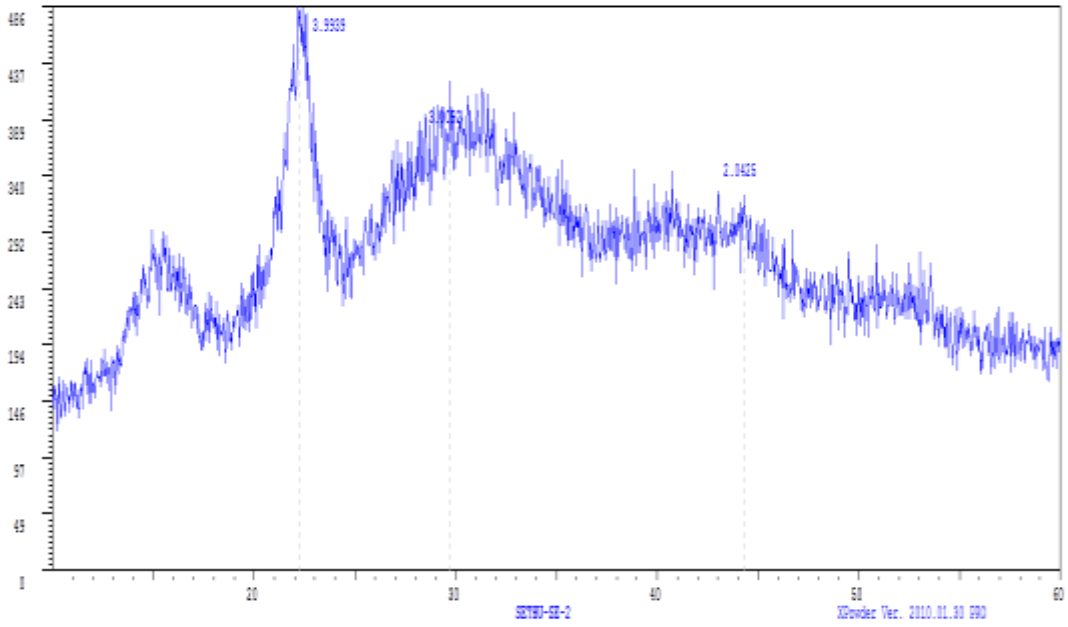

Fig. 7(b) X-ray diffraction (XRD) pattern of CdS thin film at 1.30 hrs (thiourea = 0.6g ; Cadmium =0.8 g)

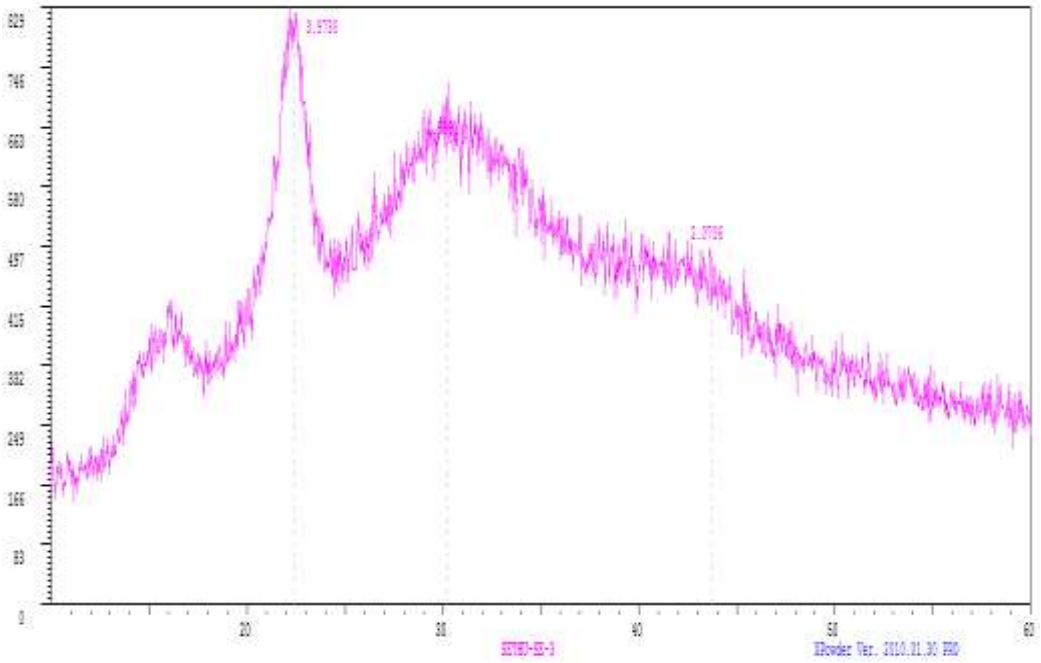

Fig. 7(c) X-ray diffraction (XRD) pattern of CdS thin film at 2.00 hrs (thiourea = 0.7g ; Cadmium =0.8 g)

