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Chemical bath deposition of ZnS thin film and its characterization

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ABSTRACT

In the present work, synthesis of ZnS thin film by chemical bath deposition(CBD) and characterization are studied; XRD analysis and SEM images and uv-visible spectrophotometry were investigated to determine the effect in preparation of ZnS thin film by CBD technique. Over the years, CdS and ZnS thin films have been intensively investigated mainly for their applications in large-area electronic devices such as thin-film field-effect transistors, magnetic recording media, electronic semiconductor devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin film solar cells) and storage (thin-film batteries). It is also being applied to pharmaceuticals, via thin-film drug delivery. So it is very interesting and attracts one to carry out such a work for the favour of various technology. Among the various methods CBD is the widely used technique; as it is advantageous over the other methods of deposition in cost easiness and control over deposition. Finally, it has been concluded that CBD is the simple as well as an excellent deposition process in which film is deposited from the aqueous solution by the reduction of metal salts.

Keywords: *ZnS, thin films, CBD, XRD, SEM.*

1. INTRODUCTION

The upcoming branch of nano science and nanotechnology that has been recently in research is the thin films, which deals with systems that have only one common property, namely one of their dimensions being small though all other physical properties of such systems may vary with the method of investigating them. In crystal, the atoms are arranged periodically whereas in amorphous there is a short range ordering i.e. no periodicity is found. In both the cases the ordering is due to the influence of forces. However a cut off of such a force with respect to the surface area is considered. The reason why thin films grasp the attention in recent research studies is that films of micrometer and sub-micrometer range can be produced.

In practice a thin film is a solid layer of material ranging from fractions of a nanometer to several micrometers in thickness where the thickness varies from 50̊A to 2000Å.An ideal homogeneous film is confined in two dimensions. The dimension along the third direction gives the film thickness. Because of the extreme thinness, they have very little strength and are not self-supportable. They are all fabricated by deposition on a suitable substrate that serves as the support.

The main criterion of choosing the substrate is that it must be compatible chemically and structurally with the film material with respect to temperature and stress reliability. Most commonly used substrates are the glass wafers. Theses wafers of silicon are coated with silica or ceramic materials etc.

Recent researches on solar cells fabrication aimed towards lowering the fabrication cost in order to decrease the price of the energy obtained. The researches were directed to use thin films technology for solar cell fabrication[1]. Suitable materials should be easily prepared and inexpensive, show stable behavior over long periods of operation. The high cost and the difficulty to obtain single crystal semiconductors give a great interest to polycrystalline semiconductors, including a wider range of compounds which could be used in different applications [2]. ZnS is an n-type II–VI compound with a wide band gap (3.5–3.7 eV) at room temperature. It is a promising material for future applications such as window layers of solar cells and coatings which are sensitive to UV light.

It is an excellent host material for electroluminescent phosphors and it is being commercially used for electroluminescent displays. Thin films of semiconductors, has been recognized as the simplest and most economical one. CBD is a technique in which thin films are deposited on substrates immersed in dilute solutions containing metal ions and the chalcogenide source. A chelating agent is used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. The technique under these conditions relies on the slow release of chalcogen ions into the solution in which the free metal ion is buffered at a low concentration. Film formation on the substrate takes place when ionic product (IP) exceeds solubility product (SP). Moreover, the content elements ZnS are nontoxic to the human body and are very cheap and abundant [3].

Previously, ZnS thin film have been deposited by different techniques, thermal evaporation [4], self-assembly technique [5], spray pyrolysis [6],electron beam evaporation [7], Photochemical deposition (PCD) [8], close-space sublimation [9], pulsed laser deposition [10], molecular beam epitaxy [11] and chemical bath deposition [12] which is used in the present study to prepare ZnS thin films.

2. EXPERIMENTAL PROCEDURE

2.1. Chemical bath deposition of ZnS

The chemical bath deposition (CBD) method uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. In a typical experiment, substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion and added base. A chelating agent is also added to control the release of the metal ion. The process relies on the slow decomposition of chalcogen source into in an alkaline solution in which the free metal ion is buffered at a low concentration. The free metal ion concentration is controlled by the formation of complex species. The dependent parameters on which the deposition rate and growth rely on include bath composition temperature and PH.

