

Studies of Structural and Optical Properties of Zinc Sulphide Thin Films

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ABSTRACT

We are explaining the preparation and properties of ZnS thin films which is mainly prepared by Successive Ionic Layer Adsorption and Reaction mechanism (SILAR). Stating the principles of SILAR, we are discussing the experimental venture we have under taken. We had the structural analysis, of the films prepared at laboratory conditions of temperature and pressure after XRD, SEM, UV, VISIBLE, NIR studies

INTRODUCTION

Thin film studies directly or indirectly advanced many new areas of research in solid state physics and chemistry, which are based on the phenomenon uniquely characteristic of thickness, geometry and structure of the film. Zinc sulphide belongs to the II-IV family of semiconducting material. It has ever increasing attention due to the wide variety of applications such as UV light emitting diodes [1], efficient phosphor in flat panel displays [2], etc. ZnS has a wide band gap and is a direct transition semiconducting material [3]. It is widely used as antireflection coatings in the solar cells [4, 5, 10]. As it is electroluminescent, used in opto-electronic devices, photo synthetic coating, blue light emitting laser diodes [6, 11] etc. Because of its non toxicity character experimental researches are going on to replace CdS by ZnS [7]. In this present work preparation of Zinc Sulphide using SILAR (SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION) method is carried out.

SILAR method for the deposition of thin films was introduced by NICOLAU in the year 1985[8]. Like stated by the name this method is based on the successive reaction of solvated ionic compound on the solution solid interface. SILAR method is one of the simplest techniques for the preparation of thin films. This is a chemical process, in which alternative adsorption and reaction of ionic reactants with intermediate rinsing. Here cationic and anionic precursors are reacting and forming a

solid compound. The precondition is that the solubility constant of the solid compound be very low, and the solubility constant of the by-product be very high [8]. Here the precursors are aqueous solutions and rinsing agent is water, which enables heterogeneous reactions between the solid phase and the solvated ions in the solution.

SILAR method is divided into 4 different steps

- i) Adsorption
- ii) Rinsing I
- iii) Reaction
- iv) Rinsing II

In the first step the cationic precursor is adsorbed on the substrate to form an electrical layer. [It means a positive charge inner ionic and negatively charged outer ionic layer is formed]. Here inner positively charged ion will be the cation for the compound and negatively charged ions are the counter part of the cation. In the second step the unabsorbed ion will be rinsed away from the diffusion layer, so a saturated electrical layer will be remained on the solid surface [8]. In third step i.e. in the reaction phase; the anionic precursor is introduced, the cation and anion will have a reaction and form a solid substance. The solubility of the substance will be very poor so that a solid chemical compound could be formed on the substrate. In the fourth step rinsing occurs, in which the counter ions of both type of precursors, which forms the by-products of the system and which has high solubility will be washed off with in water. These four steps constitute one cycle in this method. By repeating different cycles the thickness of the film can be controlled.



Fig:1 SILAR, Model No: (HO-TH-03)

EXPERIMENTAL SET UP:

SILAR the aqueous solution method has some advantages-This technique utilizes the chemical force between the ion in the liquid phase and the surface ion, so no external energy is needed for the growth of a thin film. Relatively mild conditions can be used, so under room temperature and normal pressure we can prepare films. This method utilizes uncomplicated apparatus so this is also cost effective. SILAR method is useful for the deposition of thin films of chalcogenide groups like II-IV [12]

PREPARATION OF ZnS

ZnS is formed by the reaction between Zinc chloride ($ZnCl_2$) and sodium sulphide (Na_2S) as cationic and anionic precursors respectively. $ZnCl_2$ is hygroscopic in nature so that it will absorb the moisture content from the atmosphere very easily. In that case chances to form other complex compounds are prominent. Here 0.1M $ZnCl_2$ solution is prepared by measuring suitable weight $ZnCl_2$ analytical reagent and dissolved in 250 ml distilled water which act as a solvent. Triethanol amine (TEA) could be used as complexing agent to enable increase in growth rate and hence is added. To control the PH of the solution sodium hydroxide is used.

0.05M sodium sulphate solution is also prepared by dissolving sodium sulphide flakes in 250 ml distilled water and its PH is noted. Micro glass slides of dimensions (75mm x 25mm x 1.4 mm) are used as substrate. The substrate cleaning is an important factor since it can affect the growth of the film. Substrate is washed with detergent and distilled water and immersed in dilute Nitric acid, then again washed with distilled water followed by acetone. The clean slide is washed and dried up in air. The cleaned substrates are mounted on the SILAR handle. Four beakers containing $ZnCl_2$ solution, distilled water, Na_2S solution and distilled water are placed on the SILAR bed respectively.

