Effect of IR irradiation on the various properties of chemically prepared zinc sulphide thin films

K K Ribin¹, N Navya², K Naseema³

¹,²Department of Physics, Kannur University, Edat P. O, Payyanur, India
³Deptartment of Physics, Nehru Arts and Science College, Kanhangad, India

E-mail: ¹nasribin91@gmail.com, ²nasnavya@gmail.com, ³k.naseema@gmail.com

Abstract. Zinc sulphide thin films have been deposited on glass substrate using simple low cost chemical bath deposition method at 80ºC for 2 hours. One of the samples is post irradiated with infrared radiation for one hour. Structural, optical and morphological studies were done for both samples and the results were compared. XRD pattern of the IR irradiated sample shows enhanced crystallinity. Optical band gap was found to be 3.31eV for pure ZnS and 3.93 eV for the IR irradiated ZnS thin film. The films prepared by using this facile method are suitable for optoelectronic applications.

1. Introduction
Zinc sulphide thin film has potential use in thin film devices such as photoluminescent and electroluminescent devices. In the field of optical and microelectronic industries ZnS has become an outstanding candidate, due to its high refractive index, high effective dielectric constant and wide wavelength pass band [1].ZnS is a wide band gap semiconductor of about 3.6eV, which makes it as a promising transparent material in the visible region. They are widely used for optoelectronic applications such as filters, photoelectric cells, and LED’s etc. [2]. Many deposition techniques have been used to prepare ZnS thin films, such as pulsed laser deposition, chemical vapour deposition, electron beam deposition, sputtering, chemical bath deposition, photochemical deposition and thermal evaporation [3]. Among these methods, chemical bath deposition is the most common and low cost method in producing thin films. Covalently bonded materials such as semiconductors produced either amorphous structures at low substrate temperatures or poly crystalline structures at higher temperatures [4].

The purpose of this work is to investigate the effect of IR irradiation on the structural, optical and morphological properties of chemical bath deposited ZnS thin films. Two samples were deposited at a temperature of 80ºC and one of them was exposed to infrared radiation (IR) for one hour. The structural and morphological studies were carried out using X-ray diffraction analysis, SEM analysis respectively and the optical studies were done using the UV-Vis spectroscopy for pure and IR irradiated ZnS thin films.

2. Experimental details
ZnS thin Films were prepared by using Chemical Bath Deposition technique. Good quality microscope glass slides were used for the deposition of thin films. The microscope glass slides (26x76mm, 1mm-1.2mm thick) were first washed with pure water. Then it was immersed in a detergent solution for one day. After that the slides were washed thoroughly by using distilled water. Then the washed slides
were soaked in chromic acid for 24 hours. Then they were rinsed several times with distilled water, to initiate nucleation centre for the deposition of thin film. Finally the glass substrates were dried in hot air.

After substrate cleaning, 0.2M of 50 ml Zinc acetate solution (cationic) was prepared. 0.2M of 10ml Ammonium acetate is added as buffer solution to the prepared Zinc acetate solution. 15 ml TEA is added as a complexing agent drop wise to the solution under stirring. Few drops of ammonia were added to the same solution till the colour of the solution becomes transparent. pH of the solution is maintained to 8 by adding ammonia. Then it was mixed with 0.2M of 50 ml Thiourea solution (anionic). Two cleaned glass slides were vertically immersed in the final solution taken in a beaker. Then it was kept on the hot plate for 2 hours. The temperature of the hot plate was maintained at 80ºC and the substrates were taken out at the end of the dip period and rinsed with double distilled water to remove the unreacted particles. Then the thin films were dried in air. Finally one of the deposited films was irradiated with infrared radiation for one hour.

3. Results and discussions

3.1. Structural studies

Structural analyses of the deposited samples were done using X-ray diffractometer. Figure 1 shows the XRD spectrum of the CBD grown ZnS thin film. The intensity of the peaks decreases showing less preferential orientation of the sample. The crystallinity of the sample is diminished and become amorphous. ZnS films with wide peaks on the XRD pattern were amorphous [5]. Figure 2 shows the XRD pattern of IR irradiated ZnS thin film. It is observed that IR irradiated sample has less intense peak at around 49º which corresponds to (220) reflection. This shows the sample is microcrystalline with the preference of (220) plane and mixed with amorphous structure. The diffraction peaks due to ZnS (220) plane corresponds to sphalerite type ZnS in cubic form. ZnS may exist in two major forms either cubic or hexagonal structure depending on the deposition conditions [6]. XRD spectra of ZnS thin films prepared at various substrate temperatures showed the highest peak diffraction intensity at 2θ value of 28.6º with the preferential orientation of crystallinity to (111) plane of cubic structure[7]. Akihiko Nakasaet al reported that IR irradiation enhances the crystallinity of the ITO, and it should be an inexpensive method to reduce the resistance of ITO. Therefore our work with IR irradiated ZnS thin film was in good agreement with the reported one [8]. In this work the obtained XRD graphs show higher FWHM values greater than 8, so the calculation of crystallite size and dislocation density is skipped from the structural analysis.
3.2. Optical studies
The optical properties of the deposited samples were determined from the absorbance and transmittance measurements. Figure 3 & 4 shows the optical absorbance spectrum of pure ZnS and IR irradiated ZnS thin films respectively.

![Figure 3. Absorption spectra of pure ZnS](image1)

![Figure 4. Absorption spectra of IR-ZnS](image2)

From the absorption spectra it is clear that absorbance of IR irradiated ZnS thin film is more than the pure sample in the visible region. Figure 5 and 6 shows the optical transmission spectra of the two samples. Here we got an average transmittance of 60% in the visible region for the pure sample where as it is found to be decreased in the case of IR irradiated one.

![Figure 5. Transmission spectra of pure ZnS](image3)

![Figure 6. Transmission spectra of IR-ZnS](image4)

Figure 7 and 8 shows the graphical plot of $(\alpha h\nu)^2$ versus $h\nu$ for the prepared samples. The band gap energy of both samples was found out from the intersection of the tangential line of the plotted curve with the X axis [9]. A. Djelloul et al reported the band gap energy of ZnS thin film as 3.89eV -3.96 eV [10]. The band gap energy of pure CBD grown ZnS thin film is found to be 3.31 eV and of IR irradiated sample is 3.93 eV. The broadening of band gap energy shows that the material is suitable for optoelectronic devices such as dielectric filters and solar cells [11].
Figure 7. Plot of \((\alpha h\nu)^2\) vs \(h\nu\) of pure ZnS

Figure 8. Plot of \((\alpha h\nu)^2\) vs \(h\nu\) of IR- ZnS

3.3. Morphological studies
In order to study the thin film surface and substrate coverage, Scanning electron microscope images were obtained for both samples.

Figure 9. SEM image of ZnS

Figure 10. SEM image of IR-ZnS

The SEM image of pure ZnS thin film is shown in figure 9. It shows a smooth surface with spherical grains of average size 198nm. Figure 10 shows the SEM micrograph of IR irradiated ZnS thin film. It shows a globular structure which is adhered to the surface of the substrate with large grains of average size 701nm.

4. Conclusions
Chemical bath deposited Zinc sulphide thin film was irradiated with infrared radiation for one hour. It has been found that IR irradiation enhances the crystallinity of the sample. Band gap energy of the IR irradiated sample is found to be more (3.93eV) compared to the pure sample (3.31eV). The broad band gap energies make these films a good material for optoelectronic applications. Thus IR irradiation is a simple low cost technique for modifying the properties of thin films.
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