Minor Research Project Entitled

"Optical and electrical properties of CdZnS thin films prepared by spray pyrolysis"

Completed under the financial assistance of & Submitted to **University Grants Commission Western Regional Office, Ganeshkhind, Pune – 411007**

Under the scheme of MRP (Science)

Sanction letter no.

File No. 47-456/12 (WRO) Dated: 05/03/2013

Name of the Principal Investigator

Dr. Londhe Chandrakant Trimbakrao Assistant Professor, Department of Physics

Mahatma Gandhi Mahaividyalaya, Ahmedpur Dist. - latur

BRIEF SUMMARY OF THE MINOR RESEARCH PROJECT

File Number	47-456 / 12 WRO date: 05-03-2013
Subject	Physics
Title	Optical and electrical properties of CdZnS thin films prepared by Spray pyrolysis.
Name of PI	Dr. C. T. Londhe
Institute	Mahatma Gandhi Mahavidyalaya, Ahmedpur, Dist. Latur (MS), India. Pin - 431 515

1. Introduction:

Now a day the world has to face the problem of energy crises. These are due to mainly two reasons: firstly the population of the world has increased rapidly and secondly the living standard of human beings is increased. So the human role has to hunt for the new source of energy. The sun is the ultimate biggest source of energy holding key to resolve the energy crises arising out of growing rift between our energy consumption and production. The solar energy has greatest potential of all the sources of renewable energy. The conversion of solar energy into usable form is potential challenge to the scientists. In the development of science and technology, the photovoltaic devices (solar cells) and systems have undergone revolutionary developments. Solar cell devices play vital role in converting solar energy into usable form. Many type of thin film solar cells exists today [1].

In the past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other opto-electronic device with much interest shown in the use of CdS window layer in solar cell architecture. However, the absorption of the blue portion of the solar spectrum by CdS window results in a decrease in the current density of such solar cells and UV laser diodes. For the high performance of solar cell device, it is imperative to use an appropriate window material. Ternary CdZnS thin films often exhibit improved chemical, structural and optical properties and hence are potentially useful as a window layer in solar cell. CdZns thin films have been prepared by various techniques, such as electro-deposition (1), successive ionic layer adsorption and reaction (SILAR) [2] chemical bath deposition [3,4], spray pyrolysis [5] and metalorganic chemical vapour deposition [6]. Among these, spray pyrolysis method is economical, simpler and more versatile than the others and gives the possibility of obtain films with suitable properties for optoelectronic applications and also when large areas are needed. The method is well studied and produces films that have comparable structural and optoelectronic properties to those produced using other sophisticated thin film deposition techniques [4, 7]. The technique has been applied in producing emerging materials for solar cells, sensors, laminated sheet glass for transport, protective coating, soar thermal controls in buildings and is being adopted in mass industrial production [8, 9]. In this report, the optical and electrical properties of the spray pyrolysis deposition thin films of CdZnS are studied.

2. Achievements from the project:

The work was bound to fabricate and characterize the scientifically important CdZnS thin films, as the most pertinent aspects of spray pyrolysis technique. Thin-film solar technologies have enjoyed large investment, but they have not become mainstream solar products due to their lower efficiency and corresponding larger area consumption per watt production. Semiconductor materials formed from elements of groups II and IV are extensively used in modern technology. Some semiconductors, such as Zn, Cd and S, have been studied more extensively and synthesized. The films were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis X-rays (EDAX), resistivity and optical measurement techniques and were studied for tuning of optical band gap, in different parametric conditions.

3. Summary of the findings

The CdZnS thin films were deposited on glass substrates by spray pyrolysis technique using cadmium acetate $[(CH_3COO)_2 Cd.2H_2O]$ as Cd⁺⁺ ion source, zinc acetate and thiourea $[CS(NH_2)_2]$ as S⁻² ion source, with cadmium to sulfur (Cd:S) of a appropriate molar ratio. The CdZnS thin films also deposited using cadmium chloride (CdCl₂) as Cd⁺⁺ ion source, zinc chloride (ZnCl₂) and thiourea $[CS(NH_2)_2]$ as S⁻² ion source. For deposition of CdZnS thin films, ultrasonically cleaned and dry glass substrates will be employed for deposition of thin films. The system will be optimimized for other deposition constants, such as deposition time, spray factor, nozzle to substrate distance, air pressure and the flow rate.