A large number of physico-chemical factors such as solubility product, supersaturation, type of precipitation, etc., control the growth of the deposit under a specified set of reaction conditions.

2.2. Preparation of substrate

The substrates generally selected are glass, quartz, alumina, plastics like teflon and ceramic substrates. Here we make use of glass slides as the substrate, over which ZnS is to be deposited. The choice of cleaning method depends upon the degree of cleanliness required. The steps involved in substrate cleaning are as follows:

- The glass slide is first washed with liquid soap solution and rinsed with clean water and it is dried in the oven at 75̊C for 10 min.
- Then it is cleaned using acetone and wiped with cotton, ready for use. By selecting substrates with high binding energy to the film material, one can produce highly uniform film.

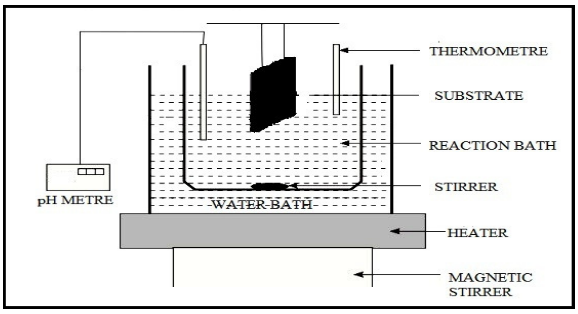

Figure - 1: Experimental set up for CBD.

2.1. Method

The chemicals used are Zinc acetate, as zinc ion source, thiourea, as sulfide ion source, Liquor ammonia-complex agent, acetone and distilled water. All the reagents are analytical grade and ready for use without further purification before utilization.

The substrate used for deposition ZnS thin films is microscope glass slides (7.7. mm x 2.2mm x 1.2mm), washed in distilled water to remove the impurities and residuals from substrate surfaces, followed by rinsing in HCl acid (50 ml of HCl in 150 distilled water) for 24 hour to introduce functional group called nucleation, which forms the basis for the thin films growth and finally washed again with distilled water. The bath temperature was maintained at 80◦C during deposition.

The substrate was immersed vertically in beaker containing, the reaction mixture and solution as shown in the figure 1. The pH level was monitored using a pH meter type. Deposition time was one hour in each experiment. The substrates were taken out, washed with distilled water and dry in air, then the deposited film from one slide was removed carefully using HCl solution.

The chemical deposition technique which also is referred to as the solution technique for the preparation of (ZnS) thin films is based on the slow release of (Zn^{2+}) ions and (S^{2-}) ions in solution. The slow release of the (Zn^{2+}) ions is achieved by the dissociation of a complex species of zinc $[Zn(NH_3)_4]^{+2}$which is formed from react ion of zinc salt (ZnSO4) with ammonia (NH_3). The (S^{-2}) ions are supplied by the decomposition of thiourea in alkaline solution (pH > 10), and react with (Zn^{2+}) ions to give zinc sulfide ZnS. Deposition occurs by an ion –by– ion process, or by colloidal particles of (ZnS) adsorbing onto the substrate .

The thickness of ZnS thin films was measured using weight method, which depends on the difference between weight of substrate before and after deposition of the film. A sensitive electronic balance was used for this purpose.

3. RESULTS AND DISCUSSION

3.1. Structural Properties

In this paper, the interesting focus falls on the preparation of good quality ZnS thin films by chemical bath deposition and to highlight that CBD is an excellent method for the purpose of getting fine quality ZnS. The ZnS film prepared was uniform, transparent and colorless. The XRD pattern for the ZnS monolayer films is shown in figure 2. Diffractogram of the thin film shows sharp peaks at 2θ values of about 28.95°, which is characteristic of the cubic structure XRD pattern of ZnS with a preferred orientation along the (111) direction. The XRD studies reveal that the film had the best preferred orientation structures. In order to obtain more structural information, the average crystallite size of ZnS is estimated by using the well-known Scherrer's formula, $D=0.94\lambda/\beta\cos\theta$. The average crystallite size was found to be 7 nm. Further the strain present in the film is 0.021, indicates the stability of the crystal structure in the prepared film.

