Structural, Morphological and Optical Properties of ZnS Thin Film Deposited by Pulsed Laser Deposition Technique

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ABSTRACT

Zinc sulphide (ZnS) thin film with thickness of about 102 nm was deposited using pulsed laser deposition (PLD) technique. The crystalline structure, morphology, optical and luminescence properties of the film were investigated by X-ray diffraction, Atomic force microscopy (AFM), UV spectroscopy and Photoluminescence (PL) spectra, respectively. XRD shows that the as deposited film is polycrystalline in nature and has a cubic crystal structure with the preferred plane of ZnS (111) of crystallite size equals to 49.6nm. AFM images show spherical shaped grain. The calculated grain size, root mean square roughness (Rq) and average roughness (Rq) of the film were found to be 84.74 nm, 11 nm and 8.3 nm, respectively. UV spectroscopy studies show good transmission characteristic with an average transmittance of 98%. The calculated band gap energy value of ZnS film is 3.7eV. PL measurements show two peaks positioned around 570 nm and 495 nm.

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. The studies on ZnS thin films are being pursued with increasing interest on account of their proven and potential applications in many thin film devices such as photo luminescent and electroluminescent devices and more recently as n-type window layer heterojunction solar cells. Among these techniques, pulsed laser deposition (PLD) technique has many advantages such as: (a) It has the ability to maintain target composition in the deposited thin films; (b) High quality films can be deposited at low temperature due to high kinetic energy of atoms and ionized species in the laser produced plasma; and (c) It is clean and low cost. It is a promising material for optoelectronic device applications such as blue light emitting diodes, electroluminescent devices and photovoltaic cells. Also, ZnS thin film has been proven as one of the promising thin film materials for detector, emitter, and modulators in optoelectronics. ZnS film can be used as a filter, reflector and planar wave guide due to its high value of refractive index, high effective dielectric constant, and wide wavelength pass band, and high transmittance in visible region. Several techniques such as molecular beam epitaxy (Deulkara, B. H., et al., 2003), atomic layer deposition (Ghosh, P. K., et al., 2007), pulsed electrochemical deposition (Durrani, S. M., et al., 2000), chemical vapor deposition (Sartale, S. D., et al., 2005; Kumar, P., et al., 2006), chemical bath deposition (Yazici, A. N., et al., 2003; Zhou, L., et al., 2009) and spray pyrolysis (Asenjoa, B., et al., 2008; Hernandez-Fenollosa, M. A., et al., 2008) have been used to produce ZnS thin films with adequate properties such as high crystallinity, low resistivity and high transmittance. Among these techniques, pulsed laser deposition (PLD) technique has many advantages such as: (a) It has the ability to maintain target composition in the deposited thin films; (b) High quality films can be deposited at low temperature due to high kinetic energy of atoms and ionized species in the laser produced plasma, and (c) It is clean and low cost (Chrisley, B. D. and G. K. Hubler, 1994). In present investigation ZnS thin film has been deposited using pulsed laser deposition method. The structural, surface morphological and optical properties of the as deposited ZnS thin film were studied.

Experimental:

Pulsed laser deposition technique was used to prepare ZnS thin film on glass substrates. The Nd:YAG excimer laser (10 ns, 6 Hz), the energy was 500 mJ. The No. of shot equel 600 pulse. The film thickness was measured by using Michelson Interferometer and found to be 102 nm. The deposition rate was estimated by the
film thickness divided by the number of laser pulses. The ZnS thin film was grown on silica glass. Since the substrates were cleaned with ethanol using the ultrasonic cleaner.

The crystalline structure was examined using X-ray diffraction (XRD) and Atomic force microscopy (AFM). X-ray diffraction (XRD) measurements were carried out using Rigaku MiniFlex II desktop x-ray diffractometer. SPM model AA 3000 Angstrom Advanced Lns., USA was used to determine the nanocrystalline topography. The optical transmission measurements were obtained using UV-Vis spectrophotometer, SP-3000 plus, OPTIMA INC. Japan. The photoluminescence spectrum of the film was recorded by Hitachi F-2500 FL Spectro-photometer.

**RESULTS AND DISCUSSIONS**

**XRD Studies:**

The XRD patterns of the ZnS thin film is given in Figure 1. The XRD patterns of the precipitated ZnS film exhibit three distinguished peaks corresponding to diffraction of the (111), (220), and (311) planes of the cubic phase (Habibullah, M., et al., 2007). The (111) plane of the ZnS crystal grew more predominantly than the other planes. No peaks from any other impurities such as ZnO or other compounds are detected. Our results are agreed with Zhang et al. and Niasari et al. (2006; 2012).

