

Low Temperature Annealing of Cadmium Sulphide Thin Films for Improving Surface-Interface Properties

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ABSTRACT

Surface morphology of materials can be changed by the application of temperature. In this work, changes in surface morphology of cadmium sulphide (CdS) thin films have been studied by annealing them at different temperatures. CdS thin films were prepared over glass substrate by spin coating technique and then annealed for 30 minutes at different temperatures (100 °C, 200 °C and 300 °C). These films were characterized by UV-Vis spectroscopy, optical microscope and Atomic Force Microscopy (AFM) before and after annealing. AFM images showed changes in the surface morphology of the films and reveals that surface roughness increases with annealing temperature.

KEYWORDS: Synthetic Membrane, Plasma Treatment, Ion Energy, Plasma Etching, Biomedical Applications.

1. INTRODUCTION

Cadmium sulphide (CdS) has gained immense interest because of its various advanced technological applications in field effect transistors,¹ light emitting diodes (LED),² environmental³ and biological sensors,⁴ photo catalysis,⁵ water purification systems,⁶ improved performance in UV-shielding,⁷ flame retardant,⁸ scratch resistance,⁹ chemical resistance,^{10–13} nanomedicine,^{14,15} photo-electrochemical activity,¹⁶ photo catalysis^{17,18} and mycobacterium activity^{19–21} etc. It is a direct band gap material, with energy band gap 2.42 eV at 300 K²² with cubic, hexagonal or mix crystal structure depending on growth and deposition.^{23–25}

Its size dependent properties²⁶ and real stage applications are got enhanced as thin films²⁷ like for synthesis of light emitting diodes (LED),²⁸ flame retardant,²⁹ dye-sensitized solar cells,³⁰ gas sensor,³¹ solar energy conversion,³² UV detectors³³ and ultrasonic sensors.³⁴

Spin coating is an easy and fast method of obtaining thin and homogeneous from solution.²³ The solution is prepared in solvent that evaporates fast at room temperature, like ethanol, acetone etc.^{8,28} Solution is poured in large amount over the substrate and then rotated at high

speed (~6000 rpm) to spread the fluid uniformly due to centrifugal force.⁸

During thermal annealing, the sample was exposed to some temperature in oven, as a result its surface morphology and structural properties changes that are useful for improving surface-interface properties.^{5,21–25} So it is important to investigate effect of low temperature thermal annealing on structural properties and surface morphology of materials. In this paper we have synthesized CdS nanoparticles using chemical root, characterized them in terms of nano range using various techniques. CdS NPs thus obtained were re-disperse an acetone and used for thin film synthesis using spin coating method. Low temperature thermal annealing was performed at atmospheric pressure to modified surface morphology and structural properties of thin films. Surface and structural modifications were characterized using AFM.

2. MATERIALS AND METHODS

0.1 M cadmium acetate (10 ml), 0.1 M sodium sulphide (10 ml) and 0.1 M ethylene diamine tetra acetate (EDTA) (20 ml) solutions were prepared in distilled water, and allowed to stir for 1 hour. Cadmium acetate and sodium sulphide solutions were then poured, simultaneously and drop wise, into EDTA solution, with continuous stirring. The mixture was stirred overnight, which was then centrifuged using distilled water, and the final solution was prepared in acetone. The particle size and

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Received: 3 March 2014

Accepted: 21 April 2014

morphology of CdS NPs are determined by transmission electron microscopy (TEM). The imaging is performed using a Technika TEM instrument operating at 200 kV. Optical Absorbance and Emission Spectroscopy was performed for NPs membranes by using a double beam UV-Vis spectrophotometer (Shimadzu 1800) and PL (RF5301 PL SHIMADZU) spectrometer respectively.

The thin films, from the so obtained solution, were prepared over glass substrate using spin coating technique at 6000 rpm. Prior to this, the substrate was thoroughly cleaned by immersing it in detergent for 15 minutes and then washed them with acetone and ethanol solution sequentially. Atmospheric thermal annealing of the thin films was done, by keeping them in oven at different temperatures (100 °C, 200 °C and 300 °C) for a constant time period (30 minutes). UV-Vis spectroscopy generates absorption data corresponding to absorption wavelength, from which energy band gap can be calculated, to ascertain formation of thin films and modification band gap. Optical properties of these films were characterized by UV-Vis spectroscopy and surface modifications were recorded using optical microscope and AFM. LABOMED microscope is used for recording optical images. NanosurfEasyScan 2 AFM was used to identify surface modification before and after annealing.