The experimental sets were prepared by changing volume concentrations of precursors. The optically important characteristics of CdS thin films varied with the wavelength and the photon energy. Study of optical conductance and band gap conform the transmission within visible range. The synthesis of CdS films using SP technique is based on slow release of Cd^{2+} ions and S^{2+} ions in an aqueous alkaline bath and the subsequent condensation of these ions on the substrate suitably dipped in bath. The slow release of Cd²⁺ ions, achieved by adding a complexing agent to the Cd salt, to form cadmium complex species, upon dissociation results in the release of Cd²⁺ ions. The S²⁺ ions are supplied by decomposition of $(NH_2)_2CS$. In the present work, CdS films are deposited at different reaction temperatures using Spray Pyrolysis technique. The morphological, Structural, electrical and optical properties of Zn doped CdS thin films are investigated.

Zn doped CdS thin films were deposited with increasing concentration (wt. %) of zinc Chloride. From figure 1 it clearly observed that the resistivity decreases with increasing Zn doping concentration in the films up to 7 wt. % after which it slightly increases.



Fig.1. Variation of electrical resistivity of CdZnS thin films with increases Zn doping concentration

The optical properties of thin films such as transmission and energy band gap are important in fabrication of solar cell. The optical transmission of CdZnS thin films are recorded using UV-Visible spectrophotometer in the wave length 300 nm - 900 nm at room temperature with increasing Zn concentration. Figure 2 shows that transmission in increases with increase in Zn concentration. The energy band gaps of the samples were calculated using relation of absorption coefficient. The energy band gap is increases with increases with increases with a solution of the energy band gap.



Fig.2. Transmission spectra of CdZnS thin films with increases Zn doping concentration

4. Scope and contributions to Society:

Silicon is the most common solar-cell material, despite the fact that it is indirect-gap and therefore does not absorb light very well. Silicon solar cells are typically hundreds of micrometers thick; if it was much thinner, much of the light (particularly in the infrared) would simply pass through. On the other hand, thin-film solar cells are made of direct band gap materials (such as Zn, CdTe or CIGS), which absorb the light in a much thinner region, and consequently can be made with a very thin active layer (often less than 1 micrometer thick).

It is an applicable Minor Research Work for CdZnS thin films fabrication. The UGC (WRO) accepted and granted the Minor Research Project proposal, it is benefited to students with Physics as a principle subject, specially to analysis the physical, electrical and optical properties of CdS thin films, and also this practical research approach will meet the prior need of manufacturers for fabricating the most applicable nanodevices, to solve the current problem of energy crises.

Thin films fabrication has a wide interdisciplinary relevance. The thickness is unique because no solid can be made flatter than a thin film. It is also unique because many of the mechanisms of the biological and physical world operate on length scales from 0.1 to 100 nm. So that the thin films have been wide potential applications in industrial, biomedical and electronics. At this dimension materials exhibit different physical properties. Scientists expect that many novel effects at the nanoscale will be discovered and used for breakthrough technologies. The vast majority of thin films based products will contain nanomaterials bound together with other materials or components, rather than free-floating nano-sized objects. Thin films have a major impact on medicine and health care; energy production and conservation; environmental cleanup and protection; electronics, computers, and sensors; and world security and defense. Thin films technology breakthrough is expected to have many environmental benefits such as reducing the emission of air pollutants and cleaning up oil spills. The large surface areas of thin films give them a significant capacity to absorb various chemicals, sunlight etc.

Conclusions:

- 1. The deposition conditions are optimized to obtain CdZnS thin films
- 2. The structural investigation using XRD reveals that formation of CdZnS thin films.
- 3. The crystalline size for CdZnS films was found to be 33nm to 38nm
- 4. From this study it observed that as Zn composition in the film goes on increases, increasing crystallite size, grain size and optical band gap energy
- 5. Electrical conductivity increases with increase temperature of the CdZnS thin films, indicating semiconducting nature.

Publications:

- C. T. Londhe, K. N. Shivalkar, M. M. Betkar, G. D. Bagde, Optical properties of CdS Thin Films, Journal of Advances in Applied Sciences and Technology, Vo. 1, Issue 2(Dec. 2014) pp 145-146.
- 2. C. T. Londhe, M. M. Betkar, Optical characterizations of CdZnS Thin Films by Spray Pyrolysis, International Journal of Computer & Mathematical Sciences, Vo. 5, Issue 3 (March 2016) pp 14-15.



ISSN : 2393-8188 (print) 2393-8196 (online) www.milliyasrcollege.org.journal.php

OPTICAL PROPERTIES OF CdS THIN FILMS

C. T. Londhe^{1*}, K. N. Sivalkar¹, M. M. Betkar², G. D. Bagde¹

¹ Physics Research Centre, Mahatma Gandhi Mahavidyalaya Ahmedpur, Dist. Latur (MS)-India.
²Shri. Kumarswami Mahavidyalaya Ausa, Dist. Latur (MS)-India

*Corresponding Author: e-mail: londhect@gmail.com

ABSTRACT:

The Cadmium Sulphide thin films were deposited by using chemical bath deposition technique with different bath temperatures. The synthesized CdS films were optically characterized by UV-visible spectrophotometer. The variation of optical energy band gap with changing concentration of $CdCl_2$ confirmed the interaction between photon energies and material properties of CdS thin films.

