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Effect of Ammonia concentration on structural and optical properties of CdS thin films prepared by CBD method

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Abstract : CdS thin films were prepared on micro glass substrates with chemical bath deposition methods for different concentration of Ammonia. The effects of Ammonia on the structural and optical properties of CdS films were examined using Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), Energy Dispersive X- ray Spectroscopy (EDAX) and Photoluminescence Analysis (PL). The SEM images shows particle size increases from 28.92 to 44.20 nm as the concentration of NH_3 increases. Also the results of the Atomic Force Microscope (AFM) the Root mean square and roughness of the CdS thin films was found to vary with the concentration of NH_3. The elemental composition analysis of the as deposited CdS thin film was investigated using EDAX with different concentration of ammonia for 2hr duration at 92^0C without annealing. It was significant to note that films deposited at optimized preparative parameters are nearly stoichiometric with average atomic percentage of Cd:S = 53.34: 46.65. The estimated Cd to S ratio value is found to be 1.14. The Photoluminescence spectrum of CdS thin film shows that the intensity decreases as the concentration increases from 0.5, 1.0, 1.5, 2.0 N of NH_3. The emission energy (eV) slightly varies with the concentration of NH_3.
Keywords: CdS thin film, SEM, AFM, EDAX and PL.

1. Introduction

CdS is an II-IV compound semiconductor; with a direct band gap of 2.4 eV [1] used as a suitable window layer for CdTe based photovoltaic devices. It has been attracted by many research communities due to its useful optoelectronics and photoconductive properties. It has many useful applications in photo resistors, optical filters, and multilayer light emitting diodes, photo detectors, gas sensors, transparent, conducting semiconductors, optical wave-guides, Non-linear integrated optical devices, light amplifiers, image intensities, phosphors, electroluminescent devices and radiation detectors [2]. CdS thin film can be prepared by many different method such as closed space sublimation [3], chemical bath deposition [4], vacuum evaporation [5], magnetron sputtering [6], Spray pyrolysis [7], Thermal evaporation, chemical pyrolysis deposition and metal organic chemical vapour deposition [8-9] and each method has its own characteristic merits and demerits in producing homogeneous and defect free thin films.

Among many methods available, CBD technique is chosen for the present study, due to its simple, inexpensive reproducible quality and it is easy to control the growth rate. Thin film properties are strongly

dependent on the method deposition, concentration of precursor, the substrate materials, temperature, rate of deposition and the background pressure. In this study influence of ammonia on CdS thin film and their structural and optical properties are discussed.

The aim of the present study is the effect of ammonia concentration with temperature of the mixer was maintained at 92^{o}C, the deposition time was 2 hours and the pH of the solution was maintained at 11.8 to deposit CdS thin films by chemical bath deposition method and to understand the growth mechanism and its impact in the structural and optical properties. The films were characterized using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy Dispersive X- ray Spectrometer (EDAX) and Photoluminescence spectra (PL) to understand the CdS morphology and structure. The emission energy (eV) was determined from photoluminescence spectra.

2. Experimental details

2.1. Substrate cleaning

The CdS thin films were growing on 7.5cm x 2.5cm X 0.1 cm microscope glass slides. The glass substrates were cleaned in an ultrasonic cleaner using acetone and alcohol. They were soaked in a chromic acid cleaning solution for 20 minutes. Further, they were cleaned ultrasonically in an isopropyl alcohol. Finally they were washed in deionized water and dried by flowing with dry nitrogen for 30 minutes.

2.2. Sample preparation

Every last one of chemicals utilized within those available examinations was explanatory review bought starting with Merck. CdS tests were ready toward silar technique. For deposition of the films 30 ml of 0.004M $CdCl_2$ solution is used as cationic precursor, 20ml of 0.005 M $SC(NH_2)_2$ solution is used as anionic precursor, 30 ml of 0.3M NH_4Cl serves as a buffer and 26 ml of (0.5, 1.0, 1.5 and 2.0N) NH_3 is the complexing agent. The temperature of the mixer was maintained at 92^{o}C, the deposition time was 2 hours and the pH of the solution was maintained at 11.8 with the pH meter for the film deposition. The glass substrates were immersed in solution contained in glass beaker placed inside a water bath. The CdS thin films were prepared on glass substrate. Then afterward the arrangement of the movies those substrates were uprooted from those shower What's more rinsed a few times over refined water to uproot At whatever follower particles also unreacted materials. Tests were dried during room temperature. The prepared thin films without annealing were examined and characterized by means SEM, AFM, EDAX and PL.