3. RESULTS AND DISCUSSION

Yellow colored precipitate was obtained after mixing of chemicals. UV-Vis absorption of the solution was recorded by Shimadzu-1800 spectrophotometer in wavelength range 200–900 nm. The maximum absorption was observed at ~490 nm (blue shifted, relative to bulk CdS) and energy band gap calculated is 2.53 eV (Fig. 1), which proves the presence of CdS nanoparticles. The photoluminescence spectrum was recorded by Shimadzu RF-5301 spectrofluorometer using 332 nm excitation wavelength. Xenon lamp is used for PL excitation. Figure 2 shows PL spectra of CdS particles. It shows two emission peaks at 520 nm

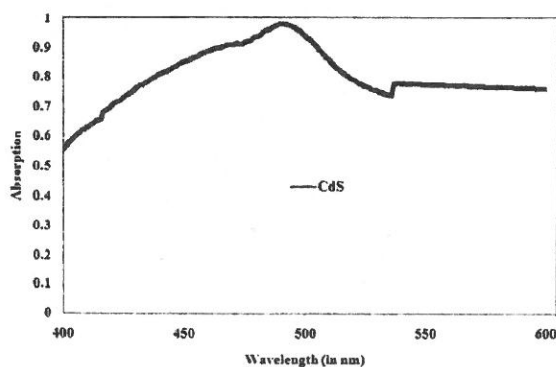


Fig. 1. UV-Vis Spectra of CdS nanoparticles.

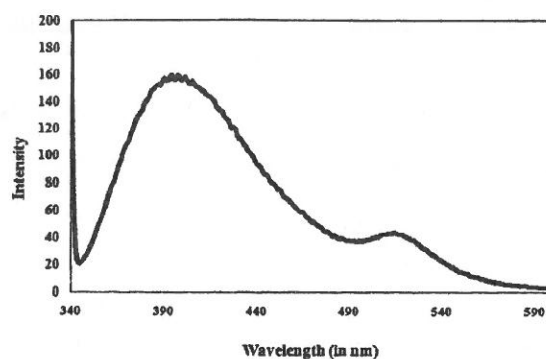


Fig. 2. PL spectroscopy of CdS particles.

and 400 nm, confirming presence of nanoparticles. CdS NPs were dispersed in acetone by ultra-sonication and then film was prepared using spin cotter. Figure 3 shows TEM image of CdS NPs synthesized having spherical shape and particle size ranging from 25–35 nm. Individual particles in TEM images can be identified easily, which shows no aggregations among CdS NPs.

The color of the thin films darkened from yellow to orange as the annealing temperature was raised from 100 °C to 300 °C. The optical microscopic images of CdS thin films (Fig. 4) taken at 40X magnification, shows that surface morphology is modified after annealing. Surface becomes rougher and some pores were formed after annealing of films.

AFM images (Fig. 5) show surface morphology of thin films. It shows that surface roughness increases with increase of annealing temperature. UV-Vis spectroscopy of annealed thin films (Fig. 6) show red shift in absorption wavelength, hence decrease in band gap, suggesting increase in size of particles with increase in annealing temperature (Table I). At temperature above 200 °C, band gap increases due to changes in crystallite size and inter-planer distance of annealed CdS films, i.e., surface-interface properties are got modified after low temperature annealing.

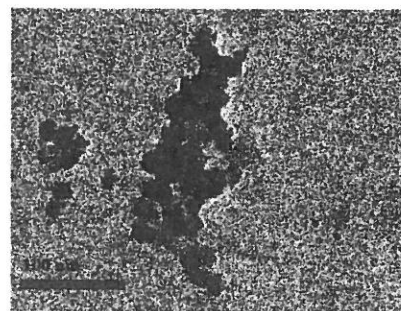
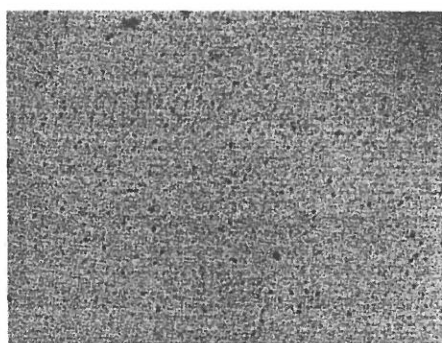
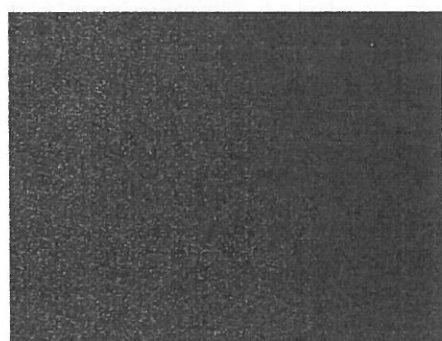