Here SILAR (model no: HO-TH-03) run by software installed on PC is used. First the substrate will dip on $ZnCl_2$ solution, the substrate immersion time in the solution is known as dipping time. This can be adjusted from 5 sec to several hours. After retrieving from a solution, there is a time delay between next dip (in next solution) i.e.: between two consecutive dips there is an exdip time, which can also be varied. By varying dip and exdip time we can control the growth rate on the substrate. The observed growth rate in the present condition was 13.54 nm/cycle. After the exdip time substrate will dip in the water, then in sodium sulphide, the anionic precursor. On fourth phase rinsing with distilled water occurs, these 4 phases constitute a cycle. As the number of cycles is changed the thickness of the film also changed. The temperature of the SILR bed can be varied from room temperature to 100 degree, so that the bath temperature of the substrate can be changed during preparation

In this work we have studied the effect of change in the number of cycles, temperature, and PH during preparation of the film. Also a change in the concentration of TEA and change in Dip and Exdip time are also verified. Films which are prepared by this method were analyzed by XRD and SEM for structural and surface morphological studies and UV-VIS-NIR for optical properties.

Structural Analysis

XRD studies are done using $\text{CuK}\alpha$ with 1.5 \AA and using SAIFXR-1104A spectrometer. XRD studies have been aimed at to check the contents of the prepared films and to confirm the film as Zinc sulphide. The comparison has been done using the standard JCPDS [a, b] data of the relevant compounds. Fig2 shows the X ray diffraction peak of ZnS thin film coated on glass substrate.

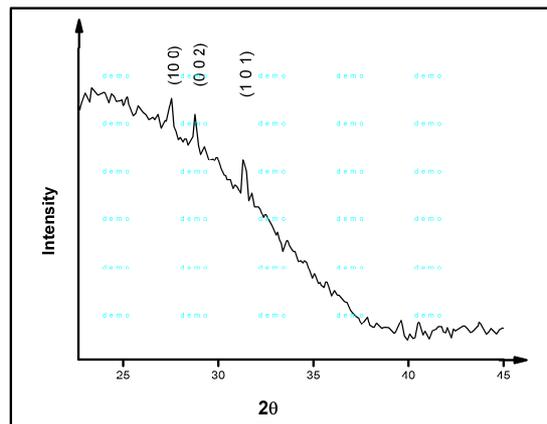


Fig2: XRD of ZnS SILAR coated film.

Deviation from amorphous nature of ZnS thin films:

Comparison with JCPDS data of the films at room temperature with different cycles (as shown a in the Fig:3) showed mostly an amorphous structure. In the figure at 2θ of 26.8° degree broad peaks has been observed for all the four films. All the films have been maintained at same laboratory conditions. But the films which are coated at higher temperatures and different cycles as in the figure:4 show a deviation from amorphous nature. At higher temperature as *dipping time adjustments* increases it shows more peaks of ZnS even when the cycles are same. The reason for the increase in crystallinity is assigned as follows. Along with ageing and increase in temperature the tendency to adhere and alignment of substance in a plane increases. When temperature increases the collisions of the cations in the solution among them and with the substrate increase, which leads to an adherence and more alignment on the glass slide.

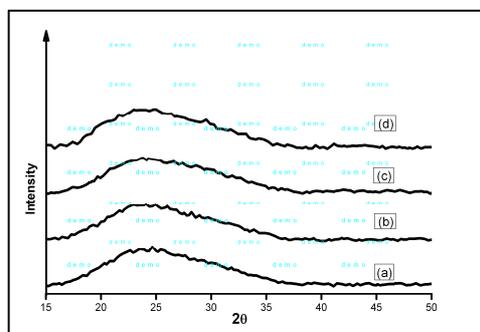


Fig.3) XRD of films all at room temperature and different cycles: a)10 b) 20 c)30 d)40