2.3. Sample Characterization

The structural and optical properties of the CdS film were characterized by using a scanning electron microscope (Model: JEOL-ISM 6390 LV) and (Model: VEGA3-TESCAN computer controlled Scanning Electron Microscopy), Atomic Force Microscope (AFM) A100 model (A.P.E Research, Italy), Energy Dispersive X-ray Spectrometer (EDAX) VEGA3 TESCAN and Photoluminescence Spectrometer (PL) Model: Savitzky - Golay, Instrument Serial Number: EL08083851, Scan mode: Emission, Data Mode: Fluorescence, Start mode (nm): 400.00 nm, and Stop mode (nm):700.00nm.

3. Results and Discussion

3.1 Scanning Electron Microscope (SEM)

SEM images of CdS thin films are shown in the different concentration of ammonia (0.5, 1.0, 1.5 and 2.0 N of NH_3) (Fig.1 and 2). The magnified microphotographs of CdS thin films reveals that the film smooth and homogeneous. It covers the entire surface area of the substrate. It has dense morphology and compact structure with uneven distribution of grains in the cluster form throughout the glass substrate with fine grained morphology. The observed grains are nearly in spherical in shape grown perpendicular to the surface of the substances. Upon closer inspection at high magnification, it is apparent that the CdS thin films are without any void, pin-hole or cracks and continuous with uniformly distributed grains which covered the substrate very well. The grains are quite small with unequal size dense, composed of largely irregular shaped and large grains comprised. This indicates poor crystallization. The particle size increases as the concentration of NH_3 increases.

This is close to the CdS thin films recorded at different concentrations of ammonia mentioned by Munikrishna Reddy et al [10]. The prepared CdS thin films particle size from SEM image found to be 24.5 - 44.2nm. Kale et al [11], Atay [12] et al reported that the prepared CdS particle size from SEM image found to be 98-179nm, which was higher than the present study and smaller than the reported by Jiankang [13].

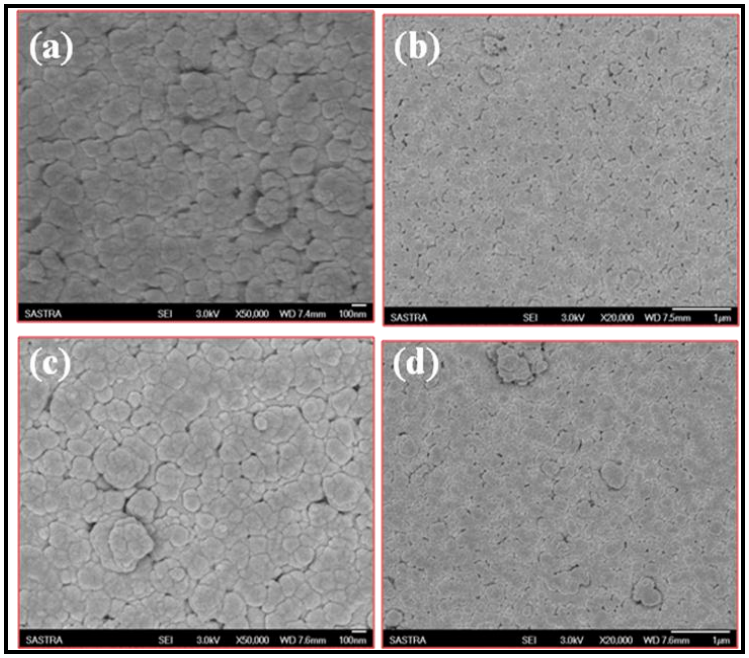

Fig.1. SEM images of CdS thin films with Nano and Micro level of (a, b) 0.5 N of NH_3 and (c, d) 1.0 N of NH_3

SEM images of a 500nm (Magnification: 50,000x) and 1µm (Magnification: 20,000x) CdS thin film of (a, b) 0.5 N of NH_3 and 500nm (Magnification: 50,000x) and 1µm (Magnification: 20,000x) CdS thin film of (c, d) 1.0 N of NH_3 deposited on glass substrate by CBD are shown in fig.1.