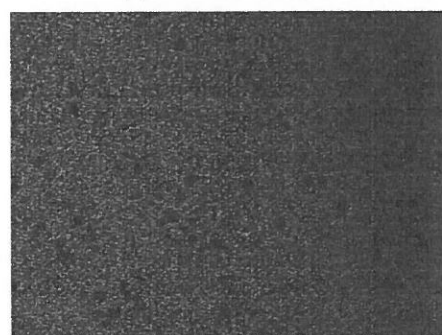
Fig. 3. Transmission electron micrographs (TEM) of CdS NPs synthesized, having spherical shape and particle size ranging from 25–35 nm.



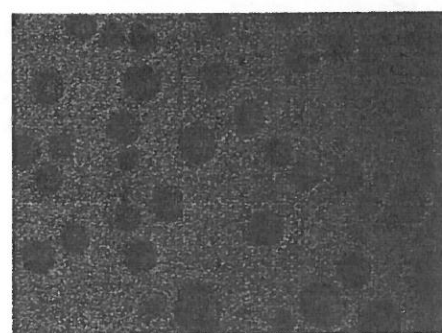
(a) Without annealing



(b) Annealed at 100 °C

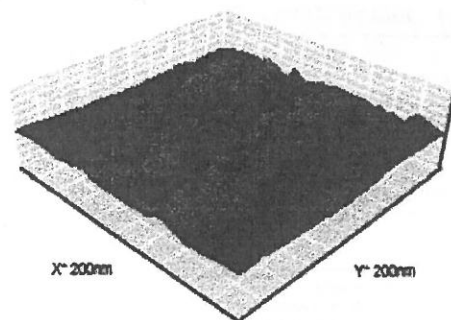


(c) Annealed at 200 °C

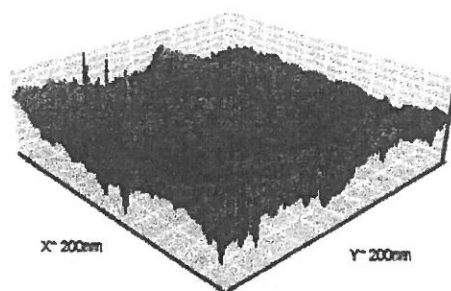


(d) Annealed at 300 °C

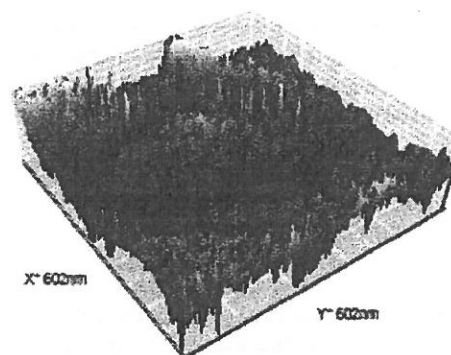
Fig. 4. Optical microscopic images of CdS thin films. (a) Without annealing, (b) Annealed at 100 °C, (c) Annealed at 200 °C, (d) Annealed at 300 °C.



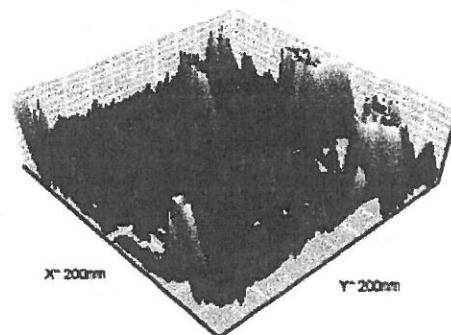
(a) Without annealing



(b) Annealed at 100 °C



(c) Annealed at 200 °C



(d) Annealed at 300 °C

Fig. 5. Atomic force microscope images of CdS thin films. (a) Without annealing, (b) Annealed at 100 °C, (c) Annealed at 200 °C, (d) Annealed at 300 °C.

