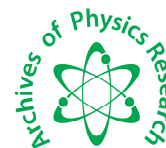




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# Photoassisted chemical deposition of nano crystalline ZnS thin films from aqueous alkaline bath

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## ABSTRACT

Photoassisted chemical deposition technique (PCD) was utilized to fabricate nanocrystalline zinc sulfide (ZnS) thin films from an aqueous alkaline solution bath. The solution comprised of zinc nitrate, hydrazine hydrate, ammonium nitrate, ammonia solution and thiourea. Samples were prepared on glass substrates by multiple dips on optimization. The as-deposited films were highly adherent and homogeneous. All the films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV spectrophotometry. Compositional studies were carried out by EDAX. The crystallinity was observed to be poor and the phases were mixed. SEM images showed uniformly distributed spherical nano grains for as-grown films. Optical studies showed gradual increase in transmittance in the visible region. The band gap of the as-prepared films was found to be 3.85eV. The morphological and optical variation of the films with temperature was also studied by annealing the samples at 200<sup>o</sup>C for 2 hours. The transmittance was found to be improved on annealing. Further we have investigated the variation in the morphology of the PCD films on different substrate like seeded soda lime glass prepared by successive ionic layer adsorption and reaction (SILAR) method. It was seen that the growth of the as-prepared films were augmented in the presence of seed. We have compared the properties of these films with that of the as-grown films by chemical bath deposition (CBD) without the assistance of UV-irradiation.

**Keywords:** Photoassisted CBD, Nucleation, Zinc compounds, Semiconducting materials.

## INTRODUCTION

Chalcogenide semiconducting materials are attracting special attention ever since its fabrication as thin film due to their significant properties. Though many techniques had been developed for

semiconductor thin film deposition, photoassisted chemical deposition (PCD) is less explored. It is a simple, controllable and effective procedure by which deposition is carried out using light. Compared to all other methods, PCD scores advantages for its cost effectiveness, capability of pattern making, use of flexible substrates and competence of large scale deposition [1,2]. In this method a substrate is immersed in the chemical bath and will be irradiated by UV light. To improve the quality and uniformity of the film, the solution is continuously stirred using a magnetic stirrer. Thus due to photo chemical reaction, there will be a compound formation and will be deposited on the irradiated region. Many films of metal chalcogenides and oxides have been fabricated in this method [3, 4]. In most of the reported cases, the deposition was carried out in acidic medium.

Zinc chalcogenides are widely used in devices for harvesting solar energy. ZnS is a direct wide band gap n-type semiconducting material suitable for ample range of optoelectronic and photovoltaic applications. The first attempt to deposit ZnS thin films by photo chemical deposition from an aqueous solution containing  $\text{ZnSO}_4$  and  $\text{Na}_2\text{SO}_3$  at pH 3.5 by Ichimura et al [5] resulted in Zn rich composition and the film was opaque. This point out that  $\text{S}_2\text{O}_3^{2-}$  ions act as a reductant under irradiation without releasing S atoms. The addition of Rochelle salt as the complexing agent improved the optical transmission of the as grown film [6]. It was also observed that the thickness of the ZnS thin films have been considerably increased with the decrease of pH of the precursors or the increase of deposition period/stirring speed [7]. The photocurrent of the as deposited films from acidic bath was made to increase by adding  $\text{Na}_2\text{SO}_3$  along with  $\text{Na}_2\text{S}_2\text{O}_3$  to trap the excess sulfur released by the latter [8].

In the present work we have deposited ZnS thin films by photo assisted chemical deposition on soda lime glass substrates by keeping the precursor solution in alkaline medium. We placed the substrate in a vertical position in the vessel containing the aqueous solution as in the chemical bath method and the UV light was allowed to fall on the substrate perpendicularly, which evade the chance of sedimentation. The preparation by double dip of 3 hour duration resulted in highly homogeneous film but with negligible thickness. In order to increase the thickness multiple depositions were carried out and the results were analyzed. We have compared those films prepared by CBD from the same reaction bath to PCD films in all aspects. The features and the enhancement in the growth of the ZnS films were studied using a seed layer prepared from SILAR, a modified version of CBD. The as prepared samples were annealed at  $200^\circ\text{C}$  to observe the variations in structure and morphology with temperature. All the resulting films were characterized in terms of surface morphology, crystallinity and optical studies.

