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TUNING THE CRYSTALLINITY OF ZnS THIN FILMS BY VARYING THE PRECURSOR CONCENTRATION

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Abstract

Progress in thin film technology depends upon the ability of selectively and controllably deposit thin films-thickness ranging from tens of angstroms to micrometers- with specified physical properties. It requires control-often at the atomic level- of film micro structure and microchemistry. Among all preparation techniques, a very attractive and cost-effective method for producing ZnS thin films due to the possibility of large area deposition at low cost is the so called chemical bath deposition (CBD) method. In the present work the ZnS thin films are coated on a glass substrate using CBD technique. Crystalline ZnS films could be obtained by chemical bath deposition at room temperature. The films are adherent and uniform. It is proved that deposition time and order of mixing contributes noticeably to the ZnS film formation. The ratio of molarities of precursor solution plays an important role in the formation of film and crystallinity. The structural characterization of the film was done by X-ray diffraction and raman studies. Surface characterization was carried out by Scanning electron micrograph. It was proved that the deposited films were ZnS from the crystalline peaks obtained from XRD results. The ZnO peaks could be successfully deteriorated by increasing the concentration of Thiourea in the bath. We got the prominent ZnS peak at $2\theta = 29.27^{o}$ for stochiometric ratio (1:1) of $ZnCl_2$ and Thiourea. Thus ZnS grains are obtained by this simple CBD method at room temperature.

Keywords: Zinc Sulfide, thin films, XRD

1. INTRODUCTION

Thin films can be deposited by number of physical and chemical techniques. Among the different methods, the chemical methods are economical and easier than that of the physical methods. Physical methods are expensive but give relatively more reliable and more reproducible results. Most of the chemical methods are cost effective, but their full potential for obtaining devise quality films has not been fully explored. But there is no ideal method to prepare thin films, which will satisfy all possible requirements. Among the chemical methods of thin film depositions, Chemical Bath Deposition(CBD) is probably the most simplest method. Chemical reaction either takes place on the surface of the dipped subsrate

or in the solution itself, where a mixing of components on the surface to be coated is required. Most of the coatings are formed in a two step fashion;

i) "Sensitizing" the surface for the nucleation reaction of the adhering coating layer.

ii) Deposition of coating by selected reactions.

Recently, the II-VI compounds semiconductor thin films (*e:g: CdS; ZnS CdSe; ZnSe*) have received an intensive attention due to their application in thin film solar cells, optical coatings, optoelectronic devices, and light emitting diodes. Zinc sulfide (*ZnS*) is a wide gap and direct transition semiconductor. Consequently, it is a potentially important material to be used as an anti reflection coating for heterojunction solar cells. In particular, *ZnS* is believed to be one of the most promising materials for blue light emitting laser diodes and thin film electroluminescent displays.

ZnS thin films are synthesized by different methods such as thermal evaporation, spray pyrolysis, sputtering, chemical vapour deposition, successive ionic layer adsorption and reaction (SILAR),and the metal organic vapour phase epitaxi (MOVPE).Among these, a very attractive method for producing ZnS thin films due to the possibility of large area deposition at low cost is the so called CBD. Ammonia and hydrazine are popular choices as the complexing agent in the CBD of thin films.

Generally ZnS crystals exist in two forms, cubic (Zinc blende) and hexagonal (wurzite).The cubic form is stable at room temperature while the wurzite the less dense hexagonal form is stable at high temperature[1].

2 EXPERIMENTAL

In the present work, the preparation of zinc sulphide (ZnS) thin film was done on a glass substrate using the CBD. The reactive substances used to obtain the ZnS layers were Zinc chloride, Ammonia solution, sodium hydroxide and thiourea and H_2O for different concentration at constant room temperature.

First the complexing agent NaOH was added to zinc chloride, then ammonia solution added. After this thiourea was added. White precipitated solution was formed. NaOH and ammonia provides the alkalinity of ZnS solution. Water was added only after mixing the reactants. During the earlier days of experiment we used only NaOH as complexing agent. But due to the lack of adherent film formation, we added ammonia in addition to NaOH as complexing agent[2]. The amount of water needed to make the total volume to 50ml is calculated and added. The substrate used is a rectangular piece of glass slide. It was cleaned first by dipping in Chromic acid and washed in pure water and rubbed thoroughly with cotton waste. It was then cleaned using distilled water and then dried. S.Kalaynasudharam et al reported that ZnS film formation needs high temperature. But in the present work, by keeping the bath one over night with substrates dipped in it, we

got adherent film at room temperature without heating.

After the film formation the film was cleaned in running water. Then we dried the film and rubbed off the film on the side which was opposite to the beaker, using Hcl. Different precursor molarities were tried to find the structural change in ZnS thin film on varying the precursor concentration. The structure was determined by X-ray diffraction studies. Morphological studies were carried out using scanning electron microscope.

3 RESULTS AND DISCUSSIONS

3.1. Raman spectrum of a ZnS thin film

Raman spectroscopy is a technique that gives information on the molecular vibration and other structural properties like crystallinity and phases of materials. In this work, the Raman excitation wavelength is 532nm.

