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Gunasekaran Munusamy
PG & Research Department of Physics, Muthurangam Government Arts College (Aut), Affiliated to Thiruvalluvar University, Vellore-2, Tamil Nadu, India., rpyeskay@gmail.com

Seenuvasakumaran Perumal
PG & Research Department of Physics, Muthurangam Government Arts College (Aut), Affiliated to Thiruvalluvar University, Vellore-2, Tamil Nadu, India., rpyeskay@gmail.com

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Structural and Optical Properties of Silar Deposited CdS and Ni, Ti & Zn DOPED CdS Thin Films

Gunasekaran Munusamy[*] *and Seenuvasakumaran Perumal*

PG & Research Department of Physics, Muthurangam Government Arts College (Aut), Affiliated to Thiruvalluvar University, Vellore-2, Tamil Nadu, India.

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Abstract: Recently, the nanostructured thin films have attracted the research community all over the world, as they show impending applications in semiconductor industry, predominantly in fabrication of optoelectronic devices. Especially, in the case of chalcopyrite heterojunction solar cells, it acts as a buffer layer. These films are also used as photoconductors, photo-resistors, transistor image magnification etc. Recently it has been found that they find application in light activated systems for large screen Liquid Crystal Display. Thin films of CdS have received considerable attention towards other device applications such as electrochemical cells, gas sensors, and metal-Schottky barrier cells. It is mainly used as optical window material in solar cell.

In the present investigation CdS & Nickel, Titanium and Zinc doped CdS thin films were deposited on a glass substrate by SILAR method at room temperature. The crystalline nature of the thin films is confirmed from X-Ray diffraction and all the thin films assume Hexagonal structure. The average particle size of CdS, CdNiS, CdTiS and CdZnS are found to be 13.86 nm, 18.08 nm, 18.77 nm and 26.04 nm respectively using Scherer formula. The corresponding dislocation density (δ) of the materials is calculated as 5.2056 X 10^{15} m^{-2}, 3.0591 X 10^{15} m^{-2}, 2.838 X 10^{15} m^{-2} and 1.4747 X 10^{15} m^{-2}. Strain is found to be 0.7283, 0.6943, 0.6501 & 0.2051. The optical band gap energy (E_g) near the edge of absorption band is calculated as 3.7191 eV, 3.8195 eV, 3.8490 eV and 3.9651 eV using Tauc relation and UV-VIS spectroscopic data. The grown thin films are subjected to different excitation wave lengths and their corresponding emission wave lengths are observed from photoluminescence spectroscopy.

Keywords: SILAR method, optical energy band gap, XRD, solar cell etc.

1 Introduction

Any solid or liquid system possesses at most two-dimensional order of periodicity called “thin film”. Thin film is a layer of materials ranging from nanometer to several micrometer ranges. Thin films can be fabricated via different methods which involve chemical reactions and the precursors are components undergoing reaction at the substrate surface. CdS thin films have received considerable attention during recent years because of their numerous excellent properties in optoelectronic fields. CdS thin film & Nickel, Titanium and Zinc doped CdS thin films has a broad range of application in important technical fields such as heterojunction solar cell etc. It has been considered to be a promising alternative to the more widely used silicon devices [1-2], such as electronic devices including light emitting diodes [3], large screen liquid crystal devices [4], gas sensors [5] and single electron transistors and field effect transistor [6, 7].

In the past decades, the efforts have been devoted for the fabrication of high quality CdS thin film and reported different chemical techniques such as Chemical Bath Deposition (CBD) [8, 9], spray pyrolysis (SP) [10], electro deposition [11] etc. have been used to fabricate thin films. In all these experiments there is wastage of chemicals and time. The deposition may not be uniform in all these methods. Recently researchers follow a novel and new thin film deposition technique called the Successive Ionic Layer Adsorption and Reaction (SILAR) method. SILAR is one of the newest solution methods used for the deposition of thin film, which is also known as a modified version of CBD. One of the potential applications of this technique is

[*]Corresponding author E-mail: rpyeskay@gmail.com

even a very large area thin films can be deposited through this method, which makes this method very attractive. SILAR method is a step-wise process of chemical deposition of thin films from aqueous precursor solutions. It is a unique method in which thin films of a compound semiconductor can be deposited by alternate dipping of a substrate into the aqueous solutions containing ions of each component. The beauty of this method is to control the thickness of the thin film easily by adjusting the number of deposition cycles. In this method substrate can be immersed separately in cationic and anionic solutions which are helpful in formation of thin films.

