Effect of deposition parameters on Structural and Optical Properties of ZnS Thin Films

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Abstract: Thin films of ZnS have been vacuum coated on glass substrates at room temperature. The crystal structure and optical properties of the films were studied using X-ray diffractometer (XRD and UV visible spectrophotometer, respectively. The X-ray diffraction patterns showed that films were polycrystalline in nature with cubic structure. The optical band gap was measured close to 3.7 eV. The influence of rate of deposition on the grain size of the films were analyzed.

Keywords: ZnS, Thermal evaporation

1. Introduction

The synthesis of binary metal chalcogenides in a crystalline form has been a rapidly growing area of research due to their important physical and chemical properties [1]. ZnS, as a typical II–VI semiconductor compound with band gap energy of 3.7 eV at room temperature, has attracted considerable attention [2]. ZnS has been used as a wide band gap material in electroluminescent and optoelectronic devices such as blue light-emitting diodes, Mn-doped electroluminescent devices, electro- optic modulator and n-window layers of solar cells [3, 4]. ZnS is also emerging as photodetector in the ultraviolet region which has application in both civil and military fields [5]. Subsequently, several techniques have been used to produce ZnS thin film such as spray pyrolysis [6], chemical bath deposition (CBD) [7], SILAR [8], molecular beam epitaxy [9], sputtering [10] and thermal evaporation [11]. Among the above mentioned methods, thermal coating is a simplest physical method. In this research ZnS thin films are coated on glass substrates by thermal evaporation method.

2. Experimental

In the present work, thin films of ZnS have been coated using thermal evaporation method. ZnS pellets of 99.9% purity were procured from Sigma Aldrich for this purpose. Films were deposited on glass substrates using molybdenum boat under 10⁻⁶ torr. The glass substrates were cleaned with chromic acid, distilled water and acetone. Stainless steel shield was used to ensure constant rate of evaporation in each trail. The deposited films were characterized using X-ray diffractometer (XRD) and UV visible spectrophotometer. X-ray pattern were obtained using Rigaku Minflex 50 X-ray diffractometer.
using CuKα radiation ($\lambda = 1.54$ Å). Transmittance and absorbance data was obtained from Shimadzu UV 1800 spectrophotometer.

3. Results and discussions

3.1. Thickness measurement

Optical thickness of the films were found using Swanepoel method [12]. For uniform thickness, the interference fringes obtained are as shown below in Figure 1. The fringes clearly are in the region of medium and weak absorption. In this region, the refractive index can be calculated from the equation

$$n = \left[ N + (N^2 - s^2)^{1/2} \right]^{1/2}$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}$$

Where $s$ is the refractive index of the substrate (for glass $s = 1.5$), $T_M$ is the maxima of the interference fringe and $T_m$ is the corresponding minima.

Thickness of the film can be obtained from the formula

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

where $n_1$ and $n_2$ are the refractive indices at two adjacent maxima at $\lambda_1$ and $\lambda_2$ wavelengths. The thickness was calculated using the above formulas for different transmission plots. The thickness values, hence, calculated were about 292 nm, 370 nm and 441 nm. Below 290 nm the films lacked uniform substrate coverage and above 441 nm they showed poor adhesion. From the above thickness values, the rate of deposition was found by dividing the thickness values by the time of deposition. Corresponding to 292 nm, 370 nm and 441 nm thickness values, 3.2 Ås$^{-1}$, 4.1 Ås$^{-1}$, 4.9 Ås$^{-1}$ rates of deposition were calculated.

![Figure 1. Transmission spectrum of ZnS film](image)
3.2. **XRD analysis**

Figure 2 shows the XRD pattern of ZnS thin films deposited at three rates of deposition namely, 3.2 Ås\(^{-1}\), 4.1 Ås\(^{-1}\), 4.9 Ås\(^{-1}\). The deposited films were polycrystalline in nature. The peaks were sharp at 2θ ≈ 29° indicating cubic structure with preferred orientation along (111) plane. Grain size was calculated from the XRD pattern using the equation

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

Where \( \lambda \) is 1.54 Å, wavelength of CuK\(\alpha \) radiation used, \( \beta \) is the full width at half maximum (in radian) and \( \theta \) corresponds to the maximum height of the peak.

![Figure 2. XRD pattern of ZnS for different rate of deposition](image_url)

**Table 1.** The grain size values for different rates of deposition

| Thickness \( t \) (nm) | Deposition Rate \( R \) (Å/sec) | 2\( \theta \) (degree) | FWHM \( \beta \) (x 10\(^{-3}\) radian) | Grain size \( D \) (nm) | Interplanar spacing \( d \) (Å) | Lattice parameter \( a \) (Å) |
|------------------------|-------------------------------|-----------------------|--------------------------------------|------------------------|-------------------------------|-------------------------------|
| 292                    | 3.2                           | 29.24                 | 5.70                                 | 25                     | 3.05                          | 5.28                          |
| 370                    | 4.1                           | 29.2                 | 9.01                                 | 15                     | 3.05                          | 5.28                          |
| 441                    | 4.9                           | 29.12                | 6.68                                 | 21                     | 3.05                          | 5.28                          |

From the above table, it is observed that, at low rate of deposition the grain size is high and it reduces with high deposition rate from 25 nm to 15 nm for 3.2 Ås\(^{-1}\) to 4.1 Ås\(^{-1}\). This is in accordance with literature [13] which says that, lower the rate of deposition, higher is the
deposition time and hence, large clusters can be formed, which finally leads to higher grain size. But from the deposition rate of 4.1 Ås\(^{-1}\) to 4.9 Ås\(^{-1}\) the grain has increased from 15 nm to 21 nm. This can be attributed to increase in thickness of the films with which crystallinity improves [13]. The lattice parameter of the films was found to be 5.28 Å.

3.3. Optical properties
The absorption spectra for three different deposition rates is as shown in Figure 3. The spectra are measured in the range of 300 to 800 nm. A strong absorption in the ultraviolet region in contrast with visible region was observed for all three rates of deposition.

\[ a h \nu = K (h \nu - Eg)^{1/2} \]

where \( K \) is a constant.

![Figure 3. Absorption spectra at various rate of deposition](image-url)
The value of absorption coefficient ($\alpha$) increased from 370 nm to 320 nm which can also be confirmed from bandgap values obtained from intersection $\alpha$ and tauc plot [14], as shown in Figure 4.

The bandgap of the films were close to 3.7 eV. It increased marginally from 3.72 to 3.75 eV with increase in rate of deposition as well as with thickness.

4. Conclusion
ZnS thin films have been successfully coated on glass substrate at various rates of deposition. The deposited polycrystalline films show cubic phase. As rate of deposition increases grain size reduces and with increase in thickness value, crystallinity improves. The deposited films have bandgap around 3.7 eV and are ideal for ultraviolet radiation detection.
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