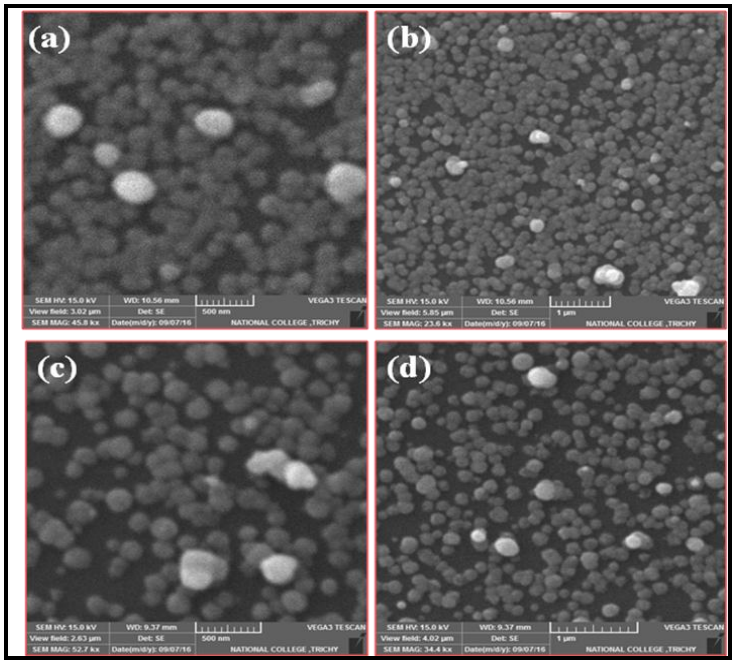

Fig.2. SEM images of CdS thin films with Nano and Micro level of (a, b) 1.5 N of NH_3 and (c, d) 2.0 N of NH_3

SEM images of a 500nm (Magnification: 45.8 kx) and 1µm (Magnification: 23.6kx) CdS thin film of (a, b) 1.5 N of NH_3 and 500nm (Magnification: 52.7 kx) and 1µm (Magnification: 34.4kx) CdS thin film of (c, d) 2.0 N of NH_3 deposited on glass substrate by CBD are shown in fig.2.

Table.1. Measurement of particle size from SEM

Concentrations of NH_3 (N)	Deposition Temperature (^{0}C)	Observed particle size from SEM (nm)
0.5	92	28.92
1.0	92	38.67
1.5	92	41.23
2.0	92	44.20

It is clear from Table.1 that as the at constant deposition temperature the observed average grain size were increased.

3.2. Atomic Force Microscope (AFM)

AFM images obtained from glass substrate immersed in different concentration of NH_3. Fig.3 (a,b,c,d) Show AFM images and cross section analysis of CdS thin films with a Ra value from 42 to 83 nm, RMS value from 69 to 127 nm and maximum peak to valley height value from 825 to 1928 nm indicating the formation of thin film on glass substrate**.** Olofinjan et al [14] reported that Root mean square values for the CdS thin film is less than 50 nm, indicating that the films are relatively smooth. Those reasonably low root mean square offensiveness esteem coupled for size of the grain demonstrates those viability of this system previously, molecule span circulation and generation for movies from claiming prominent that is generally smooth birch.

However the present study indicating that the Root mean square and roughness of the CdS thin films was found to vary with the concentration of NH_3. Therefore, the Root mean square, grain size and roughness increase as the ammonia concentration increases (0.5, 1.0, 1.5 and 2.0 N of NH_3). 3D-AFM images prove that the grains are uniformly distributed within the scanning area (10µm X 10µm) and individual grains extending upwards. This surface characteristic is important for photo detector and solar cell Anwar et al, [15] Ezekoye [16] and Islam et al [17].

The image also reveals that the film was without any cracks, pin hole, large cluster and is continuous with very well connected grains. The surface of most submicron particle is quite coarse and they are comprised. Dergacheva et al [18] reported the CdS thin film were synthesized particles has a size 22-30 nm. This is very less compare to the present study.