2 Experimental Procedures

Cadmium Sulphide and Nickel, Titanium & Zinc doped Cadmium Sulphide films (hereafter called sample A, B, C and D respectively) were grown by SILAR Technique deposited on different glass substrates. It is Noteworthy that the selected substrates do not react with the precursor solutions taken in the beakers of SILAR set up [12].

Here we used Micro slide corning glasses of dimensions of 75 mm X 25 mm X 1.35 mm as substrate. In order to roughened and remove the moisture from the surfaces, the substrates were boiled in concentrated chromic acid for 1 hour. Then the substrate is rinsed in double deionized water for 30 minutes and finally washed with acetone.

2.1Precursor Preparation

Cadmium nitrate, Nickel nitrate, Titanium dioxide and Zinc nitrate were taken as cationic precursor solution. Cadmium nitrate of known molarity is dissolved in 100 ml of double distilled water. The solution was kept in the magnetic stirrer until we get the homogenous solution and the pH value was maintained at 4.

Sodium Sulphide was taken as anionic precursor for the fabrication of all four thin films. Sodium Sulphide of known molarity is dissolved in 100 ml of double distilled water. This solution was stirred using a magnetic stirrer until we get the homogenous solution and the pH was maintained at 12.

2.2 Formation of Thin Films

The adsorption, reaction and rinsing time were set for a predetermined time to form cationic and anionic layers on the substrate to shape the thin films. A SILAR cycle involves four steps. During the first cationic dip Cd^{2+}, Ni^{2+}, Ti^{2+}& Zn^{2+} ions will be adsorbed on the glass substrate and during the third dip anionic dip S^{2-} ions will react with the Cd^{2+}, Ni^{2+}, Ti^{2+}& Zn^{2+} ions to form thin films A, B, C and D respectively. During the second and fourth dip the substrates are rinsed in double deionized water, in order to remove the loosely bound atoms if any. These four steps are called as one SILAR cycle. The process was repeated for definite cycles in order to form the thin films A, B, C and D. If the numbers of cycles are increased, then the thickness of thin films will also vary. After fabrication the thin films are subjected to different characterization techniques like X-ray diffraction for structure identification, spectroscopic studies like UV-VIS, PL to study optical properties.

3 Results and Discussion

3.1 X-Ray Diffraction Analysis

XRD studies were carried out, to study the crystallographic properties of all fabricated thin films. The presence of peaks in all diffraction patterns confirms the crystalline nature of synthesized thin films. The following table gives the summary of lattice parameters of the fabricated thin films A, B, C and D. All the films assume hexagonal structure.

The size of the crystallites in the films can be calculated using Debye Scherer's formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ, θ and β are wavelength of the X-ray diffraction, Bragg angle and Full Width at Half Maximum (FWHM) respectively for the maximum intensity peaks [13].

The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal [14]. Dislocation density can be calculated by using formula

$$\delta = \frac{1}{D^2} \quad (2)$$

Where, D is the average particle size that can be calculated by using Debye-Scherer's relation.

The dislocation densities are calculated using the above formula for the samples and listed in table 2.

Williamson–Hall (W-H) relation is used to calculate the strain of the samples. Strain is a type of crystalline imperfections which may distort the angle and may broaden or compress the observed peaks [14]. The strain relation is,

$$\varepsilon = \frac{\beta}{\tan\theta} \quad (3)$$

Where, θ and β is the Bragg angle and Full Width at Half Maximum (FWHM) of the all observed peaks.