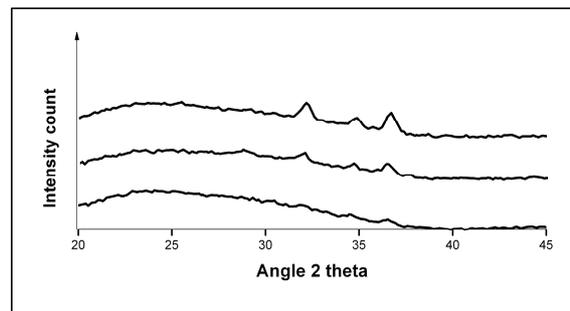


Fig.4) XRD of films at high temperature with different dipping adjustments

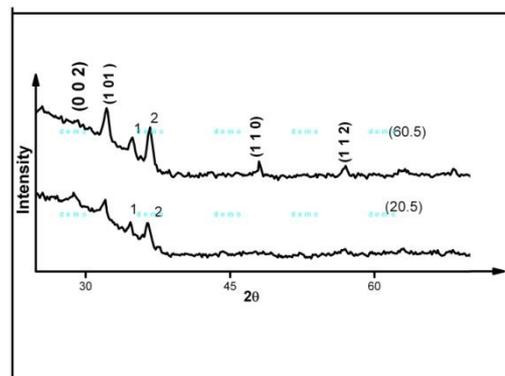


Fig5: XRD at 100 degree with 2 different cycles and dip, ex-dip times in the bracket

The XRD of samples prepared at higher temperatures are as shown in figure 4 & 5. The dipping parameters such as dipping time and ex-dip time are varied and the XRDs are as in fig.4. The dipping time plays an important role in forming crystalline films as peaks are more prominent in them than in fig.3. It confirms the hexagonal structure of ZnS with orientation marked in fig.5. It establishes the transformation from amorphous to crystalline nature as temperature increases. It could be seen that the SEM also supports the same fact (shown later). ZnCl₂ and sulphur peaks other than ZnS also appear. As the cycle increases, with decrease in dipping time, the intensity of them decreases. The reason for intensity decrease may be attributed to the lower adsorption and reaction time for ZnCl₂ and sulphur. The presence is evident from the Fig.8 (a, b) as white structures formed on the surface of the film. As the dipping time is reduced a rhombohedral nature appears occasionally [JPDS 89-2351], but not seen in others may be due to the instability of the phase. (peaks in the figure 6)

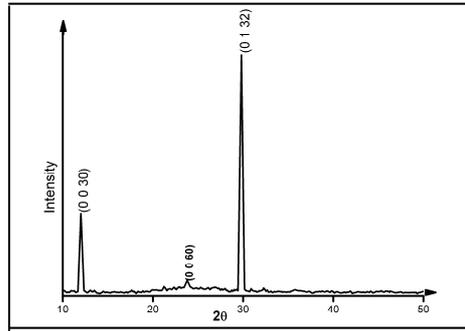


Fig:6 XRD showing Rhombohedral Structure

Morphological Analysis

Morphology is studied using SEM - JEOL microscope INSTRUMENT JSM-6390 at STIC CUSAT, Kochi, Kerala. Fig.7 shows the ageing of samples. Since ZnCl_2 is hygroscopic, the solution prepared seen to turn turbid quickly (in 1 to 2 hours). The comparison of SEM a) & b) indicates a more presence of white structures in 7.(b) which was coated using a ZnCl_2 solution prepared earlier(3days).Hence later, prepared sample ageing was only allowed and their SEM is in Fig:7 c, d. The grain size is marked in the SEM, which is increasing with ageing. The reason for the increase is obvious; a growth of the film into agglomerate, due to nucleation on the impurities, i.e., traces of ZnCl_2 & S

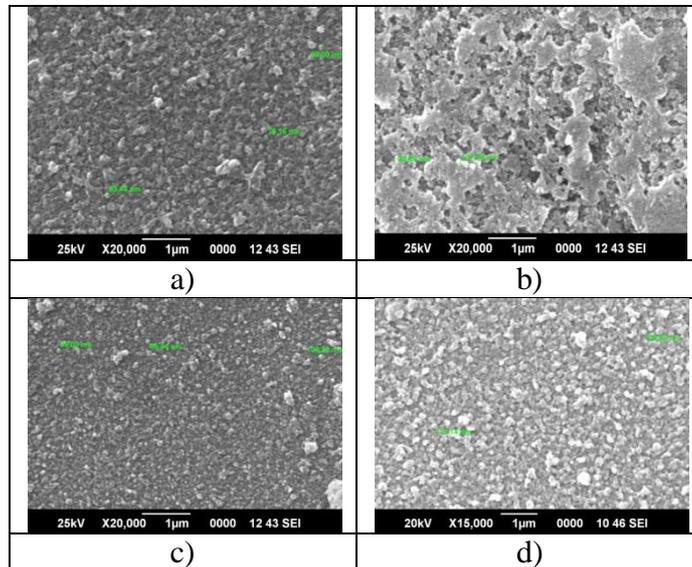


Fig.7 SEM of Samples after an ageing of a)40 days b)43 days c)45 days d)100 days all at room temperature