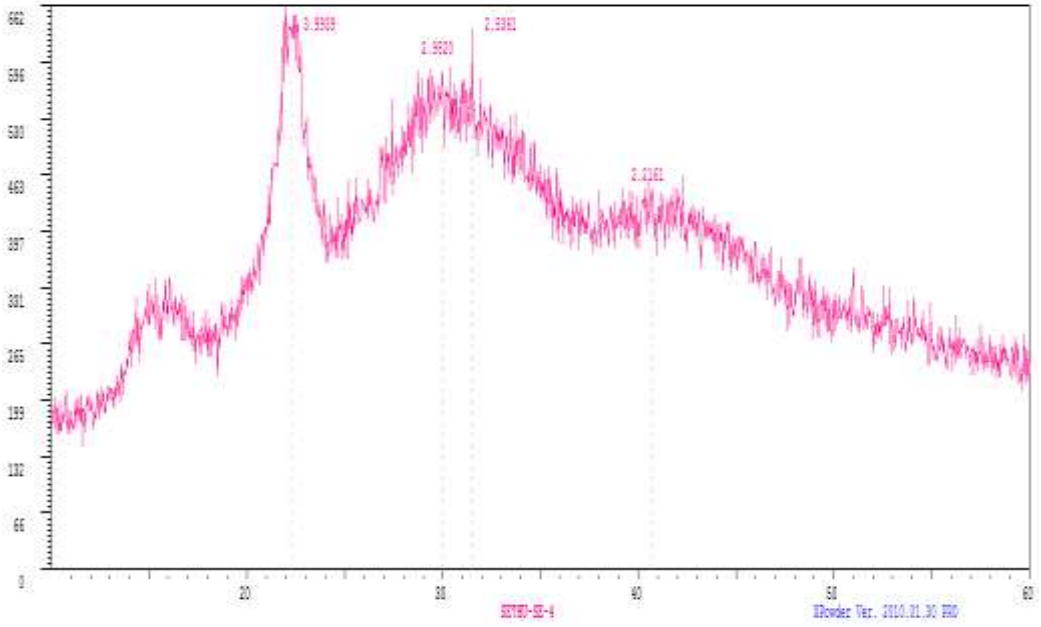

Fig. 7(d) X-ray diffraction (XRD) pattern of CdS thin film at 2.00 hrs (thiourea = 0.6g; Cadmium =0.8 g)

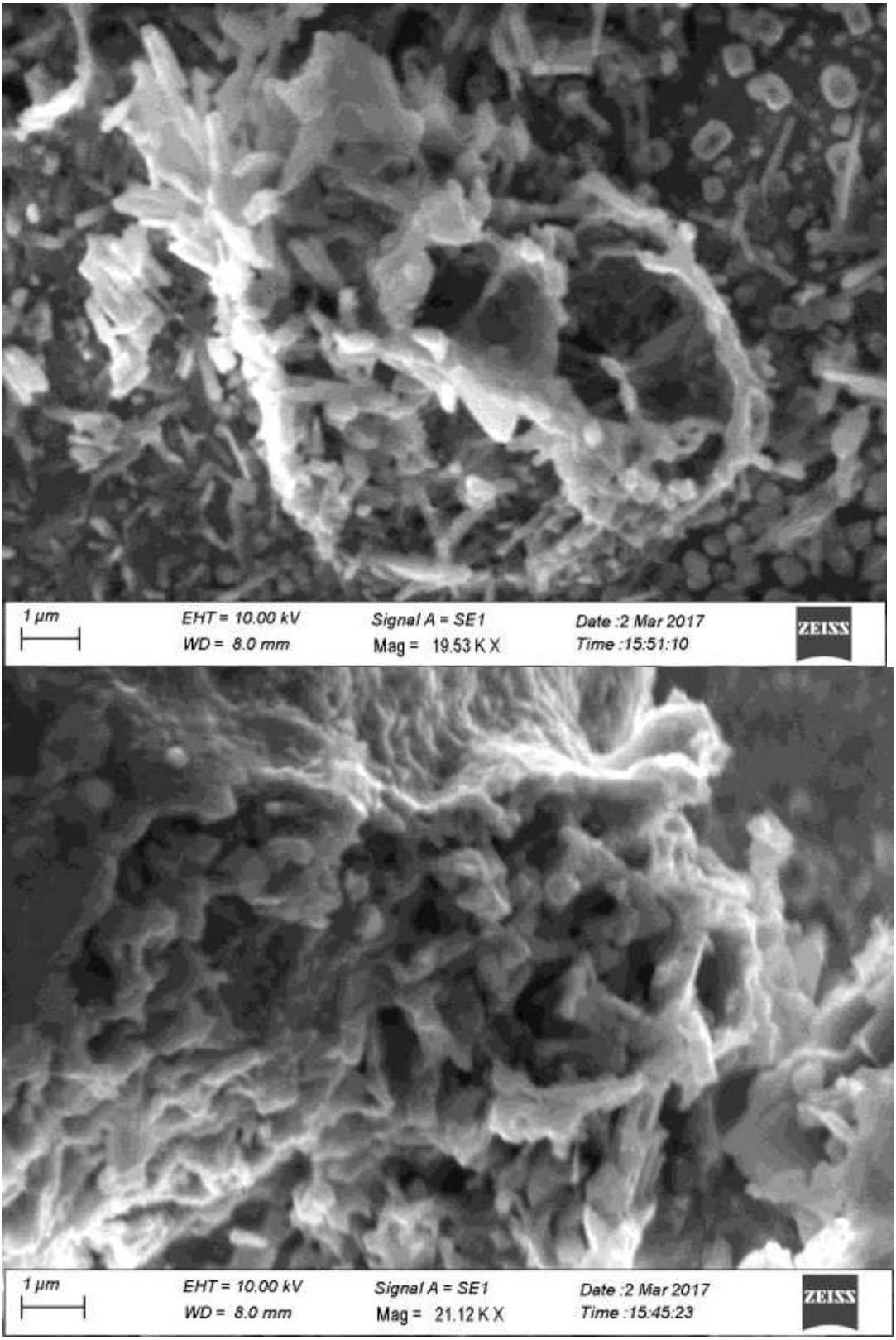

Fig.8 SEM Micrograph of CdS thin film at deposition time 1.30 Hrs. [$CdCl_2$ = 0.8g; Thiourea= 0.7 g]