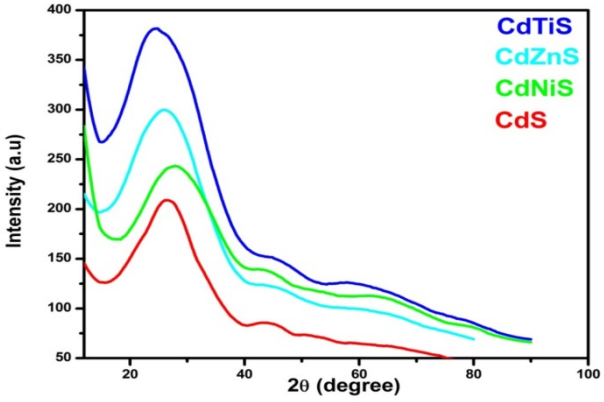


Fig. 1: XRD pattern of CdS and Ni, Zn & Ti doped CdS thin films**.**

Table 1 Lattice Parameters value of synthesized thin films by XRD**.**

SAMPLE NAME	LATTICE PARAMETER	ANGLE
A	a=b=8.578 Å & c= 5.872 Å	α=β=90°;γ =120°
B	a=b=6.728 Å & c= 4.873 Å	α=β=90°;γ =120°
C	a=b=3.74 Å & c= 4.602 Å	α=β=90°;γ =120°
D	a=b=3.9216 Å; c=6.4050 Å	α=β=90°;γ =120°

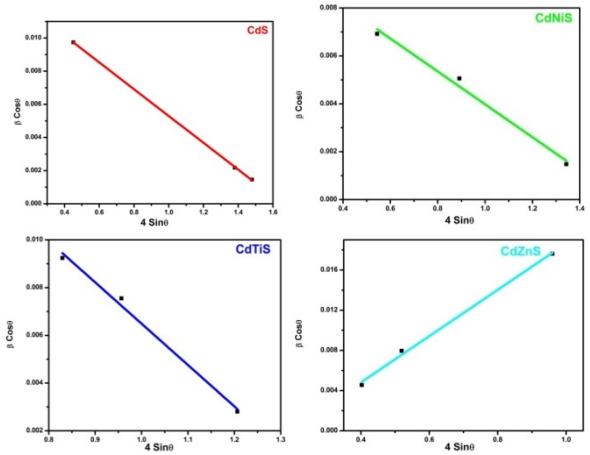


Fig.2: Strain graph of CdS and Ni, Zn & Ti doped CdS thin films.

From the figure 2 strain graph show that CdZnS show positive slope which indicate tensile load. While Pure CdS and Ni, Ti doped CdS thin films exhibit negative slope signify compressive load [16].

The table 2 gives the variation of average particle sized, dislocation density and strain for all the synthesized samples A, B, C and D.

Table 2 average particle sizes, dislocation density, strain calculated from XRD.

Sample Name	Average Particle Size (nm)	Dislocation Density (δ) X 10^{15} m^{-2}	Strain (ε) (%)
A	29.15	1.1769	0.7283
B	28.66	1.2174	0.6943
C	19.20	2.7114	0.6501
D	14.41	4.8189	0.2051

From the table we observe that when the crystallite sizes and strain values are increasing their respective dislocation density are found to be decreasing [15] calculated values are found to decrease on doping Ni, Ti and Zn with CdS, which can also be observed from the following graphs in figure 3(a) and 3 (b).

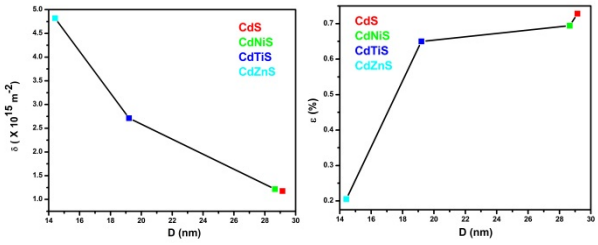


Fig. 3 (a) Average Particle Size Vs Dislocation Density & **(b)** Average Particle Size Vs Strain**.**

3.2. Optical Studies

3.2.1UV-Visible Spectral Study

The optical absorption spectra of all synthesized thin films are studied using UV-Visible spectrometer in the wavelength region 200-1100 nm at room temperature. From the graph we can observe that all grown thin films can be used for any optoelectronic device applications. The cut-off wavelengths for the samples A, B, C and D are listed in table 3.