KEY WORDS: CBD, Thin films, CdS, CdCl2, optical band gap.

1. INTRODUCTION:

CdS is an important semiconductor material plays vital role on the photovoltaic technique. It has been used as a parameter of several types of thin film solar cells such as CdTe, CdS has suitable energy band gap along with high absorption coefficient and considerable energy conversion efficiency. [1-5]

The various deposition methods have been used for preparation of semiconducting thin films. One of the suitable and non-vacuum methods is Chemical bath deposition (CBD). It is due to its simplicity, low cost and large area coatings. The technique has been widely used to deposit different verity of semiconducting materials [6]. Although other techniques have been used in deposition of CdS, Chemical bath deposition is known to enhance the performance of Cadmium Sulphide window, used in solar cell applications [7]

The optically important characteristics of CdS thin films varied with the wavelength and the photon energy. Study of optical conductance and band gap conforms the transmission within visible

range [8]. The synthesis of CdS films using CBD is based on slow release of Cd^{2+} ions and S^{2+} ions in an aqueous alkaline bath and the subsequent condensation of these ions on the substrate suitably dipped in bath. The slow release of Cd^{-2+} ions, achieved by adding a complexing agent to the Cd salt, to form cadmium complex species, upon dissociation results in the release of Cd^{2+} ions. The S^{2+} ions are supplied by decomposition of (NH₂)₂CS. [9-10]

In the present work, CdS films are deposited at different reaction temperatures using CBD technique. The optical properties of CdS deposited thin films are investigated.

2. EXPERIMENTAL:

Cadmium Sulphide thin films were synthesized using chemical bath deposition technique on clean bare glass substrates. The increasing reaction temperatures were 70, 75, 80, 85 and 90 $^{\circ}$ C was optimized for deposition. The solutions with 1M (NH₂)₂CS, 5M NH₄OH of CdCl₂ were prepared. The PH of the solution was optimized to 11 by slowly adding the aqueous NH₃.

Londhe et al.

145

Bare glass substrate were previously immersed in 4. CONCLUSION: chromosulphuric acid for 24 hr, and cleaned with acetone, rinsed with double distilled water and dried in Oven. Such cleaned glass substrates were gently mounted on substrate holder and immersed in reaction bath. The speed rotation of substrate holder was maintained at 55 rpm by means of DC geared motor for 30 minutes. The reaction beaker was kept in sand bath. Synthesized CdS thin films were optically analyzed with absorption spectra in the vicinity of absorption edge were recorded, using UV visible spectrophotometer.

3. OPTICAL CHARACTERIZATION:

The optical absorption of the Cadmium thanks to University Grants Commission (WRO), sulphide thin films have been used to evaluate the absorption coefficient (α), energy band gap (E_g) and nature of transition involved.

The spectra shows that the absorption edges are blue shifted. Blue shifting of the absorption edge confirmed that the films deposited are composed of CdS nanocrystals. The plot of $(\alpha hv)^2$ as a function [3] of hv was shown in figure1.



Fig.1 Plot of optical energy band gap versus concentration of CdCl2

The variation of optical band gap with concentration of CdCl₂ shows the interaction between the photon energies and material properties as film thickness, crystalline such size. concentration of Cd2+ ions of the CdS films.

CdS films were deposited using CBD technique at different concentration of CdCl₂ at optimized different temperatures. The optical absorption shows the blue shift of the absorption edges which showed that the prepared films are composed of CdS nano crystals. The drastic variation of optical energy band gap with concentration of CdCl₂ doping showed that the interaction between photon energies and structural and material properties of CdS thin films.

ACKNOWLEDGEMENTS:

One of the authors CTL wishes to express his

Pune for financial support under MRP.

