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Optical Properties of ZnS Thin Films

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Abstract

Zinc sulfide (ZnS) thin films of different thickness were deposited on Corning 7059 glass substrate at room temperature and high vacuum using resistive heating technique. The film properties investigated include their absorbance / transmittance / reflectance spectra, band gap, refractive index, extinction coefficient, optical conductivity, complex dielectric constant and thickness. The films were found to exhibit high transmittance (60-99%), low absorbance and low reflectance in the visible / near infrared region up to 1100 nm. However, the absorbance of the films was found to be high in the ultra violet region with peak around 360 nm. The thickness (using quartz crystal) of various films ranges from 100 nm to 400 nm. The band gap measured was found to be in the range 3.51 eV to 3.84 eV.

1. Introduction

Zinc sulfide (ZnS) is a wide gap and direct transition semiconductor [1]. Consequently, it is a potentially important material to be used as an antireflection coating for heterojunction solar cells [2]. It is an important device material for the detection, emission and modulation of visible and near ultra violet light [3,4]. In particular, ZnS is believed to be one of the most promising materials for blue light emitting laser diodes [5] and thin film electroluminescent displays [6].

Oil and gas, which are at present the main sources of energy, will eventually exhaust after sometime, necessitating the search for newer energy resources. Nuclear energy is one option, but it induces acute radiative pollution and has some technical problems. Sun is a huge source of energy that can be converted into electrical energy using the solar cells and this is the best alternative option. In this work ZnS thin films have been studied as an antireflection coating which is an essential part of the solar cell. The parameters studied include the absorbance/ transmittance/ reflectance spectra, refractive index, extinction coefficient, optical conductivity, complex dielectric constant and thickness.

2. Experimental Work

In this study resistive heating technique was used to grow the ZnS thin films on cleaned Corning 7059 glass substrates.

Leybold Heareus vacuum evaporator was used to prepare ZnS thin films. A tantalum boat was used as a support to evaporate ZnS. A quartz crystal monitor mounted near the substrate was used for insitu measurement of the thickness of the thin films as well as the evaporation rate, which was kept around 0.5 nm/s. Polster [7] found that ZnS evaporated at 0.5 nm/s has negligible absorption.

G. Hass et al [8] have reported that ZnS thin films deposited at high rates and low pressures are found to exhibit bulk values of refractive index 2.4 when evaporated at room temperature. We have, therefore, deposited our ZnS thin films with the substrate kept at room temperature.

Other conditions under which the samples were prepared are given in Table 1.

Table 1. Conditions under which the samples were prepared.

S. No.	Sample Name	Thickness (nm)	Substrate Temperature (°C)	Deposition Rate (nm/s)	Pressure (mbar)
1	ZnS-1	100	Room	0.5	$6x10^{-6}$
2	ZnS-2	200	-do-	-do-	-do-
3	ZnS-3	400	-do-	-do-	-do-

The optical absorption and transmission spectra for a range of samples of ZnS thin films (of different thickness) were obtained in uv/ vis/ nir region (up to 1100 nm) using a Hitachi U-2001 UV/ VIS Double Beam Spectrophotometer with bare (uncoated) glass slide as the reference. The measurements were done in the wavelength scanning mode under the following parametric conditions:
1. Incidence = normal
2. Temperature = room temperature
3. Reference = uncoated glass slide

3. Results and Discussion

The absorbance spectra of the thin films of ZnS, having different thickness, are shown in Figure 1. These spectra reveal that films, grown under the same parametric conditions have low absorbance in the visible and near infrared regions. However, absorbance in the ultraviolet region is high. The enhanced absorption is observed in the neighbourhood of λ = 360 nm. It has been observed that the maximum absorption peak shifts towards the longer wavelength with increasing film thickness. This suggests the decrease in the bandgap with the increasing thickness. The overall absorbance has been increased with the film thickness. This is because of the reason that in case of thicker films more atoms are present in the film so more states will be available for the photons to be absorbed. There are small absorption peaks below the fundamental edge. These small absorption peaks are an indication that some states have been created in the region between the conduction and the valance band. These states may be due to some structural defects in the films.