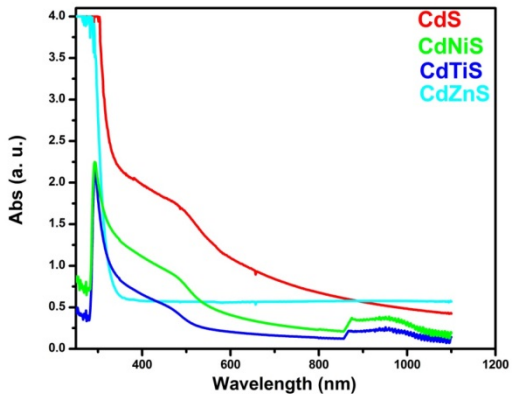


Fig.4: UV absorption spectra for CdS and Ni, Ti & Zn doped CdS thin films.

3.2.2 Determination of Band Gap

Tauc proposed a substantiate method for determining the band gap using optical absorbance data. Optical energy band gap of a semiconductor can be determined by studying the absorption of incident photons by the material. The optical absorption intensity can be measured experimentally in terms of the absorption co-efficient, the photon energy dependence of the absorption co-efficient for direct allowed and indirect transition the equation are given below

$$(\alpha h\nu)^{1/n}=A(h\nu-E_g) \qquad (4)$$

Here, *h* is Planck constant, α is the absorption coefficient, *Eg* is the band gap and A is proportionality constant. The value of the exponent denotes the nature of the electronic transition, whether allowed or forbidden and whether direct or indirect [17].

The value of n=1/2 is direct allowed transition and n=3/2,

for direct forbidden transition. For indirect allowed transitions n=2, for indirect forbidden transition *n*=3. Typically the allowed transitions dominate the basic absorption processes, giving either *n*=1/2 or *n*=2, for direct and indirect transitions respectively. Plotting the $(\alpha h\nu)^{1/n}$ versus $h\nu$ is a matter of testing *n*=1/2 or *n*=2 to compare which provides the better fit and thus identifies the correct transition type.

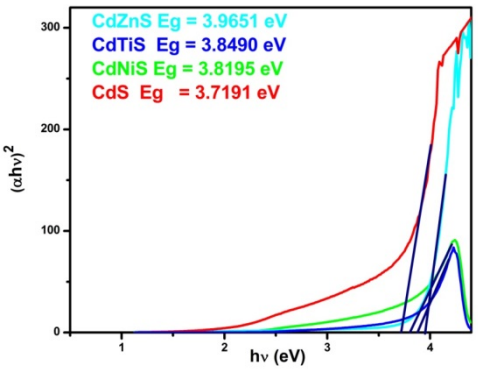


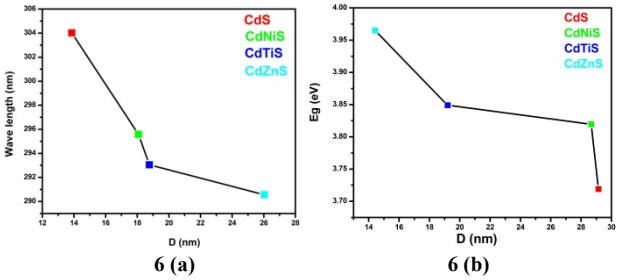
Fig. 5: Tauc plot for CdS and Ni, Ti & Zn doped CdS thin films.

From figure 4 it is observed that the CdS and Ti, Ni & Zn doped CdS have a direct allowed transition. The extrapolation of most linear region of all the graphs has been used to find the band gap values of CdS 3.7191 eV and Ni, Ti & Zn doped CdS 3.8490 eV, 3.8195 eV and 3.9651 eV respectively.