In the present effort, we have successfully deposited highly uniform, homogenous ZnS thin film by photoassisted chemical deposition method keeping the precursor solution alkaline. So far to our knowledge, this is the first report of photoassisted chemical deposition of ZnS thin films using thiourea as the sulfur source kept in basic medium instead of sodium thiosulfate as the sulfur source kept in acidic medium.

## MATERIALS AND METHODS

### 2.1 Photoassisted chemical deposition of the ZnS film

The schematic diagram of PCD setup is shown in Fig 1. Deposition was carried out in the presence of 180 W UV light, which was kept horizontal and the light was allowed to fall directly on the glass substrate placed vertically in the aqueous reaction bath through a converging lens. The absorption of UV light by glass beaker was neglected as the film formed on the curved portion of the vessel was very thin.

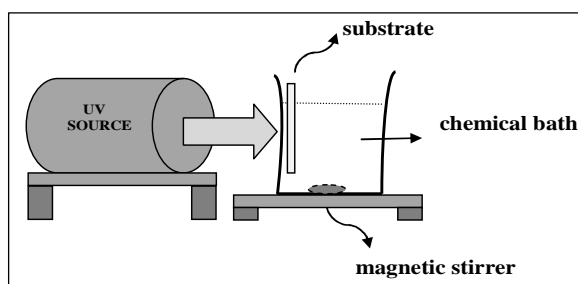
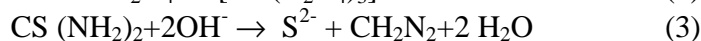
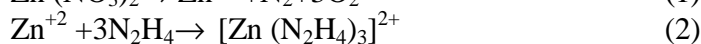
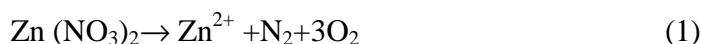


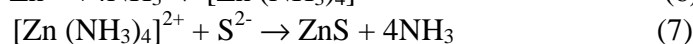
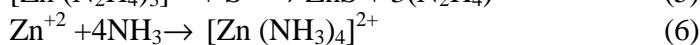
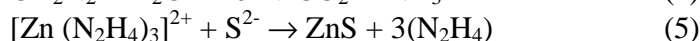
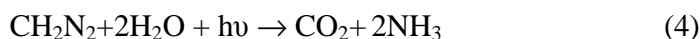
Figure 1

The substrate was cleaned very well through continuous washing in different solutions. It was first kept in extran solution for 3 hours and then in chromic acid solution for 3 hours. Finally it was washed in distilled water and dried in air. Aqueous solution comprised of 0.5M zinc nitrate  $Zn(NO_3)_2$ , 0.075N hydrazine hydrate HH, 0.25M ammonium nitrate  $NH_4NO_3$ , 17N ammonia  $NH_3$  and 0.5M thiourea CS  $(NH_2)_2$ . Here, ammonium nitrate was used as a buffer in order to accelerate the reaction. HH and ammonia were acted as complexing agents to hold the metal ions. The deposition solution without ammonia was milky white. The addition of ammonia made it transparent with a pH of 10.22. 50 ml of the precursor solution was irradiated with UV light and the solution was gently stirred using a magnetic stirrer. The deposition time was 2-3 hours for various samples on single dip. The deposited samples were washed in distilled water and dried in air using a blower at room temperature. More number of dips in similar baths was carried out to get the desired thickness.

### 2.2 Photochemistry of the deposition

It is known that thiourea decomposes on heating at about  $70^{\circ}C$  and releases toxic forms of nitrogen and sulfur oxides. In the present work as the temperature of the precursor solution doesn't exceed about  $40-50^{\circ}C$  on illumination, we expect the photolytic dissociation of thiourea into sulfur ion along with  $NH_3$  and  $CO_2$  which is risk free. HH can react with metal ions to form the metal complex easily than that of ammonia due to the high value of the equilibrium constant for the complex formation [9]. The zinc nitrate solution complexed with HH or  $NH_3$  provides the  $Zn^{2+}$  ions. The complexed Zn ion reacts with sulfur ion to form ZnS film on the substrate. The expected chemical reactions are summarized as follows.