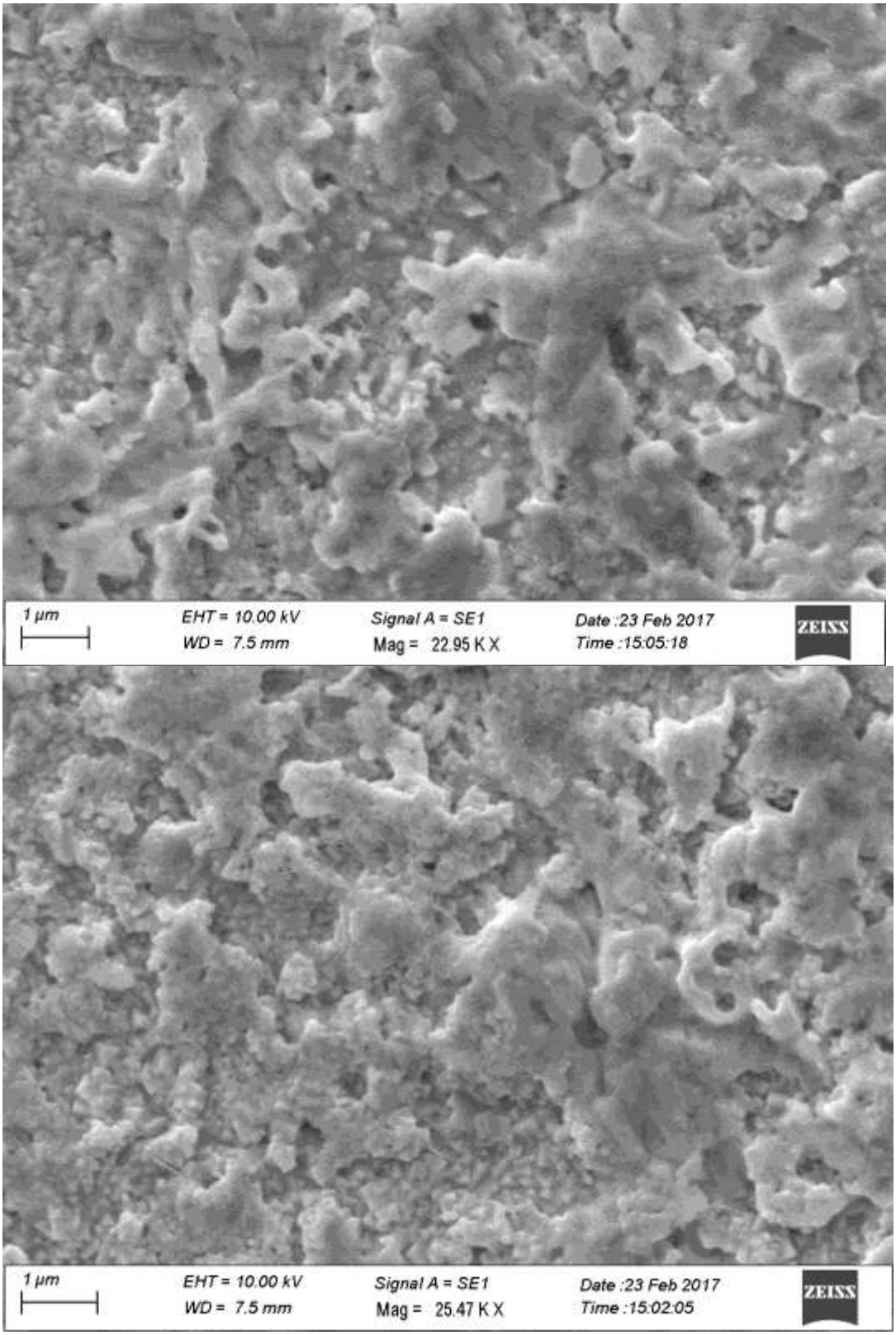

Fig.9 SEM Micrograph of CdS thin film at deposition time 1.30 Hrs. [$CdCl_2$ = 0.8g; Thiourea= 0.6 g]