![X-ray diffraction patterns of the ZnS film](image)

**Fig. 1:** X-ray diffraction patterns of the ZnS film

The average nano-crystalline size (D) was calculated using the Debye-Scherrer formula (Lifshin, E., 1999):

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

Where \( k \) denotes the Scherrer constant (the shape factor of the average crystallite and can be considered \( k = 0.90 \)), \( \lambda = 1.5418 \) Å is the wavelength of the incident Cu K\( \alpha \) radiation, \( \Theta \) is the Bragg diffraction angle, and \( \beta \) is the FWHM of the XRD peak appearing at the diffraction angle \( \Theta \). The average crystalline sizes were calculated from X-ray line broadening using (111), (220) and (311) peaks and Debye-Scherrer equation and tabulated in Table 1. The calculated values of \( D \) give an indication that the size lie within the nanocrystal range. As shown in Table 1, larger \( D \) of 49.6 nm and smaller \( \beta \) of 4.06 × 10^{-4} m^{-2} values of preferential orientation along (111) direction indicate better crystallization of the material (Habubi1, N.F., et al., 2013).

Additionally, to have more information on the amount of defects in the film, the dislocation density (d) was evaluated from the formula (Callister, W.D., 1997):

\[
\delta = \frac{1}{D^2}
\]

Where \( D \) is the grain size. This quantity, \( \delta \), is defined as the number of dislocations intersecting a unit area of a random section. It is seen from Table 1 that the \( \delta \) value of the preferential orientation of the XRD peaks along (111) direction is smaller than the other peaks. The calculated lattice constants (\( a \)) from below formula (Usharani, K., et al., 2013) of the all peaks of the film are tabulated in Table 1.

\[
a = d \sqrt{h^2 + k^2 + l^2}
\]

Where \( d \) is the interplaner distance. One can observe from the table that the lattice constant value of the preferential orientation along (111), which is 5.401 Å, is very close to the to the reported value \( a = 5.406 \) Å (Yongbin Zhao, et al., 2007).

The strain \( \varepsilon_{zz} \) of the ZnS thin film can be calculated using the following equation (Tsay, C.Y., et al., 2010):

\[
\varepsilon_{zz} (\%) = \frac{a - a_0}{a_0} 
\]

The calculated values of \( \varepsilon_{zz} \) of all peaks of the film were tabulated in Table 1. The negative value of the strain revealed the compressive strain of the ZnS thin film. This low value of compressive strain suggests that the synthesized nanocrystalline ZnS has high-quality crystal geometry.
Table 1: The diffraction angle (2θ), interplaner distance (d), FWHM (β), the grain size (D), the dislocation density (δ), lattice constants (a) and the strain ε_{zz} % of the prepared ZnS film

<table>
<thead>
<tr>
<th>Identification with (hkl) values</th>
<th>2θ (degree)</th>
<th>d (Å)</th>
<th>β×10⁻³ (rad)</th>
<th>D (nm)</th>
<th>δ×10⁻⁴ (nm⁻²)</th>
<th>a (Å)</th>
<th>ε_{zz} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>28.90</td>
<td>3.1185</td>
<td>5.7</td>
<td>49.6</td>
<td>4.06</td>
<td>5.401</td>
<td>-0.09</td>
</tr>
<tr>
<td>(220)</td>
<td>48.33</td>
<td>1.9079</td>
<td>9.8</td>
<td>30.6</td>
<td>10</td>
<td>5.396</td>
<td>-0.18</td>
</tr>
<tr>
<td>(311)</td>
<td>58.29</td>
<td>1.6355</td>
<td>6.6</td>
<td>47.6</td>
<td>4.4</td>
<td>5.424</td>
<td>0.33</td>
</tr>
</tbody>
</table>

**Surface Morphological Studies:**
Atomic Force Microscopy (AFM) is a surface analytical technique used to capture high resolution images of a surface to get microscopic information on the surface structure and to plot topographies representing the surface relief. AFM studies were carried out to evaluate the grain size and surface roughness of ZnS thin films. AFM images of ZnS film are shown in Figure 2 for two and three dimensions.