REFERENCE:

- [1] Zhang J, Sun L, Liao S, Yan C. "Size control and photoluminescence enhancement of CdS nanoparticles prepared via reverse micelle method" Solid State Commun. 124 (2002) 45-48
- [2] R S Mane, Won-Joo Lee, C D Lokhande, Byung W C and S. H. Han, "Controlled repeated chemical growth of ZnO films for dyc-sensitized solar cells" Current Applied Physics 8 (5) (2008) 549-553
- X. Wu, J. Keane, R. Dhere, D. Dehart, D. Albin, A. Duda, T. Gessert, S. Asher, D. Levi, P Sheldon "Efficient CdS CdTe Polycrystalline Thin-Film Solar Cell" Proceedings of the 17th European Photovoltaic Solar Energy Conference (2001) 995
- [4] Hodes G, Albu-Yaron A, Decker F and Motisuke P. "Three-dimensional quantum-size effect in chemically deposited cudmum selenide films" Phys. Rev. B. 6 (1987) 4215-4221
- Bertino M F, Gadipalli R R, Story J G, Williams C G, Zhang G, Sotiriou-Leventis C, Tokubiro A T, Guha S and [5] Leventis N. "Laser writing of semi conductor nanoparticles and quantum dots" Appl. Phys. Lett. 85 (2004) 6007-6010
- Hani Khallaf , Isaiah O. Oladeji , Guangyu Chai , Lee Chow "Characterization of CdS thin films grown by [6] chemical bath deposition using four different sources" Thin Solid Films 516 (2008) 7306–7312 cadmium
- Liu, F.; Lai, Y.; Liu, J.; Wang, B.; Kuang, S.; Zhang, Z.; Li, J.; Liu, "Characterization of chemical bath deposited CdS [7] thin films at different deposition temperature" J. Alloys
- Compd. 2010, 493, 305–308. Sanap V B, Pavar B H. "Optical study of effect of cudmium sources on nanocrystalline CdS thin films" Chalorgenide Lett. 7 (2010) 231 [8]
- [9] Yadav A. A., M. A. Barote, E. U. Masumdar "Studies on nunocrystalline cadmium sulphide (CdS) thin films deposited by spray pyrolysis" Solid State Sciences 12 (2010) 1173
- [10] Ravangave L. S., Biradar U. V.Misal S. D. " The Effect of Ionic Composition on Structural and Optical Properties ('dxZn1-xS Thin films ('rown by Spray pyrolysis'' International Journal of Scientific and Research Publications 2 (2012) 1.

Londhe et al.

146

JCMS

Optical characterizations of CdZnS Thin Films by Spray Pyrolysis

C. T. Londhe¹ and M. M. Betkar² ¹Physics research Centre, MGM, Ahmedpur, (MS), India. ²Shri Kumarswami Mahavidyalaya, Ausa, Dist. Latur (MS), India.

ABSTRACT:

The $CdCl_2$ based CdS films were deposited using spray Pyrolysis technique at five different substrate temperatures. The prepared CdS films were studied by UV-visible spectrophotometer. The effect of substrate temperatures on the optical properties of the synthesized thin films were studied. The variation of optical energy band gap with concentration of CdCl₂ confirmed the interaction between photon energies and material properties of CdS thin films.

Key words: CdS, CdCl₂, thin films, optical band gap, spray Pyrolysis.

1. INTRODUCTION:

The Cadmium sulphide is an interesting semiconductor material due to its very important role on the photovoltaic technique and optoelectronic devices. It has been used as a parameter of several types of thin film solar cells such as CdTe, $CuInSe_2$ for fabrication. CdS has suitable band gap and high absorption coefficient and considerable energy conversion efficiency. Moreover these films are composed of closely packed nanocrystals which make attractive for basic and applied research [1-5].

Among the different methods in preparing semiconducting thin films, the simple and non-vacuum method spray Pyrolysis has been widely used to deposit different verity of semiconducting materials [6-8]. The technique is reported to offer an excellent control to deposit uniform CdS thin films at low and higher temperatures. Although other techniques have been used in deposition of CdS, Chemical bath deposition is known to enhance the performance of Cadmium Sulphide window, used in solar cell applications [9-10].

The optical characteristics of CdS thin films varied with the wavelength and the photon energy, the optical conductance and band gap indicated that the CdS films are transmitting within visible range. In the present work, CdS films are deposited at different substrate temperatures using spray Pyrolysis technique. The structural and optical properties of CdS deposited thin films are investigated.

2. EXPERIMENTAL:

The CdS films used in the studied were deposited using chemical bath deposition technique on glass substrate. At five different reaction temperatures (265 $^{\circ}$ C, 270 $^{\circ}$ C, 275 $^{\circ}$ C, 280 $^{\circ}$ C and 285 $^{\circ}$ C M) CdS thin films were deposited. The stock solutions of CdCl₂ of 1M (NH₂)₂CS, 7M NH₄OH were previously prepared. From stock solutions 20ml of CdCl₂, 5ml of 7M NH₄OH, and 40ml of 1M (NH₂) ₂CS were employed for spray. The pH of the solution was adjusted to 11 pH by slowly adding the aqueous NH₃. Glass substrate was previously immersed in chromosulphuric acid for 24 hr, and cleaned with acetone, rinsed with double distilled water and dried in Oven. Cleaned glass substrates were mounted on hot surface for deposition. In the reaction mixture CdCl₂ was used as Cd²⁺ source, NH₄OH used as S²⁺ source and (NH₂)₂CS was used as complexing agent. The deposited CdS films were obtained at the end of the reaction. All the chemicals and reagent used were analytical grade.