Fig.8 shows the micrographs of samples prepared at high temperatures and different dipping parameter (cycles). Micrographs indicate the presence of white structures in samples with higher dipping parameter. It is due to the growth of film in

the nucleation sites. This is in agreement with the XRD study results.

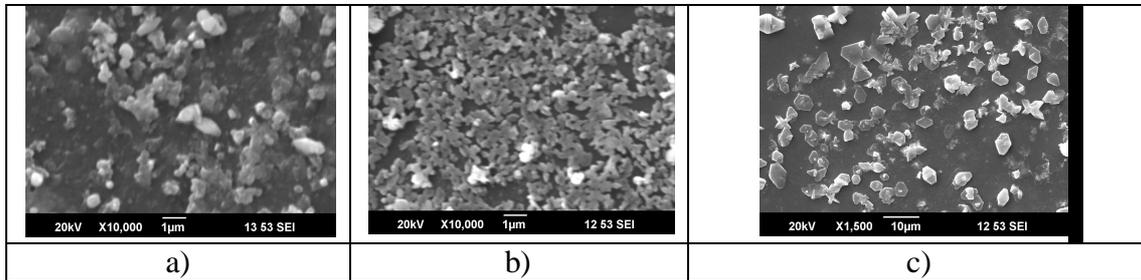


Fig.8 SEM of samples at higher temperature with different dip & exdip a) (20,5) b)(60,5) c) (60,10)

When bath temperature increases the increase in crystallinity of the sample occurs as can be seen from the Fig.8c) It has a hexagonal shapes and the agglomeration of this units can also seen in this figure.

OPTICAL PROPERTES

UV, VISIBLE&NIR spectrum of different samples are shown using the spectrometer (JASCO, Japan). The reflectance, transmittance and band gap energy spectra of samples at different conditions are given in each figure. In Fig9 (a) it shows transmission efficiency of samples at room temperature with different cycles. It is evident that when cycle increases the percentage of transmission decreases. It is due to the fact that increases in cycles consequences the increases in thickness. Similarly the bath temperatures also affect the transmission spectra seen as when bath temperature increases transmission decreases. A fundamental phenomenon is established as film becomes thicker and composed of impurities it transmits light to a lower extent.

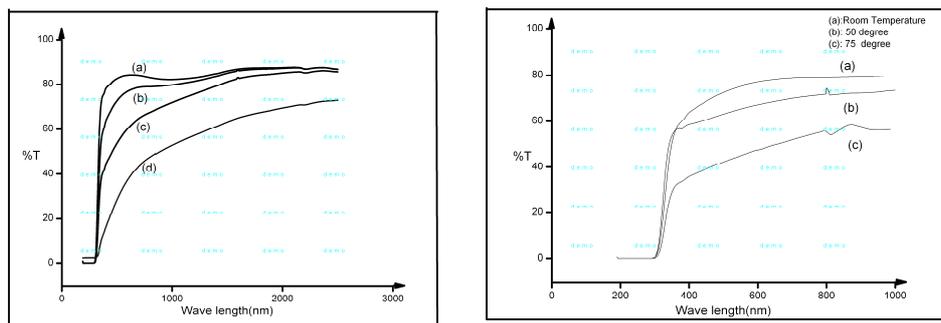


Fig 9:a) Transmittance at room temperature for different cycles b) different temperature same cycle

In the case of reflectance, it shows an increase in reflectance with increase in bath temperature. As the thickness of the film is only of the order of nanometer the

interference patterns are absent in the spectra. We have used the study to calculate mainly the refractive index and band gap energy also.