Table.2. The roughness average and Root mean square of the AFM images of CdS thin film with different concentration of NH_3

Concentration of NH_3 (N)	Average Roughness R_a(nm)	Root – Mean Square (RMS)Value R_q (nm)	Maximum peak–to-valley height (nm)
0.5	42	69	825
1.0	37	53	664
1.5	63	102	1177
2.0	83	127	1928

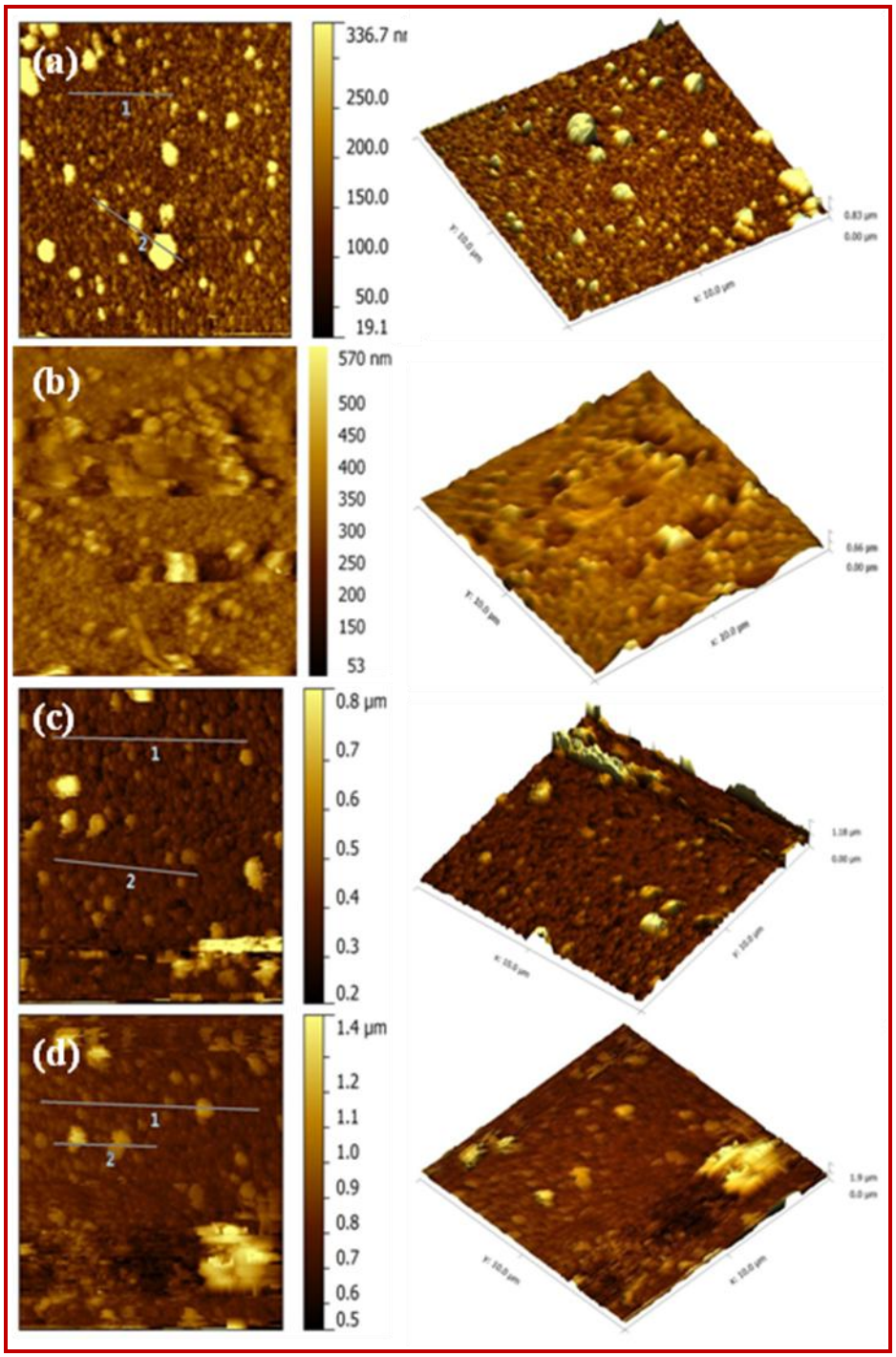

Fig.3. AFM images and 2D, 3D analysis of CdS thin films (a). 0.5 (b) 1.0 (c) 1.5 (d) 2.0 N of NH_3

3.3. Energy Dispersive X-ray Spectrometer (EDAX)

The elemental composition analysis of the as deposited CdS thin film was investigated using EDAX with different concentration of ammonia (0.5, 1.0, 1.5 and 2.0 N of NH_3) for 2hr duration at 92^0C without annealing. The pH of solution is maintained at 11.8 for the film deposition. For all samples, peaks of Cd and S exhibit the presence of these elements in the deposited thin film.