Fig. 2: AFM images of ZnS thin film for two and three dimensional

The thin film as observable in the images is made of aggregates (clusters) with a spherical shaped grain. The calculated root mean square roughness (R_{q}) and average roughness (R_{a}) of the film were found to be 11 nm and 8.3 nm, respectively. The roughness of the films is unavoidable since the grains are spherical in shape and various sizes (Anuar Kassim, et al., 2011). The calculated average grain size was found to be 84.74 nm in diameter.

**Optical Properties:**
Optical transmittance spectra of ZnS thin film in the range of (300-700) nm was presented in Figure 3, measured at room temperature in air. It is significant to note that this ZnS film was highly transparent in the visible region and its transmittance was found to be over 98%. The crystalline, structural and surface homogeneity influence the film transmission (Ates, A., et al, 2007).

Fig. 3: Optical transmittance spectra of ZnS thin film

The ability of a material to absorb light is measured by its absorption coefficient. Figure 4 shows the absorbance spectra of ZnS thin film. Absorbance coefficient α associated the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t = 102 nm) using relation (Cottrell, A., 1975): α = 2.303 A/t

\[ \alpha = 2.303 \frac{A}{t} \]
It was clearly seen that the absorbance decreases with increasing the wavelength. The sharp increase in absorbance at the wavelength \( \lambda = 370 \text{ nm} \) is due to the onset of interband transitions at the fundamental edge.

![Graph of absorbance vs. wavelength](image)

**Fig. 4:** The variation of the absorption coefficient with wavelength

The optical band gap value obtained by extrapolating the linear portion of the plots of \((\alpha h\nu)^2\) versus \((h\nu)\) to \(\alpha = 0\), Figure 5. Better linearity was observed in the former case and it was determined that ZnS film has a direct band transition. The calculated band gap value of the film was 3.7 eV and it is very close to the value of the bulk ZnS which equals to 3.65 eV (Hasanzadeh, J., et al., 2013).

![Graph of \((\alpha h\nu)^2\) vs. photon energy](image)

**Fig. 5:** The \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) for ZnS thin film

The refractive index is very important as a significant factor in optical communication and in designing devices. A roughly measurements could be estimated form the formula below formula (Ferro, R., et al., 2000) which depend only on transmission.

\[
n = \frac{1 + R}{1 - R} + \frac{4R}{(1 - R)^2} - k^2
\]

(6)

The \(n\) values of ZnS film were plotted versus the wavelength in Figure 6. It is clear that the \(n\) values of the film decreased with increasing in the wavelength.

![Graph of refractive index vs. wavelength](image)

**Fig. 6:** Variation of refractive index with wavelength of ZnS film

The extinction coefficient of the film was calculated from below equation (Benramdane, N., et al., 1997). The variation of the extinction coefficient with wavelength of the film is shown in Figure 7. It was clearly seen that the extinction coefficient decreases with increasing the wavelength.

![Graph of extinction coefficient vs. wavelength](image)
\[ k = \frac{\alpha \lambda}{4\pi} \]  

(7)

Fig. 7: Extinction coefficient variation with wavelength of ZnS film

**Photoluminescence Study:**

The photoluminescence spectrum was measured at room temperature of ZnS nanocrystalline thin film shown in Figures 8. This figure shows that the two peaks positioned are around 370 nm and 493 nm. Usually for semiconductor nanocrystals, two emission peaks can be observed, the excitation and the trapped luminescence. The excitation emission peak is sharp while the trapped emission peak is broad. The emission PL peak at about 370 nm is attributed due to the transition of electrons from the shallow states near the conduction band to sulphur vacancy present near the valence band. The other emission PL peak at 493 nm is assigned to elemental sulphur species on the surface of ZnS. This result is in agreement with Kurbatov et al (2010).

Fig. 8: PL spectrum of ZnS thin film

**Conclusions:**

Zinc sulfide thin film was prepared by PLD technique. The structural, morphological and optical properties of the coated film were studied. XRD shows that the as deposited film is polycrystalline in nature and has a cubic crystal structure with the preferred plane of ZnS (111). The crystallite size of ambient deposited ZnS waveguide for this particular plane is about 49.6 nm. AFM micrograph reveals that substrate is well covered with spherical shaped grain and average grain size of 84.74 nm. The film shows better optical transmission of 98% in the visible region. The calculated band gap value is 3.7 eV, which will be very useful for solar cell. PL measurement at room temperature showed that the two peaks positioned are around of 370 nm and 493 nm.

**REFERENCES**