Table I. Band gap of films at different temperature.

Thin film	Band gap calculated (in eV)
Unannealed	2.15
Annealed at 100 °C	2.00
Annealed at 200 °C	1.85
Annealed at 300 °C	1.82

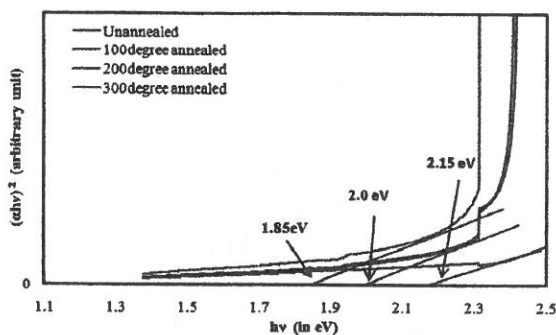


Fig. 6. UV-Vis spectrograph of CdS thin films-unannealed, and annealed at 100 °C, 200 °C and 300 °C.

4. CONCLUSIONS

The study investigates the effect of annealing temperature on CdS thin films. CdS nanoparticles were prepared by wet chemical method. Their thin films were prepared over glass substrate by spin coater. Upon annealing the thin films at 100 °C, 200 °C and 300 °C for constant time (30 minutes), it was found that particle size and surface roughness increases with increase in temperature. These results are useful for applications in semiconductor industry as many of their applications (e.g., as LED) are temperature dependent. These results are also useful to study thermal annealing effects on structural properties for analysis and modifications of surface-interface properties of materials.

Acknowledgments: The authors are thankful to Centre for Converging Technologies and University Science Instrumentation Centre of University of Rajasthan, Jaipur for providing research facilities for carrying out this work. Authors are also thankful to INSPIRE AORC program of DST, Government of India for providing fellowship to Ravi Agarwal to carry out his Ph.D. research work.