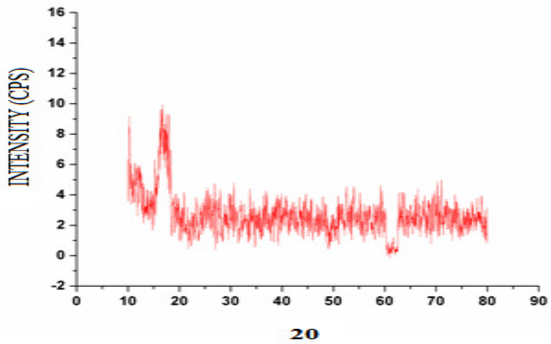

Figure - 2: XRD pattern of ZnS thin film.

3.2 Surface Morphology

The surface morphology of the thin film plays a crucial role in any optoelectronic devices. In the present study the surface morphology of the prepared ZnS film is observed by SEM as shown in Figure 3. Surface of the film appears like smooth, uncolored, reflecting and well adhered to the glass substrate. As discussed in the XRD section the film contains the nano-sized crystalline structure of the atoms, which is verified by the SEM.

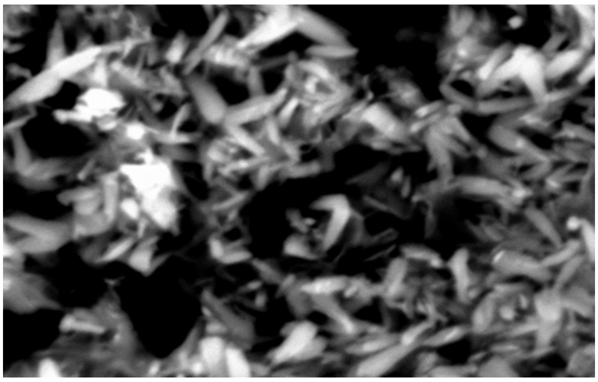

Figure - 3: SEM image of the ZnS thin film.

3.3. Optical Properties

The optical properties of ZnS film were observed using the Transmission spectra of the film, which is measured using UV-VIS spectrophotometer. The transmission spectrum of the ZnS film is shown in Figure 4.ZnS thin film have a wide direct band gap in the UV region, so it can be used as a key material for blue light emitting diodes and other optoelectronic devices such as electroluminescent displays. The optical study represents the UV absorption spectra which show the absorption peak at around335 nm. The obtained band gap from the graph was found to be 3.72 eV. SEM images revealed uniform deposition of the ZnS material over entire glass substrate with spherical grains distributed over the surface. From optical absorption spectra it is clearly seen the peak position around ~335 nm wavelength. Optical band gap calculated from the graph was found to be 3.72 eV corresponds to the ZnS thin film. SEM micrograph shows that uniform deposition with spherical grains covering entire surface of substrate.

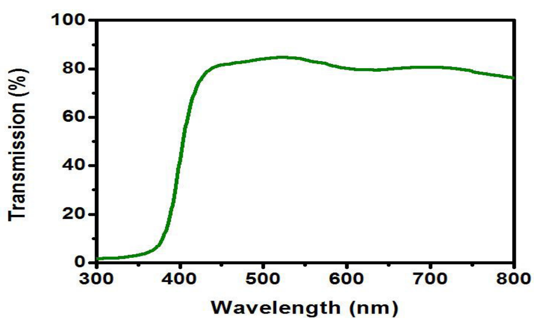

Figure - 4: Transmission spectrum of the ZnS films.

4. CONCLUSION

Cubic uniform ZnS thin films were prepared using CBD and the characterized using different analytical techniques. The grown ZnS films are crystallized in the cubic structure and were aligned perpendicular to the (111) plane. The SEM shows the uniform film over the glass substrate. The ZnS film exhibited good optical properties with a relatively high transmittance of 80% in visible region, and the optical band gap is about 3.72 eV. The optical study represents the UV absorption spectra which show the absorption peak at around335 nm. SEM images revealed uniform deposition of the ZnS material over entire glass substrate with spherical grains distributed over the surface, proves its future use in many optoelectronics devices. From all the instrumental characterizations, it is concluded that CBD is advantageous over other methods of deposition in cost easiness and has a good control over deposition. It is the simple deposition process in which film deposited is of good quality from the aqueous solution by the reduction of metal salts

5. REFERENCES

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