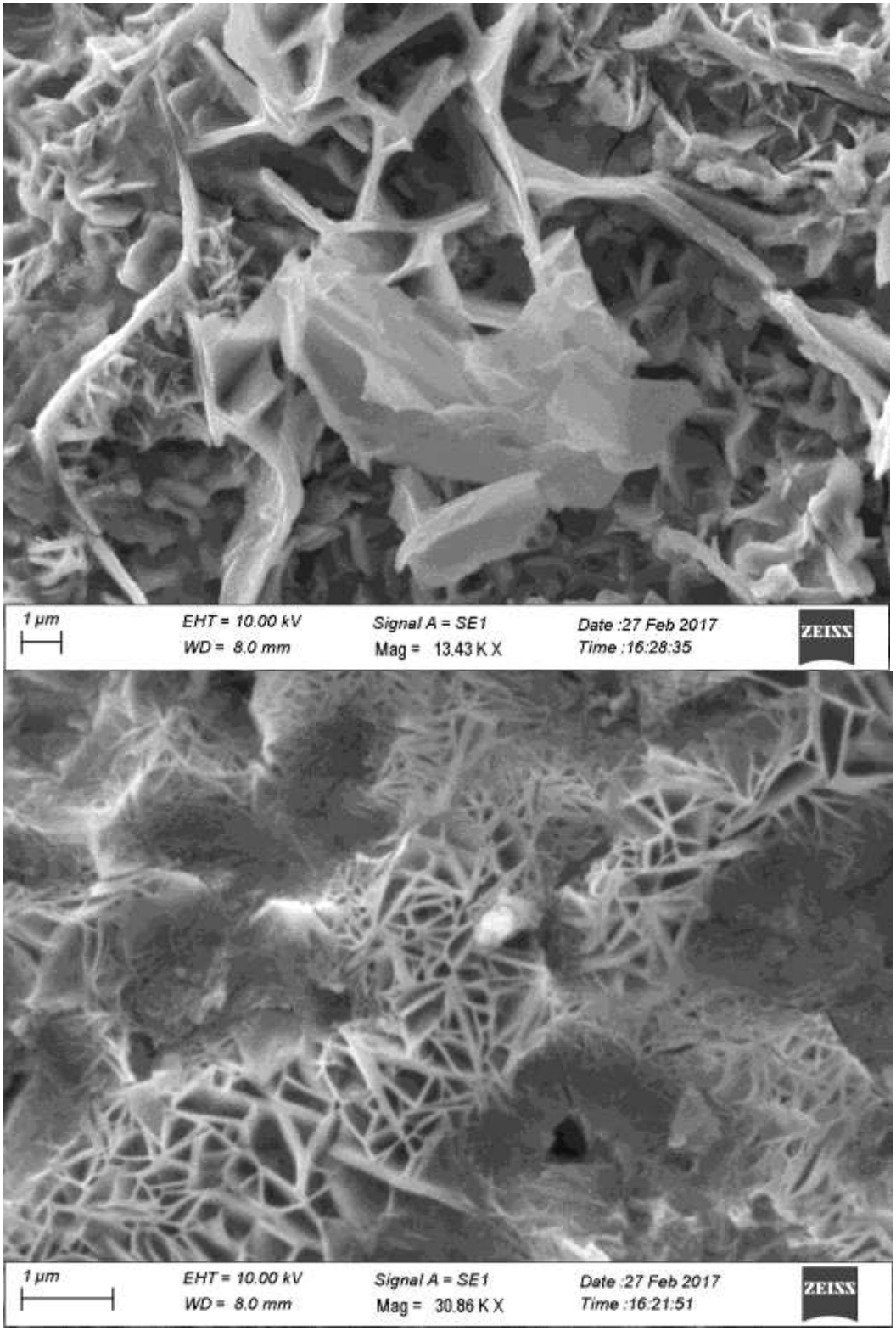

Fig.10 SEM Micrograph of CdS thin film at deposition time 2.00 Hrs. [$CdCl_2$ = 0.8g; Thiourea= 0.7 g]