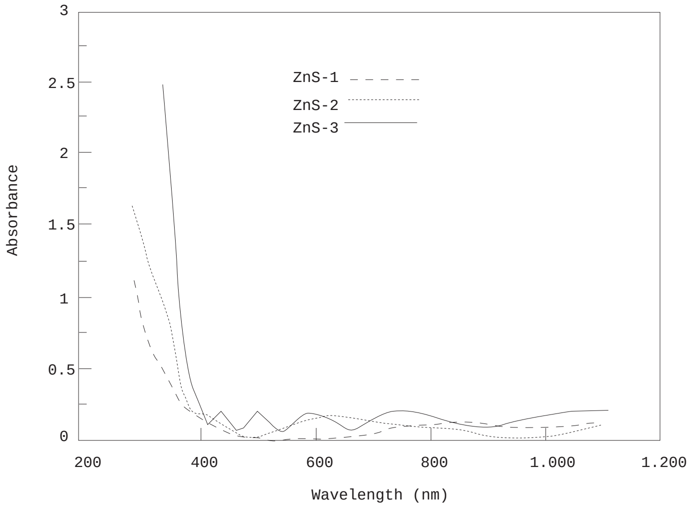

Figure 1. Absorbance versus wavelength of incident radiation.

The theory of optical absorption gives the relationship between the absorption coefficient α and the photon energy hv, for direct allowed transition as

$$\alpha = (hv - Eg)^{1/2}. \quad (1)$$

Using the fundamental relations of photon transmission and absorbance,

$$I = I_o e^{\alpha t},$$

where t is thickness and

$$A = log I_o / I,$$

we have $\alpha = 2.303A/t$.

Equation (1) gives the band gap E_g, when the straight portion of α^2 versus hv plot is extrapolated to the point $\alpha = 0$.

Figure 2 gives the variation of band gap with the thickness of the films. ZnS thin films grown here have band gap in the range 3.51 eV 3.84 eV. These values are in good agreement with the values 3.44 eV, 3.5 eV, 3.6 eV, 3.68 eV and 3.7-3.8 eV reported by Seppo Lindroos [9] using successive ionic layer adsorption and reaction (SILAR) technique, Ryoki

Nomura [10] using metal organic vapour phase epitaxy (MOVPE), T. Yamaguchi [11], S. Biswas [12] and I. C. Ndukwe [13] using chemical bath deposition (CBD) technique. Figure 2 also shows that the band gap is decreasing with the increasing thickness of the films. There is the possibility of structural defects in the films due to their preparation at room temperature; this could give rise to the allowed states near the conduction band in the forbidden region. In case of thick films these allowed states could well merge with the conduction band resulting in the reduction of the band gap.

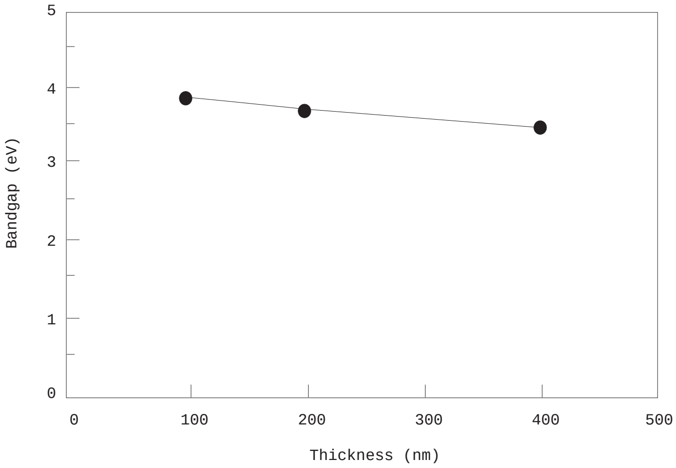

Figure 2. Bandgap versus thickness of the thin films.

Figure 3 shows the optical transmittance spectra for the ZnS thin films. All the films demonstrate more than 60% transmittance at wavelengths longer than 400 nm, which is comparable with the values for the ZnS thin films deposited by Seppo Lindroos [9] using SILAR method, I. C. Nduckwe [13], T. Yamaguchi [11] using chemical bath deposition method. Below 400 nm there is a sharp fall in the %T of the films, which is due to the strong absorbance of the films in this region. It has been observed that the over all %T increases with the decrease in the film thickness. This happens due to the over all decrease in the absorbance with the decrease in film thickness. A rise and fall in the transmittance above 40 0nm is observed. A similar behaviour (rise and fall in the transmittance) is reported by S. Y. Kim [14] for TiO_2 thin films prepared using electron beam evaporation and is claimed to be due to interference of the light transmitted through the thin film and the substrate. These variations have been observed to increase with film thickness.