References and Notes

- Y. Sanchuan, L. Xuesong, L. Jingqun, W. Dihua, L. Meihong, and G. Congjie, *Separation and Purification Technol.* 76, 283 (2011).
- H. S. Nalwa (ed.), *Encyclopedia of Nanoscience and Nanotechnology*, American Scientific Publishers, Los Angeles (2004/2011), Vols. 1–2.
- H. S. Nalwa and S. Miyata, *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, India (1996), Vols. 1–2.
- H. S. Nalwa, *Polymer Optical Fibers*, American Scientific Publishers, Los Angeles (2004), Vols. 1–2.
- H. S. Nalwa, *Polymeric Nanostructures and Their Applications*, American Scientific Publishers, Los Angeles (2004), Vols. 1–2.
- H. S. Nalwa, *Handbook of Organic Conductive Molecules and Polymers*, John Wiley and Sons, USA (1997), Vols. 1–4.
- J. Singh, W. M. Saied, R. Kaur, and I. Badea, *Rev. Nanosci. Nanotechnol.* 2, 275 (2013).
- S. Khandelwal, G. A. Kumar, R. Agarwal, and N. K. Agrawal, Effect of Transition Metal on Luminescence Quenching of ZnS Nanoparticles, *Proceedings of the International Conference on Emerging Trends of Research in Applied Sciences and Computational Techniques (ETRASCT' 14)*, Published by Int. J. of Engineering Research and Technol., Jodhpur, Rajasthan, India (2014), February, pp. 98–103.
- N. K. Agrawal, R. Agarwal, G. A. Kumar, Y. K. Vijay, and K. C. Swami, Study of Enhancement of Bio-Compatibility of Argon Plasma Irradiated: Polycarbonate Ag Nanocomposites Polymer Membranes, *Proceedings of the International Conference on Emerging Trends of Research in Applied Sciences and Computational Techniques (ETRASCT' 14)*, published by Int. J. of Engineering Research and Technol., Jodhpur, Rajasthan, India (2014), pp. 92–97.
- H. Ji, J. Choi, G. Lim, B. Parida, K. Kim, J. H. Jo, and H. S. Kim, *J. Nanosci. Nanotechnol.* 13, 7806 (2013).
- G. A. Kumar, N. K. Agrawal, S. Khandelwal, and R. Agarwal, Highly Optimized PMMA-TiO₂ Nanocomposites via Solution Casting, *proceedings of the International Conference on Emerging Trends of Research in Applied Sciences and Computational Techniques (ETRASCT' 14)*, Published by Int. J. of Engineering Research and Technol., Jodhpur, Rajasthan, India (2014), pp. 109–113.
- N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *Adv. Sci. Eng. Med.* 6, 698 (2014).
- N. K. Agrawal, R. Agarwal, S. Khandelwal, Y. K. Vijay, and K. C. Swami, ZnO Nano Composites Polystyrene Membranes: Plasma Treatment and Characterization, *Proceedings of the International Conference on Emerging Trends of Research in Applied Sciences and Computational Techniques (ETRASCT' 14)*, Published by Int. J. of Engineering Research and Technol., Jodhpur, Rajasthan, India (2014), February, pp. 104–107.
- S. J. Lee, D. H. Kim, J. K. Kang, D. Y. Kim, H. M. Kim, and Y. S. Han, *J. Nanosci. Nanotechnol.* 13, 7839 (2013).
- A. Goyal, V. Sharma, A. Sharma, R. Agarwal, K. B. Sharma, and S. L. Kothari, *J. Nano and Electronic Physics* 3, 254 (2011).
- L. J. Ghil, T. Y. Youn, N. R. Park, and H. W. Rhee, *J. Nanosci. Nanotechnol.* 13, 7912 (2013).
- P. Agarwal, R. Agarwal, and N. K. Agrawal, *Proceedings of 58th DAE-Solid State Physics Symposium, AIP proceedings*, Patiala, Punjab, India (2013), December.
- N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *J. Mat. Sci. Sur. Eng.* 1, 4 (2013).
- W. M. King, P. A. Cantor, L. W. Schoellenback, and C. R. Cannon, High-retention reverse-osmosis desalination membranes from cellulose acetate, *Membranes from Cellulose Derivatives*, Interscience Publisher, New York (2001), Vol. 1.
- N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *J. Mat. Sci. Sur. Eng.* 1, 23 (2013).
- A. Sveshnikov, I. Klicmanová, P. Demo, and Z. Kožfšek, *Adv. Sci. Eng. Med.* 5, 569 (2013).
- S. U. Maheshwari, S. V. Kumar, and N. Nagiah, *Adv. Sci. Eng. Med.* 5, 1305 (2013).
- N. K. Agrawal, R. Agarwal, Y. K. Vijay, and K. C. Swami, *Journal of Materials Science and Surface Engineering* 1, 32 (2014).
- P. Agarwal, A. Mehta, S. Kachhwaha, and S. L. Kothari, *Adv. Sci. Eng. Med.* 5, 709 (2013).
- M. Hatami, K. V. Rao, M. Ahmadipour, and V. Rajendar, *Adv. Sci. Eng. Med.* 5, 1039 (2013).

26. J. K. Beasley, The evaluation and selection of polymeric materials for reverse osmosis membranes, Interscience Publisher, New York (1997), Vol. 1.
27. S. Vijay, J. K. Vijayavargiya, A. Sharma, and Y. K. Vijay, *Adv. Sci. Eng. Med.* 5, 1058 (2013).
28. N. K. Agrawal, K. Awasthi, Y. K. Vijay, and K. C. Swami, *Adv. Electrochem.* 1, 98 (2013).
29. N. K. Agrawal, M. Singh, Y. K. Vijay, and K. C. Swami, *Adv. Sci. Eng. Med.* 6, 595 (2014).
30. Y. Haldorai, S. Chitra, and J. J. Shim, *Adv. Sci. Eng. Med.* 5, 1044 (2013).
31. R. Agarwal, N. K. Agrawal, and R. Singh, *Adv. Sci. Eng. Med.* 6, 203 (2014).
32. M. R. Anwar, K. Vattipalli, E. Myrah, R. Asmatulu, and S. Prasad, *Adv. Sci. Eng. Med.* 5, 633 (2013).
33. K. Hyun and K. S. Soo, *J. Mem. Sci.* 286, 193 (2009).
34. R. Kolenák and M. Martinkovic, *Adv. Sci. Eng. Med.* 5, 527 (2013).