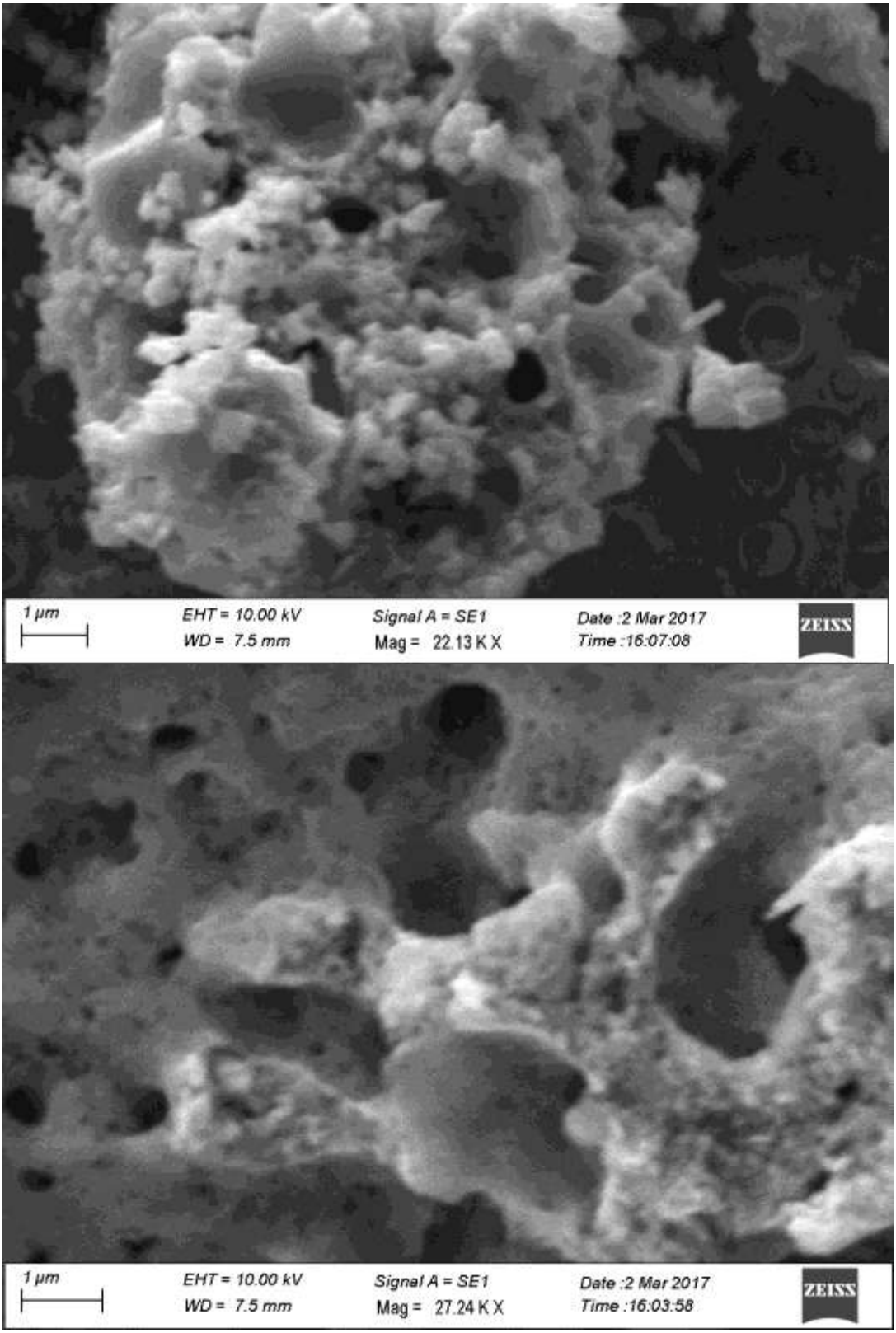

Fig.11 SEM Micrograph of CdS thin film at deposition time 2.00 Hrs. [$CdCl_2$ = 0.8g; Thiourea= 0.6 g]

1.3.4 SEM Analysis

The scanning electron microscopy is a convenient technique to study the micro structure of thin films. SEM confirms the homogeneous film formation for both the durations 1.30 and 2 hours. SEM micrographs observed for different magnifications between 13 and 30 Kx. Fo better accuracy, magnification is maintained above 10 nm. The cross section area is 1 µm in width. Low deposition duration led to small, uniform grain size and shape. It also provides good adhesion to the substrate. Grain sizes were about 2 to 50 nm. The SEM

micrograph given in Figures (8,9,10,11) possess a cubical morphology and an irregular pattern without any void, pin hole or cracks and cover the entire substrate. It is observed that, the CdS thin films exhibit crystalline natue clearly in high sulphur concentration ie., thiourea of 0.7g and no crystalline natue in low sulphur concentration ie., thiourea 0.6g in the deposition duration of 1.30 hrs and 2 .00 hrs respectively. The grains are thickly packed, dense, smooth and without any visible holes. SEM micrograph of CdS thin film at deposition duration 2 hous reveals. The the formation of nano rod clusters[20-21].

1.3.5 AFM Analysis

Atomic force microscopy analysis were performed to observe the morphological characteristics of the CdS thin film deposited at 0.7g and 0.6g sulphur concentrations in the 1.30 hours deposition duration.Figures 12(a,b) and 13(a,b) show the 2D and 3D AFM images of the CdS film ,with a scaning area of 1 µm for the 0.7g and 0.6g sulphur concentrations respectively.Figures 14(a,b) and 15(a,b) show the particle height histogram and partical sizes are exhibited in randomly orientad and have uniform grain sizes.Root mean square height (Sq),maximum height (Sz) and arithmetic mean height (Sa) of the deposits are observed and results are displayed in table 2.Maximumpeak height is 46.3 nm, maximum pit height 15.8nm, so the maximum height will be 62.1 nm for the film having 0.7g thiourea concentration for deposition duration 1.30 hous .Its arithmetic mean height will be 2.92 nm and root mean square height will be 4.09 nm.Skewness and kurtosis is 1.48 and 12.3 respectively fo the film having 0.7g thiourea concentration for deposition duration 1.30 hours.Maximum peak height is 72.4nm, maximum pit height is 62.1 nm,so the maximum height will be 62.1 nm 134.5 nm fo the film having o.6g thiourea concentration for deposition duration 1.30 hours.Its arithmetic mean height will be 12.2 nm and root mean square height will be 15.7 nm.Skewness and kurtosis is 0.327 and 4.09 respectively for the film having 0.6g thiourea concentration for deposition duration 1.30 hous.Skewness and kurtosis are having higher values for the film having 0.7g than 0.6g thiourea concentration for deposition duration 1.30 hours. the maximum height,arithmetic mean height and root mean square height is heigher for the film having 0.6g and 0.7g thiourea concentration for deposition duration 1.30 hours.So smooth surface is observed for the film of 0.7g sulphur concentration comparatively.The CdS particals are randomly distributed on the surface.

Table 2 Particle Height Parameters of TEA and Ammonia added CdS thin film

Parameters	**Height**	**Cadmium Chlorite (0.8 g)**	
		a) Thiourea (0.7 g)	**b) Thiourea (0.6 g)**
Root mean square height	**Sq**	4.09 nm	15.7 nm
Skewness	**Ssk**	1.48	0.327
Kurtosis	**Sku**	12.3	4.09
Maximum peak height	**Sp**	46.3 nm	72.4
Maximum pit height	**Sv**	15.8 nm	62.1
Maximum height	**Sz**	62.1 nm	134 nm
Arithmetic mean height	**Sa**	2.92 nm	12.2 nm