### 2.3 Characterization of films

The structural profile of all deposited samples was characterized by XRD using an X-ray diffractometer with Cu-K $\alpha$  radiation of wavelength 1.5405Å<sup>0</sup> as the source. The morphological studies have been carried out by Scanning electron micrograph of JEOL Model JSM6490 and the composition was analyzed using EDAX analyser attached with SEM. The thickness of the samples was found out from the cross sectional SEM. The optical properties like absorption and transmission spectra were taken using a Varian Carry 5000 UV-Vis-NIR spectrophotometer in the range 200-2000 nm.

## RESULTS AND DISCUSSION

### 3.1 Film growth

Seeded and non-seeded soda lime glasses were used for the preparation of samples. We have undertaken the deposition of ZnS films by varying the pH of the precursors from 8-12 and optimized the pH as 10.22. Double dip and multiple dips have been carried out at the optimized pH with gentle stirring. The obtained films are highly uniform and have a cloudy white color. The film thickness increases with increase in the pH of the solution at the cost of uniformity. The homogeneity of the film also depends on the stirring speed.

It is familiar that the same precursors can be used to deposit ZnS thin films by CBD method. But the deposition starts only after 70<sup>0</sup>C. Hence it is clear that the deposition of ZnS thin film by PCD is due to the activation of chemical reactions at room temperature by the irradiation of UV light. The UV light in PCD can ideally replace the heat supplied to the aqueous solution in CBD. Further the pH value of the precursor is highly sensitive in CBD. In CBD it changes due to evaporation at higher temperature. But the photo assisted decomposition of thiourea provides more NH<sub>3</sub> to keep the pH same during the deposition of many hours. Further the control over CBD depositions is rather small when once it is started. In PCD the deposition can be controlled by the removal or intermittent illumination of source of light. It is also seen that after the completion of reactions in CBD, the vessel containing the solution got some precipitate of the components at the bottom. But in the case of PCD, even after the reaction of 5-6 hours, the reaction solution can again be used for further deposition. Chemical bath deposition is inefficient to convert the preparatory materials effectively into the thin film form either due to the homogeneous reaction or the deposition on the reaction vessel. But in PCD, heterogeneous reaction predominates and the deposition on the vessel is very thin.

Samples have been prepared by CBD with the same precursor solution kept at 70<sup>0</sup>C to compare the various characteristics with the samples of PCD. To enhance the nucleation sites on the glass substrate and to reduce the number of dips for the desired thickness nanocrystalline ZnS films were deposited on a seed layer prepared from SILAR and was termed as ZnS Seed.

### 3.2 Structural and morphological studies

Double dipped, multiple dipped and annealed samples of ZnS thin film were analyzed by X-ray diffractometer. The profile of PCD samples prepared by double dip was depicted in Fig. 2. It confirms the weak crystalline nature of the as deposited film. Normally zinc sulphide exhibit two major structures, cubic and hexagonal. Cubic structure is less stable and hexagonal structure is prominent at higher temperatures. The peak at  $2\theta=26.962^\circ$  showed agreement with standard JCPDS data (File no: 89-2942) having orientation at (100) plane with a d value of 3.305 with hexagonal structure, which is in accordance with the other reports [10]. No discernible peak has been seen on the annealed sample and it appeared to be amorphous (not shown). This may be due to the lack of sufficient thickness of the as prepared film. The broad hump is due to the background of glass substrate.