Table 3: Cut off wavelength measured by UV-Vis spectrum and energy band measured by Tauc plot.

Sample Name	Average Particle Size (nm)	Cut off Wavelength	Energy Band Gap (eV)
A	29.15	304.0204	3.7191
B	28.66	295.5797	3.8195
C	19.20	293.0475	3.8490
D	14.41	290.5610	3.9651

Figures 6 (a) & (b) shows the graphs drawn between the cut-off wavelength vs average particle size and optical band gap vs. average particle size.



6 (a) 6 (b)

Fig. 6 (a): Average Particle Size Vs Cutoff Wave length & **(b)** Average Particle Size Vs Energy Band gap.

From the table 3 we can find that the optical band gap value increases as the average crystallite size of the particles decreases [18][19][20].

3.3 Photoluminescence Study

Light emission from compound semiconductors has been an important phenomenon due to its technological applications [21]. Most of the optoelectronic component devices such as light emitters or photo detectors are being fabricated using semiconductors having a direct band gap with high efficiency like CdS thin films. These films are also used in solar cells as light absorbing panels. Photoluminescence **(**PL) analysis of the CdS thin film over glass substrate was performed to analyze the purity of deposition [22]. The photoluminescence spectrum ranges between 350-800nm for the different emission peaks are shown in figure 7.

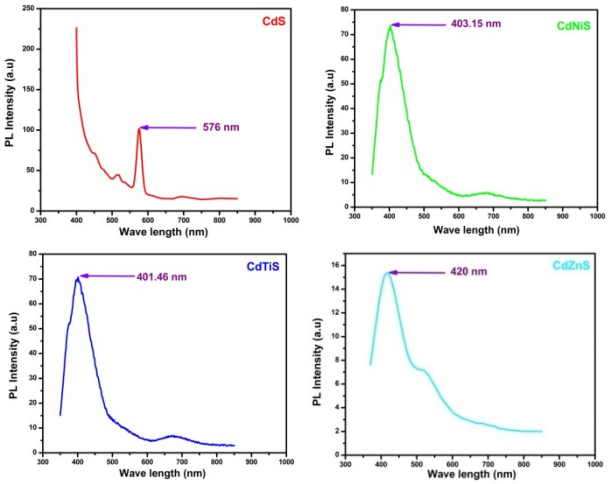


Fig. 7: Photoluminescence for CdS and Ni, Ti & Zn doped CdS thin films**.**

Table4: Emission Wavelength measure by Photoluminescence**.**

Sample Name	**Emission Wavelength (nm)**	**Colour**
A	576	Yellow
B	403.15	Violet
C	401.46	Violet
D	420	Violet

3.4 Surface Morphology

The morphological studies of the nanomaterials have been carried out from scanning electron microscope (SEM). SEM enables the investigation of specimens with a resolution down to the micro meter scale. The surface morphology of the thin films was recorded at different magnifications are 1 µm, 5 µm, 10 µm and 20 µm.

Figure 8(a) shows the SEM micro graphs evident that the CdS films at 1 µm, 5 µm & 10 µm range. Among these three images 10 µm range shows the film is deposited on

glass substrate is homogeneous and the CdS nano particles can occupy the glass substrate without any space in the grown film.

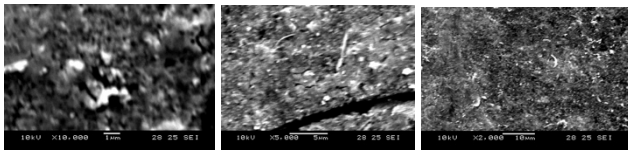


Fig.8 (a): SEM images of grown CdS thin film at the range of 1 µm, 5 µm & 10 µm.

Figure 8(b) shows that the CdNiS films form of flowers and texture like structures, which was speculated that the agglomeration of flower shapes but different size. All the grains appear different shapes at different magnification values. The three different magnifications are 1 µm, 5 µm and 10 µm.

