Preheated substrate effects on the structural and optical properties of chemically prepared ZnS thin films

K Deepa1,2, K C Preetha3, A C Dhanya1 and T L Remadevi2

1School of Pure and Applied Physics, Kannur University, Kerala, India-670327
2Pazhassi Raja NSS College, Mattannur, Kerala, India-670702
3Sree Narayana College, Thottada, Kannur

email:deepa00hari@gmail.com

Abstract. Nanocrystalline zinc sulphide thin films were prepared by an improved chemical bath deposition technique in which glass substrates were thermally treated prior to the deposition process. The microscopic glass slide was heated to 200°C before mounting into the chemical bath. The films prepared with and without preheating the substrate were characterized using various techniques and their properties compared. Structural analysis of the films was done using powder X-ray diffraction technique. Films deposited without preheating were amorphous whereas preheating the substrate resulted in the deposition of highly crystalline film with wurtzite structure having an intense (100) orientation. Morphological analysis using scanning electron microscope revealed the densification of the films deposited on preheated substrate indicating that the nucleation rate was higher in this case as compared to films deposited without preheating. Gravimetric analysis of the films confirmed that preheating results in the deposition of thicker films. The optical analysis of the samples was done using UV-Vis-NIR spectroscopy. All the films had a very low absorbance in the visible region. A red-shift in absorption edge was observed on preheating the substrate which indicates a decrease in band gap. However the transmittance in the visible region decreased on preheating the substrate. Room temperature photoluminescence spectra exhibited UV and violet emission for both the samples. The luminescence intensity was found to increase on preheating.

1. Introduction
Zinc sulfide (ZnS), which is a II-VI semiconducting compound, has received much attention owing to its potential uses [1-2] in a wide variety of applications. In opto-electronics, it can be used as light-emitting diode in the blue to ultraviolet spectral region due to its wide band gap at room temperature. Furthermore, ZnS films are used as light source for viewing screens and buffer layer for CIGS solar cells. Large area deposition of high quality ZnS films is required for it to be effectively used in solar cells and electroluminescent devices. There are many deposition techniques to fabricate ZnS thin films [3]. Among them chemical bath deposition (CBD), is more popular due to its simplicity, low cost and uniformity for large area deposition of high quality films. It is often difficult to obtain crystalline ZnS thin films of appreciable thickness using CBD technique. In most cases multiple depositions are required to obtain films of appreciable thickness and larger grain size. In this work the substrates were...
preheated to a temperature of 200°C before mounting into the chemical bath. The films obtained in this single step deposition process were thicker and highly crystalline. It is confirmed that the nucleation, growth and morphology of thin films is affected by the thermodynamic conditions of the interfaces between the substrates and reaction solution [4].

2. Experimental
Nanocrystalline ZnS thin films were deposited using conventional and very popular chemical bath deposition technique. Aqueous solutions of 0.2M zinc acetate and 0.6M thiourea were used as cationic and anionic precursors. Triethanolamine and trisodium citrate were used as complexing agents. Thoroughly cleaned microscopic glass slides were used as substrates. Two identical substrates were immersed simultaneously into the chemical bath one of which was thermally pretreated to a temperature of 200°C for 15 minutes. The bath was maintained at a temperature of 80°C and deposition was carried out for two hours. The slides were removed, thoroughly rinsed and dried using hot air blower. The as prepared samples were characterized using X-ray diffractometer, UV -Vis –NIR spectrophotometer, Scanning electron microscope and spectrofluorometer.

3. Results and discussion
The films deposited on both the substrates appeared to be smooth and homogenous. The thickness of these films as determined using gravimetric technique was 43 nm for the one deposited on untreated substrate and 200 nm for the other.

3.1 Structural analysis.
Figure 1 depicts the XRD pattern of the as prepared samples. In general zinc sulphide crystallizes in cubic and hexagonal form. Cubic form is stable at room temperature whereas the hexagonal form is found to be stable at higher temperatures. ZnS film formed on untreated substrate was amorphous owing to very fine grains. The film on preheated substrate showed good crystallinity with an intense peak at 26.806° corresponding to (100) orientation of wurtzite structure. Another less intense peak occurred at 53.901° corresponding to (1 0 38) orientation. The average grain size using Debye Scherer formula was calculated to be 35nm. The improved crystallinity in the latter case could be attributed to the higher thickness of the deposit.

3.2. Morphology.
The SEM images of the samples are shown in figure 2. The film on pretreated substrate exhibits more uniform morphology compared to the other film. The grains appear to be tightly packed indicating densification of the film when preheated substrate was used. It is clear that

![Figure 1. XRD pattern of ZnS samples](image_url)
thermal treatment of the substrate has enhanced the nucleation which resulted in a more compact film with decreased porosity.

3.3. Optical analysis. The transmission and absorption spectra of the samples in the UV-Vis-NIR region are shown in figure 3. The transmittance of the film deposited on preheated substrate in the UV-Vis region was found to be less than that deposited on normal substrate. This can be attributed to the higher thickness of the former sample. The improved thickness of the film has also caused a shift in absorption edge implying a reduction in band gap from 3.65eV to 3.45eV. Figure 4 shows the photoluminescence emission spectra of the samples at an excitation wavelength of 325nm. The samples exhibit emission at 376nm and 400 nm. The photoluminescence spectra of ZnS films depends on preparation conditions, defects present, crystallite size and shape and stoichiometry. The intensity of PL spectra usually decreases with increase in thickness and crystallinity of the film[4]. In this work the PL intensity was found to be more for the film on preheated substrate though it was more crystalline. Probably preheating of the substrate could have resulted in film with improved stoichiometry [5]. Poor stoichiometry often results in low intensity luminescence peaks [6].

![Figure 2](image1)

**Figure 2** SEM micrographs of ZnS thin films (a) without and (b) with preheating

![Figure 3](image2)

**Figure 3** (a) Transmittance and (b) absorbance spectra of ZnS Thin films
4. Conclusion

Highly crystalline ZnS thin films were deposited chemically on thermally treated glass substrates. The effect of thermodynamic conditions prevailing at the substrate solution interface is found to affect the properties of the film. The films prepared using this single step facile method exhibited good optical properties and are feasible for photovoltaic and optoelectronic applications. The effect of varying preheating temperature on the properties of ZnS thin films is open to investigation.

References

[1] Mach R and Mueller G O 1991 Semicond. Sci. Technol. 6 305.
[2] Varitimos T E and Tustison R W 1987 Thin Solid Films 151 27
[3] Dedova T, Krunks M, Volobujeva O and Oja I 2005 Phys. Stat. Sol. (c) 3 1161
[4] Prathap P, Revathy N, Venkata Subbaiah Y P and Ramakrishna Reddy K T 2008 J Phys:Condens.Matter 20 035205
[5] Long F, Wei-Min Wang, Zhan-kui Cui, Li-Zhen Fan, Zheng-guang Zou and Tie-kun Jia 2008 Chem.Phys.Letters 462 84-87
[6] Denzler D, Olschewski M and Sattler K1998 J.Appl.Phys.84 2841S