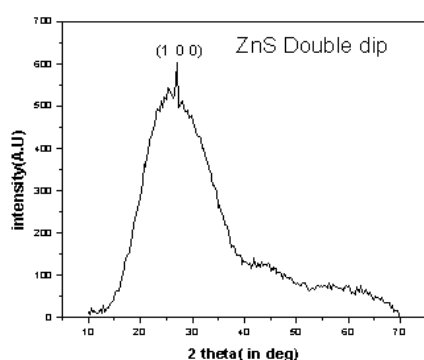


Figure 2

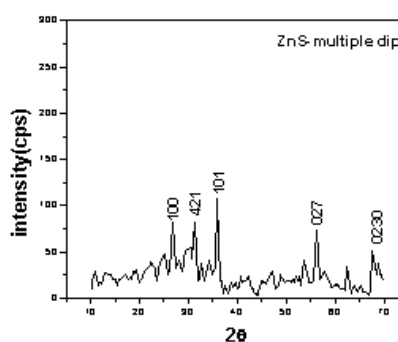


Figure 3

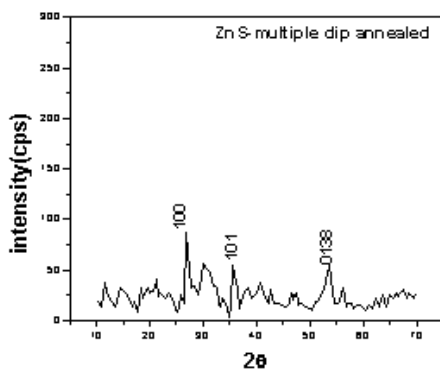


Figure 4

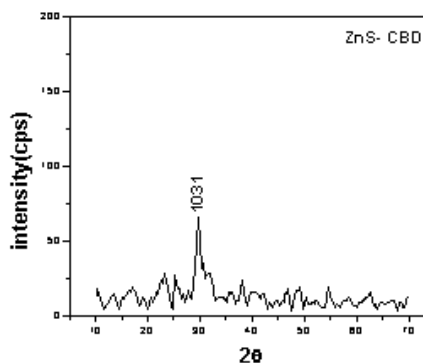


Figure 5

The XRD reports of the as prepared and annealed samples of multiple dips were shown in fig.3 and fig.4. Due to the increased thickness, crystallinity of the films was improved in both cases as compared to those obtained from double dip. One major zinc sulfide peak with hexagonal structure was found to be common in both (100) at  $26.96^\circ$  with a d value of 3.31. Two minor peaks oriented at (0 2 7), (0 2 30) planes at  $65^\circ$ ,  $67.65^\circ$  with d values 1.63, 1.38 in the as prepared samples could also attribute to the same phase of Zinc sulfide. Continuous illumination of the bulb resulted in the formation of zinc oxide and a corresponding peak at  $35.85^\circ$  having an orientation of (1 0 1) was also seen in the diffractogram of both the samples. It is expected that both homogeneous and heterogeneous nucleation may occur during the film formation. The

plane (4 2 1) present in the XRD profile (Fig 3) corresponding to sulphur may be due to the heterogeneous growth on the substrate.

It was seen that the peak intensity improved on increase in the film thickness. The thickness of the as grown sample of ZnS by double dip and multiple dips were 561.43nm and 1.52 $\mu$ m respectively from the cross sectional SEM measurement.

Figure 5 illustrates the XRD sketches of samples prepared from the same bath by CBD multiple dip at 70<sup>0</sup>C. The as deposited film showed a single peak at 30<sup>0</sup> with an orientation of (1 0 31) plane with rhombohedral structure. Both the samples from the same chemical bath showed different preferential orientations with different phase. Multiple dipped PCD samples were found to be polycrystalline than the multiple dipped CBD samples.

It could be concluded that though the films were of highly uniform and homogeneous, as most of the samples did not reveal well defined peaks, the crystallinity was poor and the observed phases were mixed. The amorphous nature of the samples may also be considered as nano crystalline which were made up of nanocrystallites [11].

The morphology of the as prepared and annealed samples for double dips was shown in Fig. 6a and 6b. The film grains were found to carpet the substrate and are uniformly spherical in shape. Double dipped samples contain spherical grains of both individual and clustered forms with a grain size of 110-120 nm. The growth of the film by this method is slow; initially the grains may not be distributed equally on the surface of the substrate. There may be more nucleation centres on the substrate where the light directly falls. Due to these, the surface contains unequally distributed clusters and individual spherical grains. Since the thickness is small, individual grains are more in number than that of clustered ones. After annealing to a temperature of 200<sup>0</sup>C, the grains were almost equally rearranged on the surface of the substrate. Using the heat energy, there may be cluster formation among the individual grains which resulted in the increase in grain size to 130-140nm. .

The SEM picture depicted in Fig.7a showed the morphology of multiple dipped samples which clearly indicated the packed nature of the grains and it dropped the clarity in spherical shape to find out the grain size. In the case of multiple dipped samples, increased thickness resulted in the enhancement in the number of clustered grains on the substrate. As we increase the number of dips, number of uniform grains increased which improved the crystallinity of the films.

Seeded substrates for PCD have been prepared from SILAR. The cationic and anionic precursor solutions were zinc sulphate and thio acetamide. The seeded substrates were kept in the precursor solution for illumination by UV light. The SEM photograph 7 (b) of the seed sample exhibits a cloudy nature. Since the initial nucleation was done by SILAR technique, the growth was faster. On illumination by UV light the molecules stick easily on the regions where the seeds are present. As a result there was an unequal deposition on the surface during the induction period. Due to large scale cluster formation, it was unable to get the grain size compared to others.