It was significant to note that films deposited at optimized preparative parameters are nearly stoichiometric with average atomic percentage of Cd:S = 53.34: 46.65. The estimated Cd to S ratio value is found to be 1.14. No, detectable change in the computational changes are observed during the increase of ammonia concentration. The spectra confirm the presence of composition of Cadmium and Sulphur in the film. No other impurity peaks are detected in the spectrum which is an indication of the chemical purity of the

sample. Thus, EDAX results indicate the CdS thin films of (0.5, 1.0, 1.5 and 2.0 N of NH_3) with higher Cd-rich (Cd/S = 1.14) were formed by chemical bath deposition. EDAX analysis shows that the films are cadmium rich. This may be due to the fact that the reacting of cadmium is greater than sulphur. Bedir et al [19] and Hasnet et al., [20] reported that the quantitative results of pure CdS thin film from EDAX analysis was (Cd/S = 1.09) close to the present study.

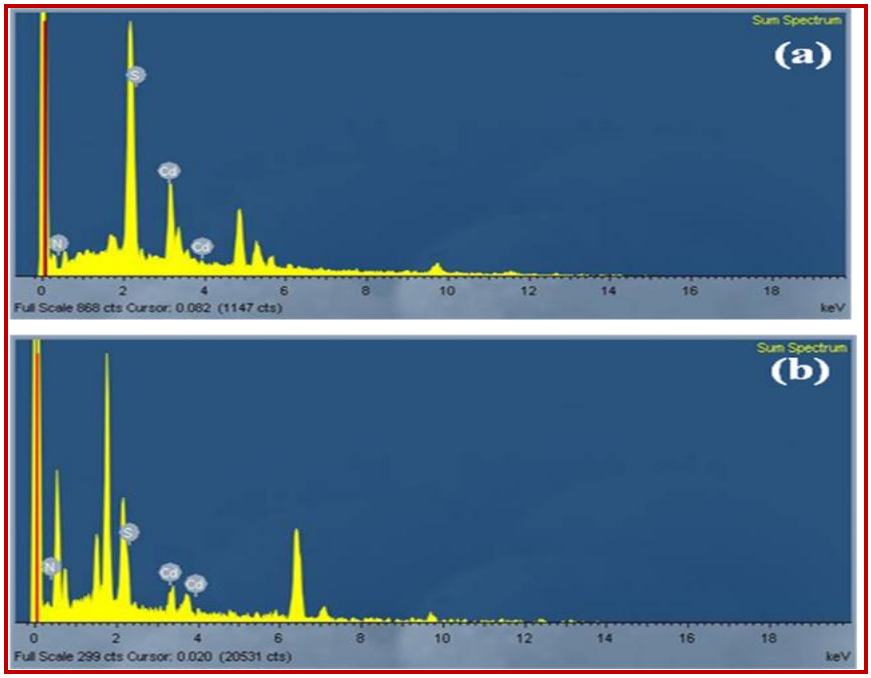

Fig. 4. EDAX Spectrum of CdS thin films (a). 0.5 N of NH_3 (b). 1.0 N of NH_3

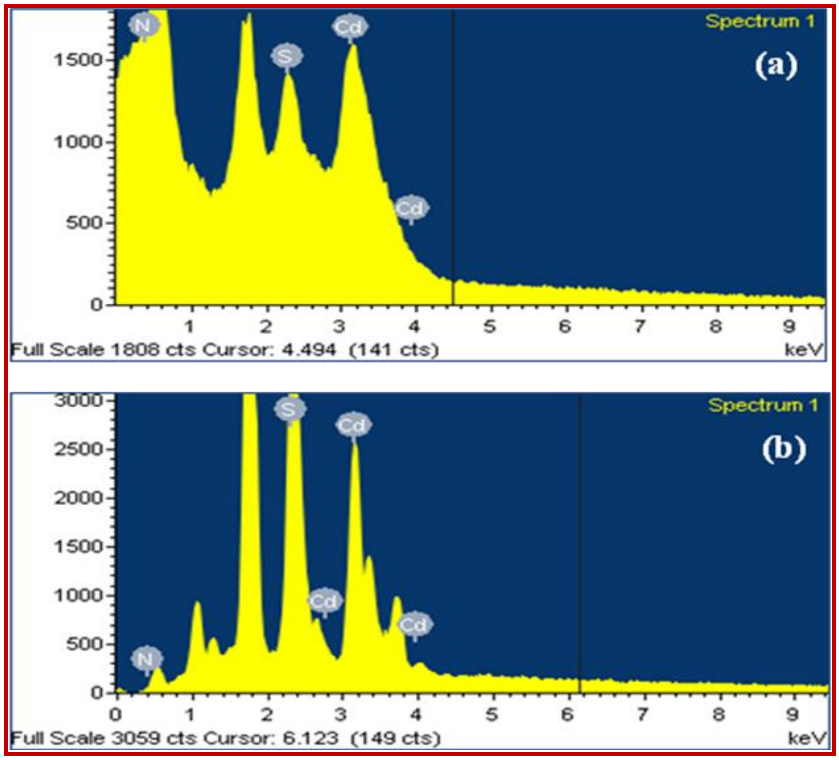

Fig. 5. EDAX Spectrum of CdS thin films (a). 1.5 N of NH_3 (b). 2.0 N of NH_3

Table. 3. EDAX Spectrum results

Concentration of NH_3 (N)	Element	Atomic percentage obtained by EDX analysis (%)	Cd/S ratio	Conditions
0.5	Cd S	50.12 49.88	1.00	Cd-rich
1.0	Cd S	50.72 49.28	1.02	Cd-rich
1.5	Cd S	54.12 45.88	1.17	Cd-rich
2.0	Cd S	58.43 41.57	1.40	Cd-rich

3.4. Photoluminescence Spectra (PL)

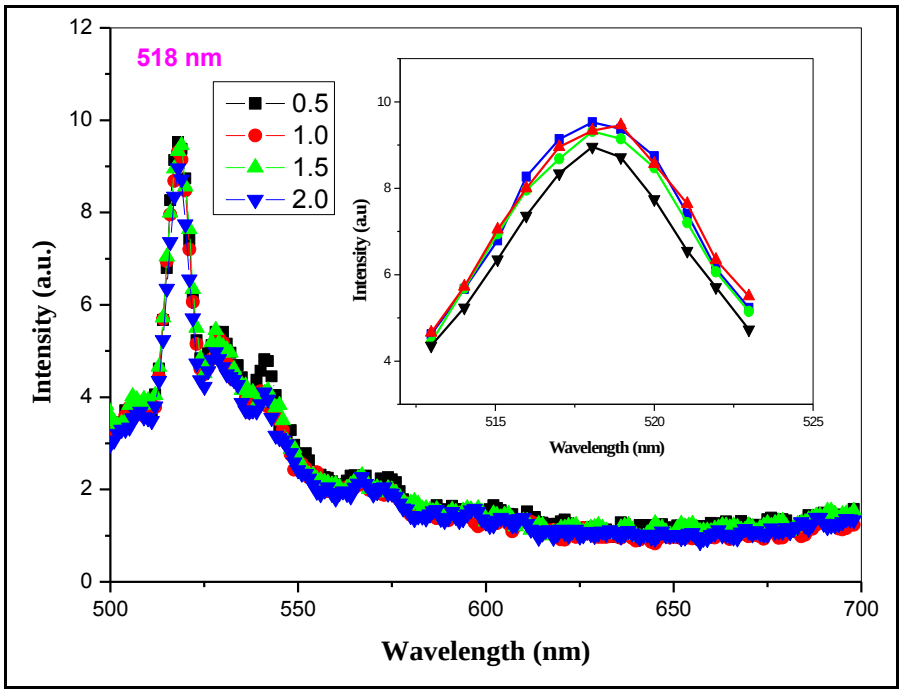

Fig. 6. Photoluminescence spectra of CdS thin films of 0.5, 1.0, 1.5, 2.0 N of NH_3