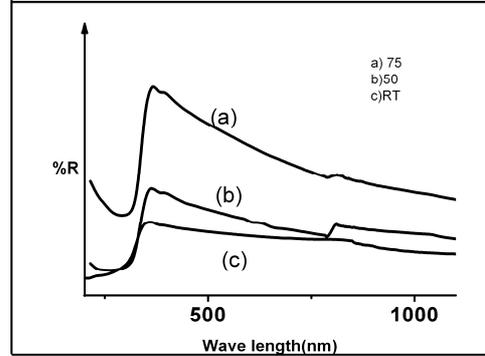


Fig10: Reflectance at different temperature and same cycle

From the figure refractive index is calculated using the equation $R = \left[\frac{(n-1)}{(n+1)} \right]^2$ as in [6].

Where R is the reflectance and n is refractive index. It is varied from 1.9 to 2.4 when temperature increases. Film property is different from the bulk and hence it's optical parameter also. The refractive index value enables a probe into the layer coating as an antireflection film in wider fields which we do not elaborate here.

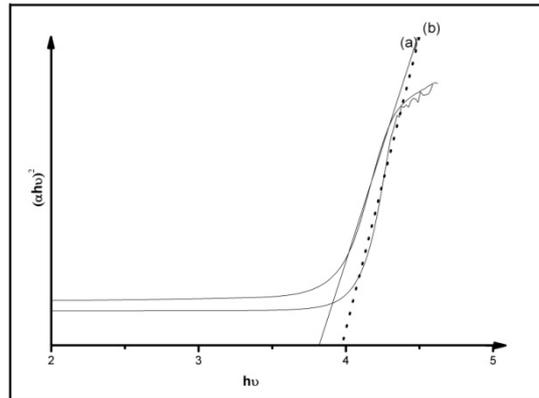


Fig:11 a) Band gap energy with 2 different temperature

The Study of optical absorption leads to the explanation of band gap energy of the film ZnS. In this experiment optical absorption for different cycles and dipping parameters with in the wave length region 250-700 nm were studied.

Band gap energy is calculated using the formula

$$\alpha = A (h\nu - E_g)^n$$

$h\nu$ as in [9].

$h\nu$ is the photon energy, E_g band gap energy A, n are constants. For allowed direct transition $n=1/2$, and for all allowed indirect transitions, $n=2$.

The plots of $(\alpha h\nu)^2$ vs $(h\nu)$ are shown in figure: 11 a) for ZnS films. Band gap energy is determined from this graph. The linear nature indicates the existence of direct transition. It can be seen that band gap energy is little higher in this case that is varied from 3.7 to 3.91 with different dipping parameter. When temperature increases the crystalline size also increases which consequences the decrease in band gap energy [7]. Our result is in agreement with this. Band gap is a parameter highly useful in semiconductor fields and so it may be helping in further use as in diodes. The higher values of band gap are shown by the films of low thickness.

CONCLUDING REMARKS

All studies are done at laboratory conditions of temperature and pressure; coated on glass microslides. It is seen that more thick and uniform films are obtained when the system is used at higher bath temperature during coating. Ageing is done at local environment which suspected to be more of oxygen content. But the result analysis show precipitation of sulphur at the surface rather than oxidation. It may be due to zinc chloride and sodium sulphide as reactants. For clear solution we have used sodium hydroxide. The result was more dense film in the first case and more clear film in second case, with a bluish coloration enabling us to conclude that the solution is to be more alkaline for good films. Films at room temperature with different cycles show mostly an amorphous structure. But the films which are coated at different temperatures and different cycles as in the figure(2) show a deviation from amorphous nature. At higher temperature as *dipping time adjustments* increases it shows more peaks of ZnS even when the cycles are same. The comparison shows that for the fresh samples with higher bath temperature have a change in their phase from amorphous to hexagonal with broader peak. The SILAR method is fit for producing films of lesser thickness and is good on bath heating during the deposition. It could be concluded that stabilization needs time or temperature. The ZnS films coated by this method is confirmed to produce rhombohedral (which is rare and unstable) at its prime functioning of SILAR. The phase change has been attributed to agglomeration during the growth of the films which gets stabilized in ageing, and heating as supported by XRD&SEM. The grain size has been calculated in the different phases which are explaining the growth of the film. The nucleation may be due to sulphur or $ZnCl_2$ as resulted from the reactants (supported by XRD) and also as described in SILAR mechanism. The absorption spectra gives an energy gap of 3.7 to 3.91 eV, in agreement with theory. The refractive index is assigned to be 1.9 to 2.4 for a zinc sulphide film, may not be differing from bulk. The studies make it more interesting to probe into its use in electronics and coating industry

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