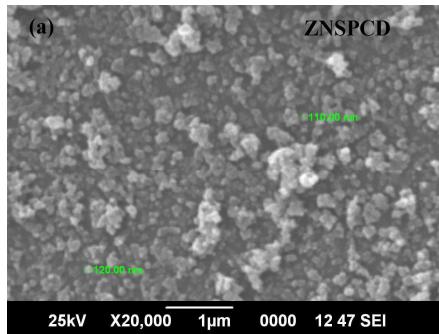


Figure 6(a)

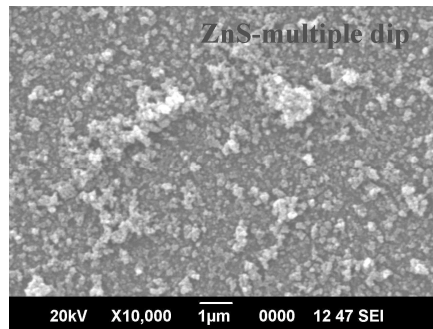


Figure 6(b)

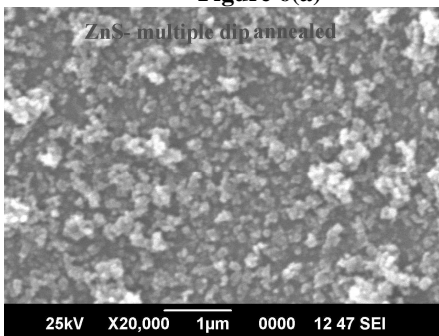


Figure 7(a)

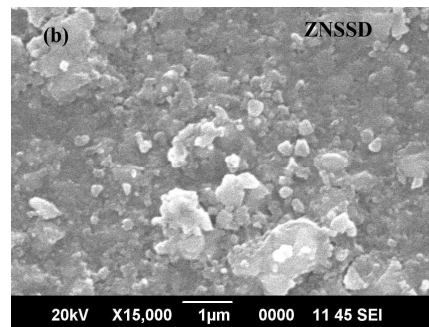


Figure 7(b)

### 3.3 Optical studies

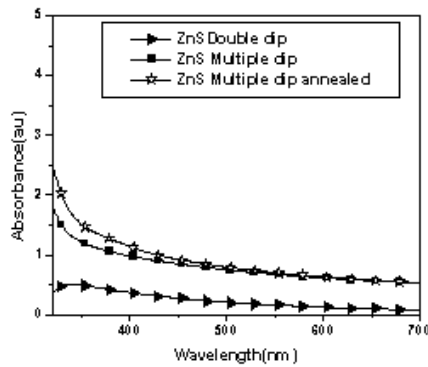


Figure 8(a)

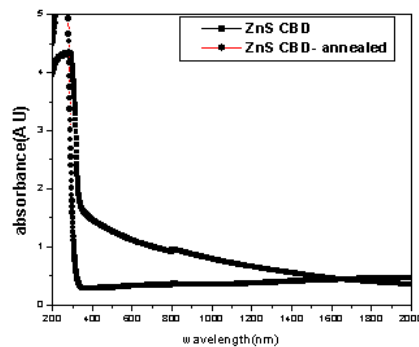


Figure 8(b)