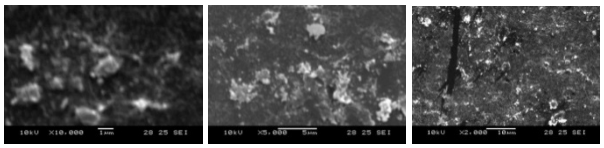


Fig.8 (b): SEM image of CdNiS thin film at the range of 1 µm, 5 µm & 10 µm.

Figure 8(c) shows the SEM image of CdZnS thin film at 1 µm range, 5 µm range & 10 µm range shows the film is deposited on glass substrate is homogeneous with high purity of the nano particles and some parts of the grown film peeling or cracks on the film surface.

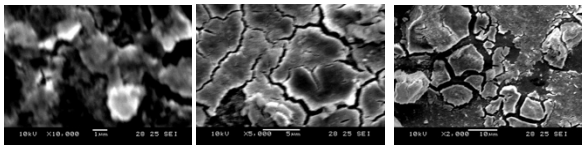


Fig. 8(c) SEM images of grown CdZnS thin film at the range of 1 µm, 5 µm & 10 µm.

Figure 8(d) shows the SEM image of CdTiS thin film at 5 µm range, 10 µm range& 20 µm range Some Pinholes and cracks particles are observed clearly in the SEM images.

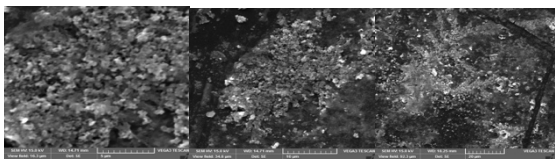


Fig. 8(d): SEM image of CdTiS thin film at the range of 5 µm, 10 µm & 20 µm.

4 Conclusions

In this study, CdS thin film and Nickel, Titanium & Zinc doped CdS thin films were deposited on a clean glass substrate by SILAR method. The structural properties of these thin films were investigated by XRD. The XRD confirms their crystalline nature and all the films assume Hexagonal structure. The average particle size is found to be 13.86 nm for pure CdS thin film and 18.08 nm, 18.77 nm& 26.04 nm for Ni, Ti & Zn doped CdS thin films respectively. The strain (ε) for the samples A,B, C & D are found to be 0.7283, 0.6943, 0.6501 & 0.2051 respectively and the dislocation density (δ) of them are 5.2056 X $10^{15}$$m^{-2}$, 3.0591 X 10^{15} $m^{-2,}$ 2.838 X 10^{15} m^{-2} and 1.4747 X 10^{15} m^{-2}. Using UV-VIS spectroscopic data the cut-off wavelengths and the optical energyband gap (E_g) at the edge of absorption band for all the listed four samples were found to be 3.7191 eV, 3.8195 eV, 3.8490 eV and 3.9651 eV using Tauc relation. The grown thin films are subjected to different excitation wave lengths and their corresponding emission wave lengths are observed from photoluminescence spectroscopy. So we conclude that, CdS and doped CdS are all direct band gap materials may find applications in the construction of the solar cells. The surface morphology is studied from SEM. The SEM picture reveals the homogeneous layer, flower, texture structure, Pinholes and cracks micro structural changes in CdS and doped CdS thin films.

References

[1] H.R. Motinho, D. Albin, Y. Yaan, R.G. Dheo, X. Li, C. Perkis, C.S. Jiang, Thin Solid Films 436, 175 (2003).H. Metin, R. Esen, "Semicond. Sci. Technol., **18**, 647 (2003)".

[2] J. Barman, J. P. Borach and K. C. Sarma, "Effect of pH Variation on Size and Structure of CdS Nanocrystalline Thin Films," Chalcoginide Letters., **11(5)**, 265-266(2008)".

[3] G.S. Vorobjov, V.O. Zhurba, A.S. Krivets, J. Nano- Electron. Phys., **2(4)**, 47 (2010).