3. RESULT AND DISCUSSIONS:

CB deposited CdS films are analyzed for optical studies optical absorption spectra in the vicinity of absorption edge were recorded, using UV visible spectrophotometer (Simadzu).

14 C. T. Londhe and M. M. Betkar

JCMS

Optical Characterization:

The optical absorption of the CdS films have been studied to analysis the nature of transition.involved. Following figure 1 shows the optical absorption spectra of five CdS films of different concentration of CdCl₂.



Figure 1 Optical absorption spectra of CdS thin Films

The spectra shows that the absorption edges are blue shifted. Blue shifting of the absorption edge confirmed that the films deposited are composed of CdS nanocrystals. The absorption spectra was found to be decreased.

4. CONCLUSIONS:

Thin and uniform CdS films were deposited using spray pyrolysis technique for five different concentration of $CdCl_2$ at optimized temperature. The optical absorption shows the blue shift of the absorption edges which showed that the prepared films are composed of CdS nano crystals. The variation of absorption spectra with concentration of $CdCl_2$ showed that the interaction between photon energies and structural and material properties of CdS thin films.

ACKNOWLEDGEMENTS:

One of the authors, C T Londhe thankful to University Grants Commission (WRO, Pune) for granting of financial support under MRP.

REFERENCES:

- [1] Zhang J, Sun L, Liao S, Yan C. 2002 Solid State Commun. 124 45-48
- [2] R S Mane, Won-Joo Lee, C D Lokhande, Byung W C and Sung-Hwan Current Applied Physics 8(5) 549-553 2008
- [3] Bertino M F, Gadipalli R R, Story J G, Williams C G, Zhang G, Sotiriou-Leventis C, Tokuhiro A T, Guha S and Leventis N. 2004 Appl. Phys. Lett. 85 6007–6010
- [4] X. Wu, J. Keane, R. Dhere, D. Dehart, D. Albin, A. Duda, T. Gessert, S. Asher, D. Levi, P. Sheldon 2001 Proceedings of the 17th European Photovoltaic Solar Energy Conference, Munich, Germany, October 22-26 995
- [5] Hodes G, Albu-Yaron A, Decker F and Motisuke P. 1987 Phys. Rev. B. 6 215-4221
- [6] Ugwu I. and D.U. Onah, M. 2007 The Pacific Journal of Science and Technology 8
- [7] Hani Khallaf, Isaiah O. Oladeji, Guangyu Chai, Lee Chow 2008 Thin Solid Films 516 7306-7312
- [9] Sanap V B, Pawar B H. 2010 Chalcogenide Lett. 7 (27) 231
- [10] Ghosh T, Bandyopadhyay S, Roy K K, Kar S, Lahiri AK, Maiti AK, Goswami K 2008 Cryst. Res. Technol. 43 959–963

15 C. T. Londhe and M. M. Betkar

References

[1] A.R. West, 'Solid State Chemistry' John willey and Sons, Singapore, (2003)

- [2] G. Laukaitish, S. Lindroos, S. Tamulevicius, M.Leskela, M. Rackitis, Appl. Surf. Sci. 161, 396, (2000).
- [3] P. U. Asogwa, Chalcogenide Letters, **7**(8), 501 (2010).
- [4] T. Prem kumar, K. Sankaranarayanan, Chalcogenide Letters, 6(10), 555 (2009).
- [5] L.S. Ravangave, U.V. Biradar, S.D. Misal, Int. Jour. Of Sci. and Research Publications, Vol.2, Issue 6, (2012).
- [6] Patricia B. Smith, J. Vac. Sci. Technol. A 10, 897 (1992).
- [7] T. Yamaguchi, Y. Yamamoto, T. Tanaka, A. Demizu, A. Yoshida, Thin solid films, 281/281, 375, (1996)
- [8] R. U. Osuji, Nig. J. of Solar Energy 14, 90 (2003).
- [9] S.C. Ezugwu, F.I. Ezema, P.U. Asogwa, Chalcogenide Letters, 7(5), 3415 (2010).

(Dr. C. T. Londhe)

Principal Investigator