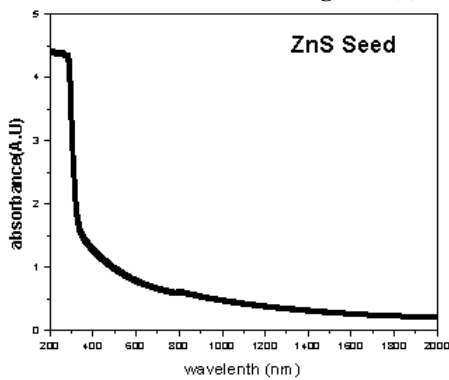


Figure 9

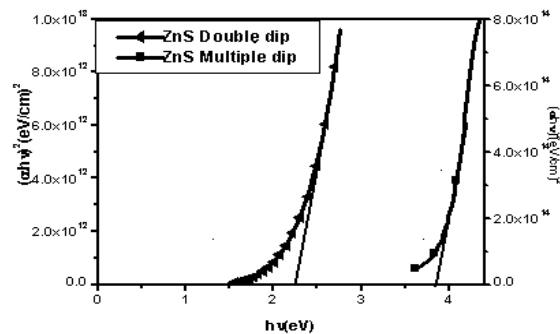


Figure 10

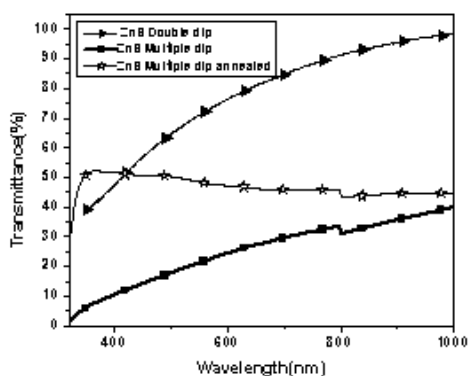


Figure 11(a)

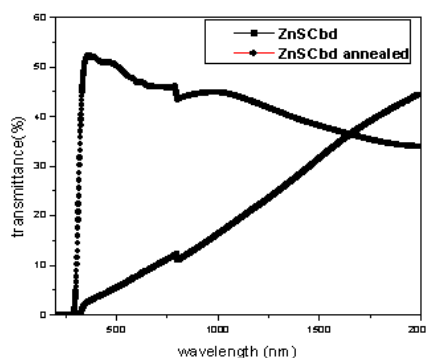


Figure 11(b)

The optical studies of the samples were carried out over a wide wavelength range. The absorption spectra of ZnS double dip, ZnS multiple dip and the annealed samples from PCD and CBD were shown in Figure 8(a) and 8(b) with wavelength along X axis and absorbance along Y axis. There was no much difference in the absorbance of PCD samples, but annealed CBD samples showed a lower absorbance in the entire visible and IR region. It is evident from Fig.9 that the absorbance was found to be unaltered in the case of seeded substrate.

The absorption coefficient ( $\alpha$ ) is related to the band gap of the material by the equation

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (8)$$

for allowed direct transition. A is the parameter which depends on the transition probability. In the case of direct transition in the fundamental absorption,  $(\alpha h\nu)^2$  showed a linear dependence on the photon energy  $h\nu$ . The intercept on energy axis gives the direct band gap energy. The absorption coefficient can be deduced from the absorption spectra using the relation

$$\alpha = 2.303A/t \quad (9)$$

where 't' is the thickness of the as deposited thin film. Extrapolating the linear portion of the graph between  $(\alpha h\nu)^2$  and  $h\nu$  to the X- axis, we have obtained the direct band gaps as 2.23eV and 3.85eV respectively for double dipped and multiple dipped samples, which is shown in Figure 10.

Transmission spectra of various samples were depicted in Figure 11(a) and 11(b). The higher transmittance of double dipped sample was due to the small thickness and good stoichiometry as seen from EDAX. But the multiple dipped samples showed linearly increased transmittance in the visible and IR region, which got improved on annealing. On annealing it showed more or less constant transmission in the entire visible region and hence could be used as a window layer in heterojunction solar cells. The features of transmission remained same in CBD samples in the visible region. It is speculated that the absence of uniform transmittance in the visible region for the entire multiple dipped as grown samples were attributed to the poor stoichiometry.



## CONCLUSION

Nanocrystalline ZnS thin films were prepared by the novel and rarely explored photoassisted chemical deposition technique keeping the precursor solution in alkaline medium. Here the substrate was kept vertical and the UV light was allowed to fall perpendicular on to it. In order to increase the thickness, the same substrate was repeatedly immersed in the same solution without intermediate washing and drying. Structural and optical variations of double dipped and multiple dipped samples were studied and compared with those obtained by chemical deposition method. Morphologies of the annealed samples and seeded samples were also analysed with SEM results. It was found that both structural and optical properties vary with annealing. Grain size was found to be increased on annealing. The wider band gap of the multiple dipped sample showed that the crystallites are comprised of nano grains. The broad band gap of ZnS thin films can achieve higher spectral response in the blue region and hence offer the possibility of using as a buffer layer in solar cells. We could establish that PCD can facilitate smooth, uniform, highly adherent and homogenous film with good grain structure owing to its time-consuming nature.

## Acknowledgement

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