[4] N. I. Achuko and C. C. Ugwuegbu, "Optical Properties of CdS Thin Films Obtained by Chemical Bath Deposition," International Journal of Academic Research, **6**, 368-374(2011).

[5] J. Levinson, F.R. Shepherd, P.J. Scanlon, W.D. Westwood, G. Este, M. Rider, J. "Appl. Phys., **53**, 1193 (1982)".

[6] U. Pal, R. Silva-Gonzalez, G. Martinez-Montes, M. Gracia-Jimenez, M.A. Vidal, S. Torres, "Thin Solid Films., **305**, 345 (1997).

[7] J.H. Schon, O. Schenker, B. Batlogg, "Thin Solid Films., **385**, 271 (2001)".

[8] S.S. Kale, C.D. Lokhande, "Mater. Chem. Phys., **62**,103 (2000)".

[9] S.D.Sartale,C.D.Lokhande,. Growth of copper sulphide thin films by successive ionic layer adsorption and reaction method. "Matter.Chem.Phys.,64(1999)".

[10] TBanerjee M. Chongad L. and Sharma A. "Structural and Optical Properties of Pure and Copper Doped NiS Nanoparticles" Research Journal of Recent Sciences., 2(ISC-2012), 326-329 (2013)".

[11] J. Sa´nchez-Gonza´lez, A. Dı´az-Parralejo, A.L. Ortiz , F. Guiberteau, "Determination of optical properties in nanostructuredthin films using the Swanepoel method",

[12] B.R.Sankapal,R.S.Mane, and C.D.Lokhande, "Photoluminescence Specroscopy Of CdS and GaSe"Mater.Res.Bull., **35**,177-184(2000)".

[13] Linhtowlers R. A. Stradling and P.C.KlippsteinGrowth and characterization of semiconductors, "Bristol., 135(1990)".

[14] T. Banerjee M. Chongad L. and Sharma A. "Structural and Optical Properties of Pure and Copper Doped NiS Nanoparticles" Research Journal of Recent Sciences Vol. 2(ISC-2012), 326-329 (2013)".

[15] Particle size effects on structural and optical properties of BaF2nanoparticles Adriano B. Andrade, Nilson S. Ferreiraab and Mario E. G. Valerio "RSC Adv.,**7**, 26839(2017)".

[16] Aydin Selte and BuraxOzkal "Crystalline size and strain calculations of hard particle reinforced composite powders (Cu/Ni/Fe-WC) synthesized via mechanical alloying" "Proceedings of the Estonian Academy of Science., **68(1)**, 66-78(2019)"

[17] B.R.Sankapal,R.S.Mane, and C.D.Lokhande, "Photoluminescence Specroscopy Of CdS and GaSe" "Mater.Res.Bull., **35**,177-184(2000).

[18] Anjali Jain Deotale and R. V. Nandedkar "Correlation between Particle Size, Strain and Band Gap of Iron Oxide Nanoparticles" "Materials Today: Proceedings., **3**, 2069 – 2076(2016).

[19] Madan Singh, Monika Goyal and Kamal Devlal "Size and shape effects on the band of semiconductor compound nanomaterials" "Journal of Taibah University for Science ., **12(4)**, 470 – 475(2018).

[20] Said Benramache, Ali Arif, OkbaBelahssen and AbderrazakGuettal "Study on the Correlation between crystalline size and optical gap energy of doped ZnO thin film" "Journal of Nanostructure in Chemistry, **3**, 80(2013).

[21] T Theivasanthi, N Kartheeswari and M Alagar, "Chemical Precipitation Synthesis of Ferric Chloride Doped Zinc Sulphide Nanoparticles and Their Characterization Studies" "Research gate, 03/2013, DOI 10, 7598/cst 2013.207".

[22] P. Mitra and S. Mondal," Structural and Morphological Characterization of ZnO thin Films Synthesized by SILAR" "Theoretical and Applied Physics., **1**,17-31(2013).