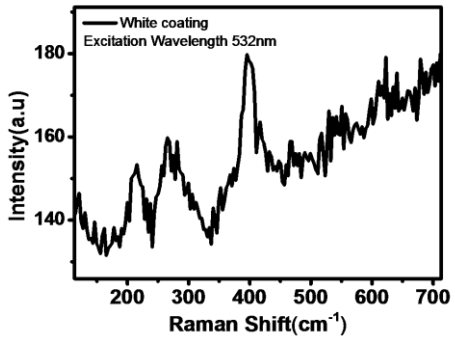


Fig. 1 Raman spectra of a ZnS thinfilm

From the spectra, it is observed that there are two broad peaks at 217cm-1, 254 cm-1 and at 400cm-1. The hexagonal ZnS unit cell belongs to the point group symmetry. Non-polar E2 mode is one of the four modes of zone-center optical phonons. E2 mode is associated with two frequencies. The higher-frequency E2 mode is associated with the sulphur atoms. Lower -frequency E2 mode is associated with Zn atoms. We got peak at lower (217 &254 cm-1)and higher frequencies(400 cm-1). Brafman and Mitra have reported that the modes A1(TO) and E1(TO) can occur at the same wave number 273 cm−1 [6]. J.Diaz-Reyes et al reported that for ZnS above 380 cm-1,acoustic and optical combinations can occur [7]. They assigned the broad weak peak at 436 cm−1 to TA+LO at L point for flat phonon dispersion.

3.2. XRD spectrum of ZnS thin films

X-Ray diffraction studies were carried out on ZnS thin films and scans were carried out in the range $2\theta = 10^{o}$-80^{o}. The X-ray diffraction patterns of thin films deposited at different precursor concentrations are shown below. In this XRD, the prominent peak obtained is at 33.9^{o} . But this peak is due to diffraction peak of hexagonal ZnO grains on the surface. Usually ZnS thin films prepared in room temperature conditions are amorphous.

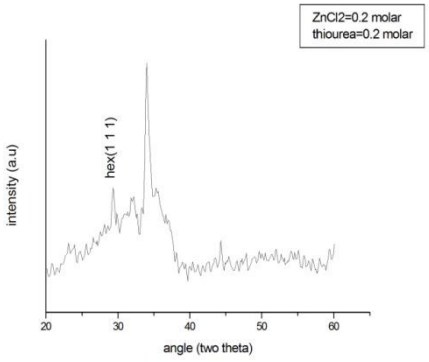


Fig. 2. XRD pattern of ZnS sample 1

In this sample, there is a small peak at 2θ =29.34^o and it corresponds to (111) plane of the hexagonal ZnS phase [JCPDS data file number :72-0163 (ZnS/ hexagonal)Grain size of ZnS grain is 22.63 nm.

But in this sample, as the preferential orientation is due to the ZnO grains, we have to increase the concentration of sulphur in thin film sample to obtain ZnS grains. Hence we purposefully increased thiourea concentration.

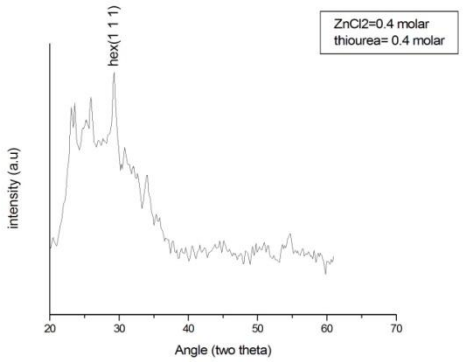
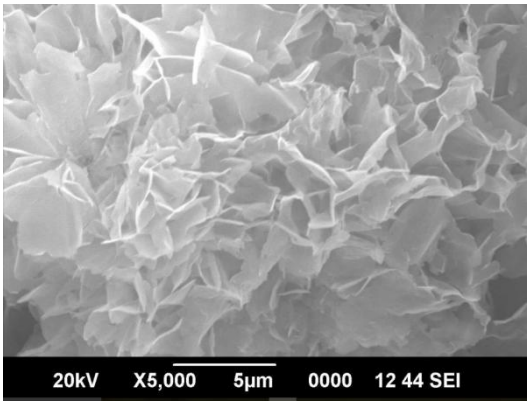


Fig. 2. XRD pattern of ZnS sample 2

We obtained a sharp peak of ZnS at 2θ=29.244. Hence the preferential orientation is towards the hexagonal (1 1 1) plane. The size of ZnS grain is 15.38 nm. It should be noticed that the peak corresponding to ZnO grain has got vanished.

3.3. SEM image of a ZnS film

Sem micrograph of a ZnS sample with high thiourea concentration is shown below.



From the scanning electron micrographs of the sample, the deposited films looks like flower shaped and the grains are also hexagonally shaped, confirming the XRD results. From the images we can observe that the film is less smooth, because of the presence of grain boundaries. That may be the reason for low conductivity of ZnS thin films. The hexagonal structure is more evident in the SEM image.

4 CONCLUSIONS

The effect of concentration of precursor solutions used for making the chemical bath on physical properties of the ZnS films are studied. Here ammonia and NaOH are used as complexing agents in chemical bath to provide alkalinity for the reaction.

While making the chemical bath the order of mixing of precursor solution and complexing agents are important. The films are deposited after 24 hours of dipping. We were able to prepare the films at room temperature without any heating. Most papers reported amorphous ZnS thin films at room temperature. From present study, crystalline ZnS films could be

obtained by room temperature chemical bath deposition. The films are in good, quality, adherent and uniform. There is a good agreement between XRD and microstructure studies. It is also proved that deposition time contributes noticeably to the ZnS fim formation.

The ratio of molarities of precursor solution plays an important role in the formation of film and crystallinity.

It was proved that the deposited films were ZnS from the crystalline peaks obtained from XRD results. The ZnO peaks could be successfully deteriorated by increasing the concentration of Thiourea in the bath. We got the prominent ZnS peak at $2\theta = 29.27^{o}$ for stochiometric ratio (1:1) of $ZnCl_2$ and Thiourea. All papers reported amorphous ZnS thin films at room temperature. The grain size is calculated to be around 15nm.

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