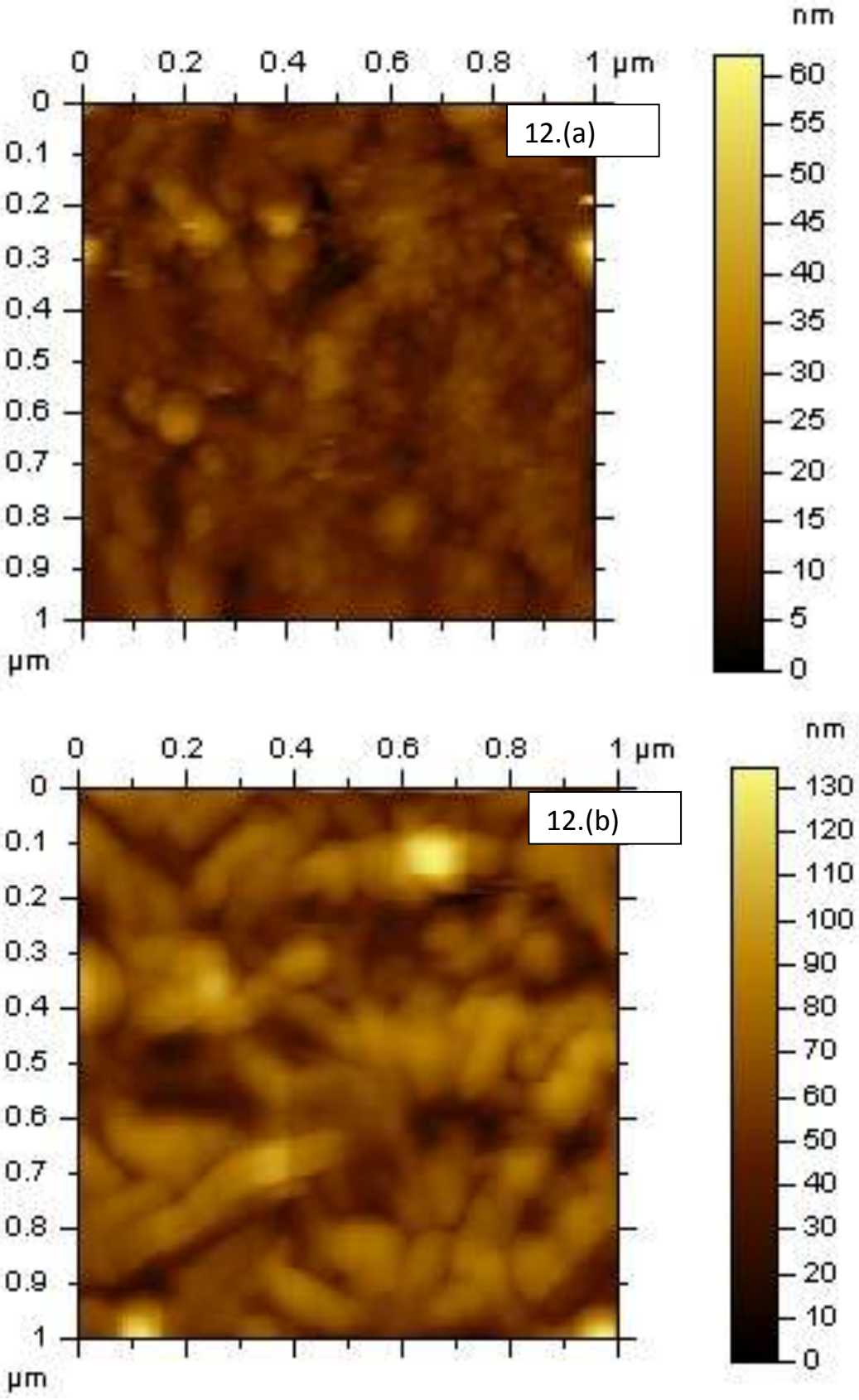

Fig.12(a,b) 2D, AFM images of CdS thin film at deposition time 1.30 Hrs. [a)$CdCl_2$ = 0.8g; Thiourea= 0.7 g;b) $CdCl_2$ = 0.8g; Thiourea= 0.6 g]