Fig.6. shows the Photoluminescence spectrum of CdS thin film deposited over glass substrate by CBD method with different concentration of NH_3 was recorded at room temperature in the range of wavelength between 400nm to 700nm. The PL spectra originate from the recombination of surface states. The excitation and emission spectrum of the CdS thin film was obtained. The CdS thin film was excited at 407.359 nm corresponding energy Eg = 3.04 eV, in violet band with maximum intensity. The emission peak was observed at 518.307 nm with low intensity levels in green band corresponding Eg = 2.39 eV, the emission of near band edge (NBE) excitonic peak [21] (karimi et al). The origin of green band emission is due to radioactive recombination of electrons and holes via the surface/defect states present [22] (wang et al). This is close to the band gap (2.43 eV) of pure CdS as observed from the absorption spectrum. Pushpalatha et al [23] reported that, the green band at 2.39 eV is due to the transition from donor states near conduction band to the valance band i.e. due to donor acceptor transition.

The intensity decreases for the CdS thin film depends on concentration of NH_3.The observed band gap energy (2.39 eV) for green band from PL studies confirmed the CdS thin films. PL emission lines are not sharp peaks but are broad bands, because of the presence of many recombination sites. Surface area and defect concentrations; hence the individual PL emission lines will have a range of energies and form a broad band. The peak at 518.307 nm has the emission of green light with energy of 2.39 eV is due to the recombination of

electrons trapped inside a sulfur vacancy with hole in the valance band of the CdS is responsible for green band emission for CdS. This is useful to design a suitable window material in fabrication of solar cells and photonic device applications [24].

Table.4. Emission wave length and emission energy with various concentrations of NH_3

Concentrations of NH_3 (N)	Intensity (a.u)	Emission wavelength (nm)	Emission energy (eV)
0.5	9.709	518.312	2.392
1.0	9.189	518.138	2.393
1.5	9.267	518.390	2.392
2.0	8.867	518.390	2.392

From the table it is observed that the intensity decreases as the concentration increases from 0.5, 1.0, 1.5, 2.0 N of NH_3. The emission energy (eV) slightly varies with the concentration of NH_3.

4. Conclusion

The CdS thin films have been prepared by simple chemical bath deposition method. Microstructure of the prepared film is investigated by SEM and EDAX spectra confirmed the particle size found to be 28.92 to 44.20 nm and presence of compositional elements such as Cd and S. AFM images and cross section analysis of CdS thin films with a Ra value from 42 to 83 nm, RMS value from 69 to 127 nm and maximum peak to valley height value from 825 to 1928 nm indicating the formation of thin film on glass substrate. The Root mean square and roughness of the CdS thin films was found to vary with the concentration of NH_3.The Photoluminescence spectrum of CdS thin film, the peak at 518.307 nm has the emission of green light with energy of 2.39eV. This is useful to design a suitable window material in fabrication of solar cells and photonic device applications.

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References

1. N. Romeo, A. Bosio, V. Canevari, Recent progress on CdTe/CdS thin film solar cells, Solar Energy. 2004;77:795-801.
2. D.Kathirvel, Preparation and characterization of cadmium sulphide thin films prepared by vacuum evaporation deposition and chemical bath deposition Ph.D thesis, Anna University, p.85. 2012.
3. J. Schaffner, E. Feldmeier, A. Swirschuk, Influence of substrate temperature, growth rate and TCO substrate on the properties of CSS deposited CdS thin films, Thin Solid Films. 2011;519:7556-7559.
4. J.N. Ximeelo-Quiebras, G. Contreras-Puente, Physical properties of chemical bath deposition CdS thin films, Solar energy Mater. Solar cells. 2002;82:263-268.
5. Salah Abdul-Jabbar Jassim, Abubaker A. Rashid Ali Zumaila, Influence of substrate temperature on the structural, optical and electrical properties of CdS thin films deposited by thermal evaporation, Results in Physics. 2013;3:173-178.
6. F. Lisco, P.M. Kaminski, A. Abbas, K. Bass, The structural properties of CdS deposited by chemical bath deposition and pulsed direct current magnetron sputtering, Thin Solid Films. 2015;582:323-327.
7. A. Rmili, F. Ouachtari, A. Bouaoud, A. Louardi, Structural, optical and electrical properties of Ni-doped CdS thin films prepared by spray pyrolysis, J. Alloys compd. 2013;557:53-59.
8. S. A. Tomas, O. Vigil, J. J. AlvaradoGil, R. LozadaMorales, Influence of thermal annealings in different atmospheres on the band gap shift and resistivity of CdS thin films, J. Appl. Phys. 1995;78:2204.