Figure 4 shows the optical reflectance spectra for ZnS thin films. The reflectance has been found by using the relationship

$$R + T + A = 1.$$

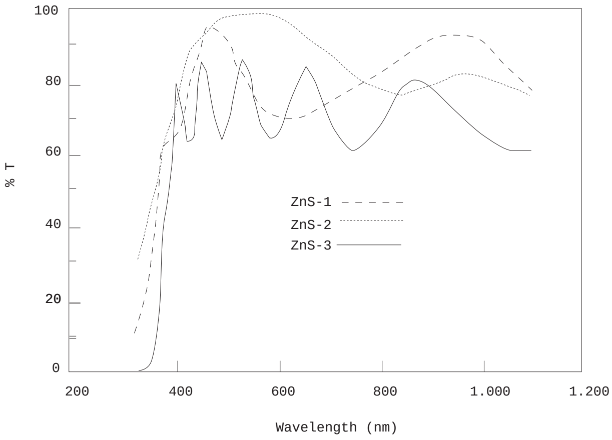

Figure 3. Transmittance versus wavelength of incident radiation.

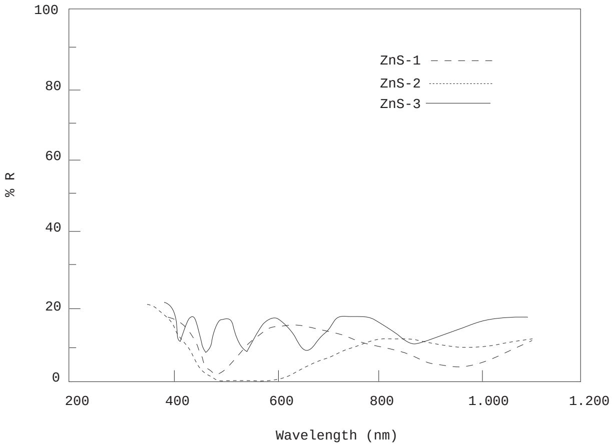

Figure 4. Reflectance versus wavelength of incident radiation.

The reflectance of ZnS thin films is small in the near infrared and visible region. The over all reflectance of the film increases with the film thickness.

For normal reflectance [15], we have,

$$R = (n-1)^2/(n+1)^2,$$

where R is the normal reflectance; using the above relation the refractive index n was determined.

Figure 5 shows the variations in the refractive index with the incident photon energy. The increase in the film thickness results in the over all increase in the refractive index. This increase is due to the over all increase in the reflectance with the film thickness. The peak value of the refractive index for the ZnS thin films of various thickness vary in the range of 2.61 to 2.64, which is in good agreement with the value 2.62 reported by I. C. Ndukwe [13].

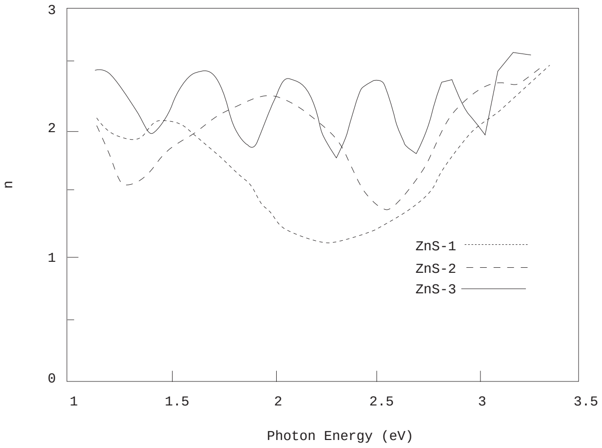

Figure 5. Refractive index versus incident photon energy.

The extinction coefficient k could be found using the relation [15],

$$k = \alpha\lambda/4\pi,$$

where $'\lambda'$ is the wavelength.

Figure 6 shows the variations of extinction coefficient with the photon energy. The rise and fall in the extinction coefficient is due to the variation in the absorbance.