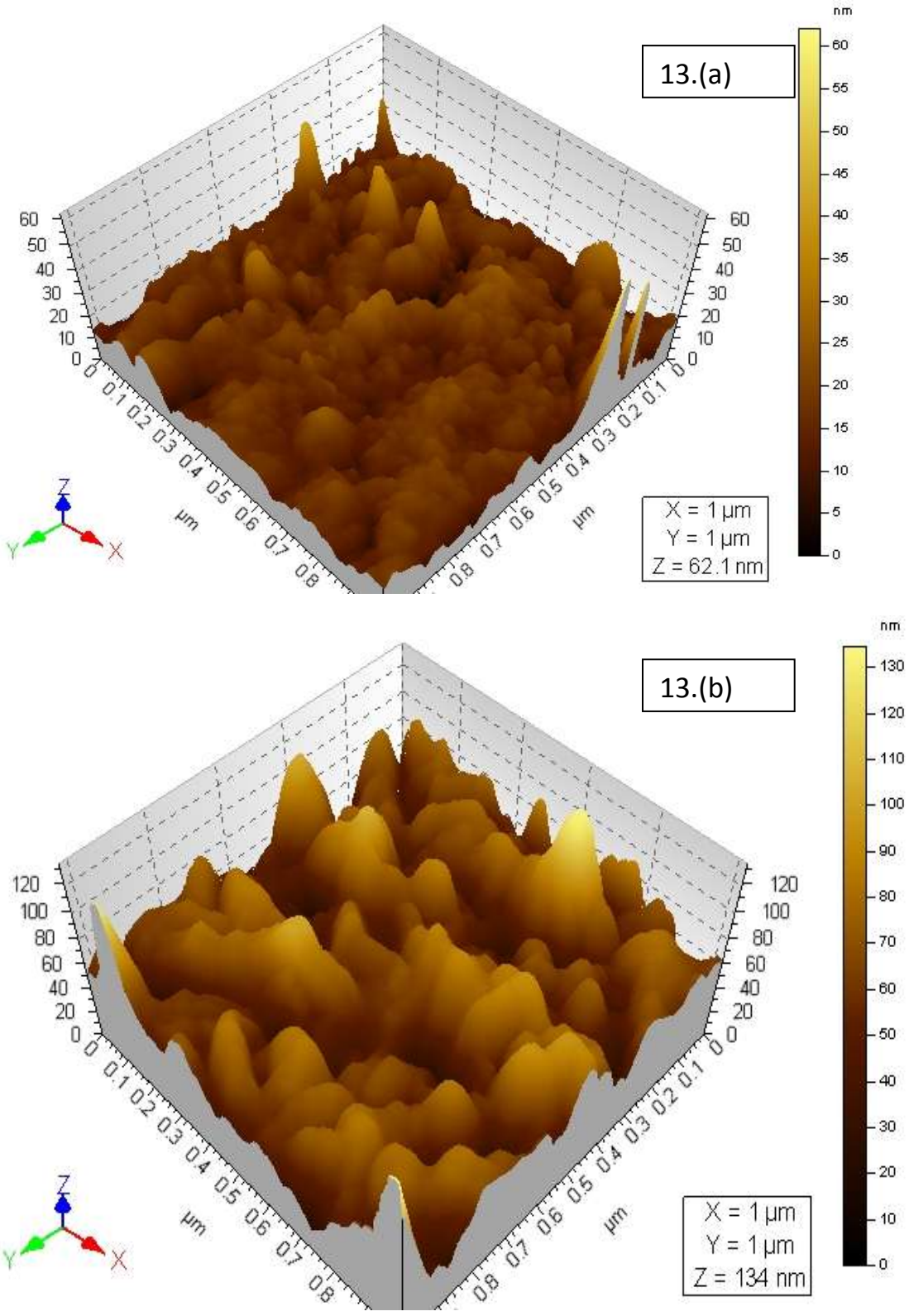

Fig.13(a,b) 3D, AFM images of CdS thin film at deposition time 1.30 Hrs. [a)$CdCl_2$ = 0.8g; Thiourea= 0.7 g; b) $CdCl_2$ = 0.8g; Thiourea= 0.6 g]