9. N. Amin, T.Isaka, T. Okamoto, A. Yamada, Doping effects of dimethyl –tin-dichloride on material properties of CdS films and an formation of CdS/CdTe hetro structures, J. Appl. Phys. 1999;38:1.
10. Y. Munikrishna Reddy, M. Nagendra Vara Prasad, Properties of CdS Chemically Deposited thin films on the Effect of Ammonia Concentration, J. Appl. Phys. 2013;4(4):01-07.
11. Milind Kale and Deelip Bhavsar, Synthesis and Characterization of Nanostructured (CdS) Te, Thin Films for solar cell Application, Int. J. Eng. Sci. Res. Tech. 2014;3(4):7012-7015.
12. F. Atay, V. Bilgin, I. Akyuz, S. Kose, The effect of In doping on some physical properties of CdS films, Mater. Sci. Semicond. Proc. 2003;6:197-203.
13. Jiankang.Li, Preparation and properties of CdS thin films deposited by chemical bath deposition, Ceramics International, 2015;41:5376-5380.
14. Bolutife Olofinjana, Gabriel Egharevba, Bidini Taleatu, MOCVD of Molybdenum Sulphide Thin Film via Single Solid Source Precursor Bis-(Morpholinodithioato-s,s')-Mo, Journal of Modern Physics. 2013;2:341-340.
15. Anwar H. Ali, Sarah A. Jassem, Preparation and Study of CdS thin films at different concentration thiorea by chemical bath deposition (CBD) method, WSN. 2015;23:73-89.
16. B. A. Ezekoye, K. O. Ighodalo1, V. A. Ezekoye, Nanocrystalline Cadmium sulfide (CdS) thin film synthesized at different dip times by chemical bath deposition technique, Int. J. Phys. Sci. 2015;10(13):403-412.
17. M.A. Islam, F.haque, K.S. Rahma, N. Dhar, Effect of oxidation on structural, optical and electrical properties of CdS thin films grown by sputtering, Optic. 2015;126:3177-3180.
18. M. B. Dergacheva, K. A. Mit, K. A. Urazov, Electron Microscopic Study of Thin CdS Films, Journal of surface investigation, 2013;7:1270-1276.
19. Metin Bedir, Re K Kayali, Mustafa Oztas, Effect of the Zn Concentration on the Characteristic Parameters of Zn_xCd_{1-x} S Thin Films Developed by Spraying Pyrolysis Method Under the Nitrogen Atmosphere, Turk. J. Phys. 2002;26:121-126.
20. A. Hasnat, J. Podder1, Optical and alectrical characteristics of pure Cds thin films for different thickness, J. Bang. Aca.Sci. 2013;37(1):33-41.
21. Meysam Karimi, Mohammad Rabiee, Fathollah Moztarzadeh, Controlled synthesis, characterization and optical properties of CdS nanocrystalline thin films via chemical bath deposition (CBD) route, Curr. Appl. Phys. 2009;9:1263-1268.
22. Szu-Ko Wang, Ting-Chun Lin, Sheng-Rui Jian, Effects of post-annealing on the structural and nanomechanical properties of Ga-doped ZnO thin films deposited on glass substrate by rf-magnetron sputtering, Appl. Surf. Sci. 2011;258:1261-1266.
23. H.L. Pushpalatha, S. Bellappa, T.N. Narayanaswamy, R.Ganesha, Structural and optical properties of CdS thin film obtained by chemical bath deposition and effect of annealing, Indian J. Pure and Appl. Phys. 2014;52:545-549.
24. M. Muthusamy, S. Muthukumaran, Effect of Cu-doping on structural, optical and photoluminescence properties of CdS thin films, Optik. 2015;126:5200-5206.

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