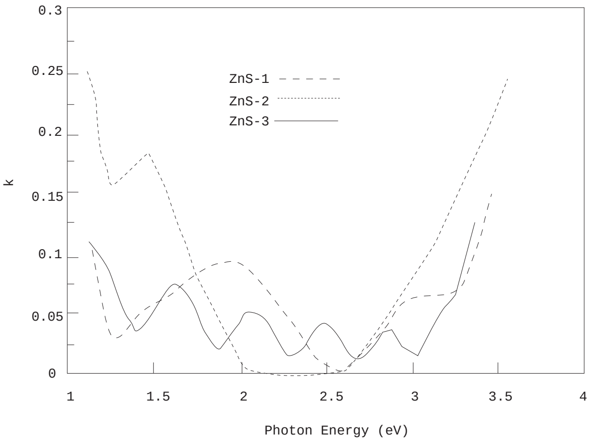

Figure 6. Extinction coefficient versus incident photon energy.

Figure 7 shows the variation of optical conductivity with the incident photon energy. The optical conductivity was determined using the relation [16]

$$\sigma = \alpha nc/4\pi,$$

where c is the velocity of light.

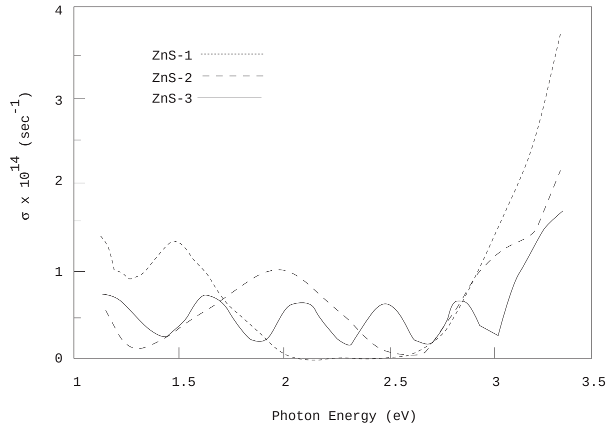

Figure 7. Optical Conductivity versus incident photon energy.

The increased optical conductivity at high photon energies is due to the high absorbance of ZnS thin films in that region.

The real and imaginary parts of the dielectric constant were determined using the relation [17],

$$\varepsilon_c = \varepsilon_r + \varepsilon_i = (n + ik)^2,$$

where ε_r is the real part and is the normal dielectric constant, ε_i is the imaginary part and represents the absorption associated of radiation by free carrier.

Figures 8 and 9 show the variations in the real and imaginary parts of the dielectric constant with the incident photon energy. The range of variation of dielectric constant is in agreement with the observations of I. C. Ndukwe [13]. Different shapes of the curves for the real part of the dielectric constant have been observed. This is due to the different effective thickness of the insulator. The imaginary part confirms the free carriers contribution to the absorption.

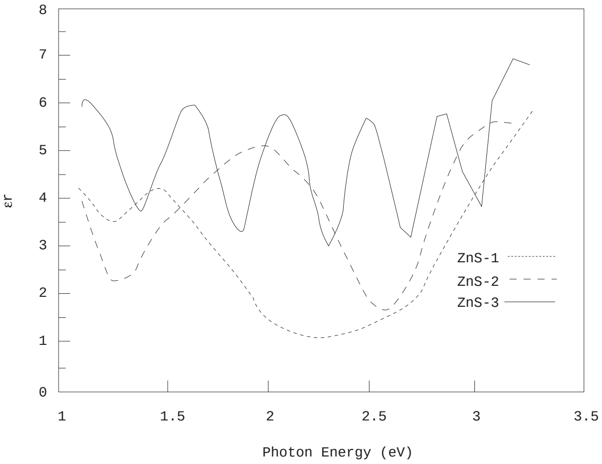

Figure 8. Real part of the dielectric constant versus incident photon energy.

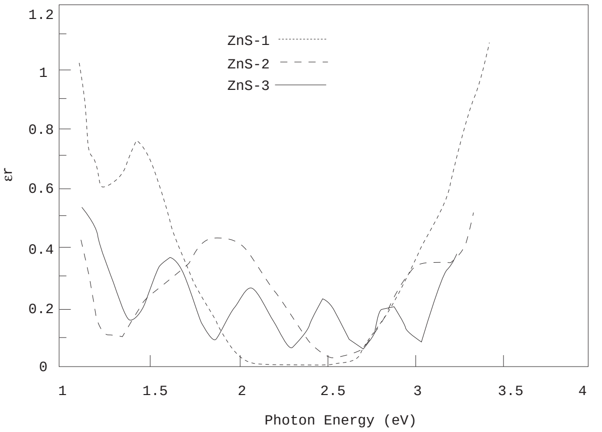

Figure 9. Imaginary part of the dielectric constant versus incident photon energy.

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