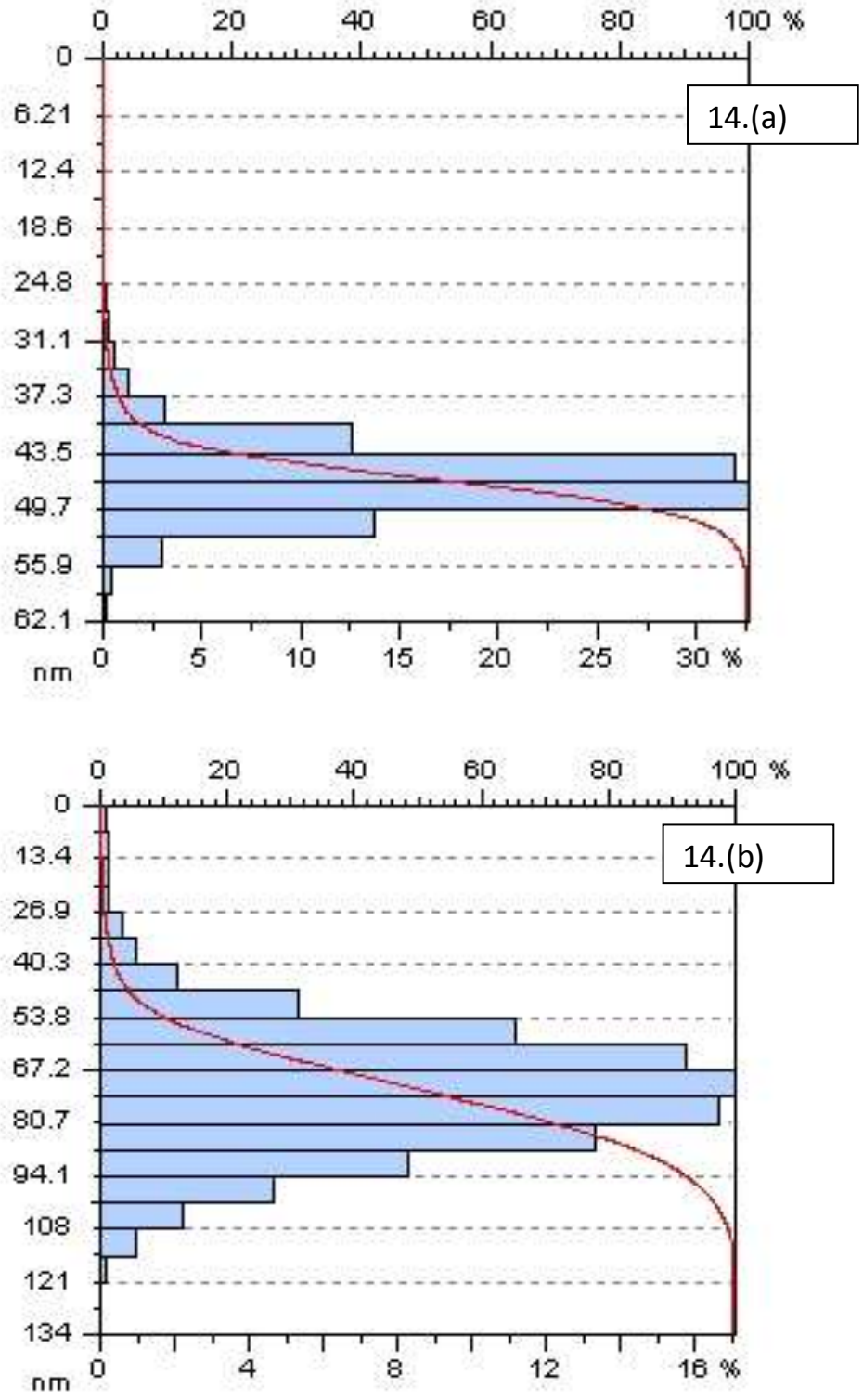

Fig.14 (a,b) 2D, AFM images, particle size histogram of CdS thin film at deposition time 1.30 Hrs. [a)$CdCl_2$ = 0.8g; Thiourea= 0.7 g; b) $CdCl_2$ = 0.8g; Thiourea= 0.6 g]

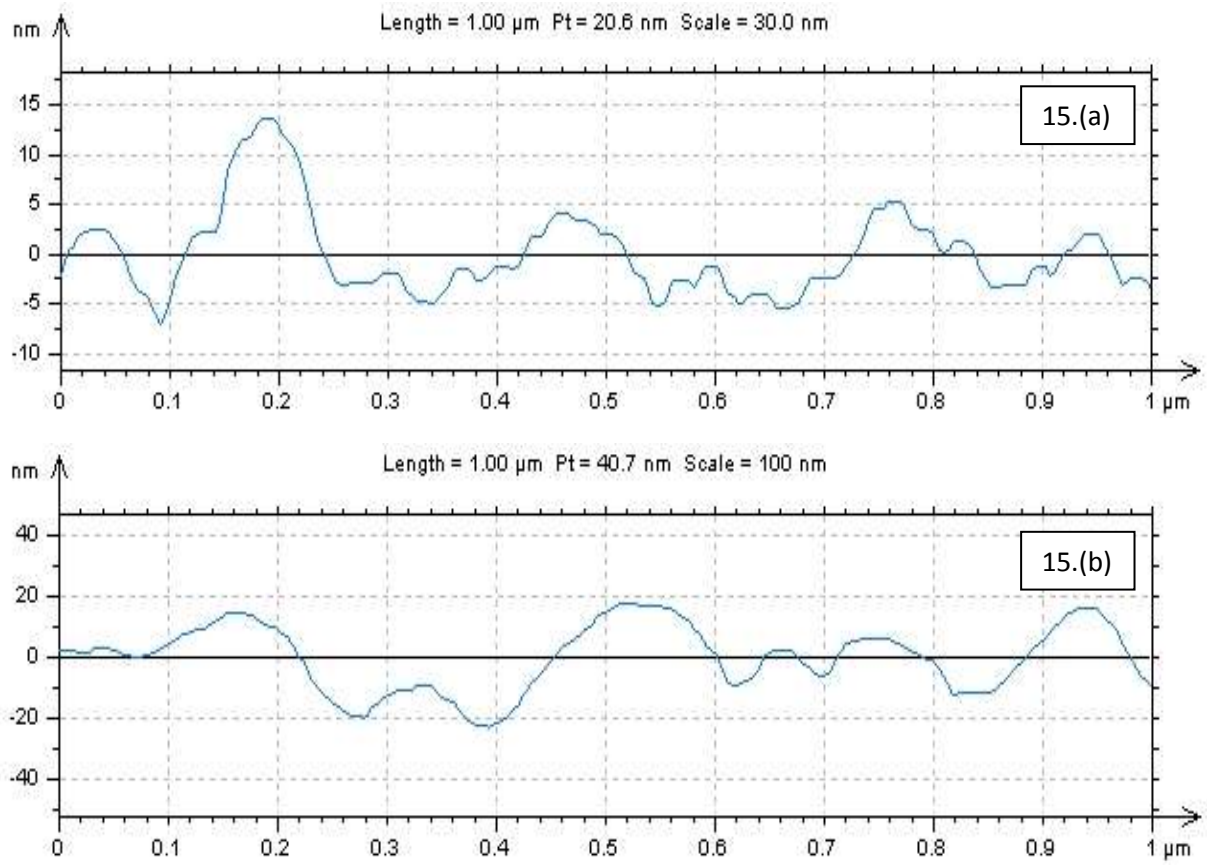

Fig.15 (a,b)2D, AFM Micrograph, particle size of CdS thin film at deposition time 1.30 Hrs. [a)$CdCl_2$ = 0.8g; Thiourea= 0.7 g; b) $CdCl_2$ = 0.8g; Thiourea= 0.6 g]

1.4 Conclusion

Cadmium sulphide thin films were deposited by solution with the complexing agents TEA and ammonia on clinical glass substrate using the CBD method at room temperatue. The results of optical absorbance, transmittance, band gap analysis, stuctural, mophological and topographical studies were discussed.These CdS thin films are having good optical bandgap.Increasing concentration of sulphur content is good for optical window material.X-ray diffraction (XRD) analysis reveals average crystaline size is 8 nm. The CdS partical were randomly distributed on the surface of the films.Thier sufaces were homogeneous and the films were uniformly deposited .These characteristics recommend this material for solar cell and optoelectronic applications.

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