NIGERIA JOURNAL OF PURE AND APPLIED PHYSICS

Nigeria Journal of Pure & Applied Physics, Vol. 6, No. 1, pages 33 – 39, 2015

OPTICAL, ELECTRICAL AND SOLID STATE PROPERTIES OF NANO CRYSTALLINE ZINC SULPHIDE THIN FILMS FOR DEVICE APPLICATIONS

S. S. Oluyamo[†] and O. A. Abdulsalam

Condensed Matter and Statistical Physics Research Unit, Department of Physics,
School of Sciences, The Federal University of Technology, P.M.B. 704 Akure.
[†]Corresponding Author's Email: ssoluyamo@yahoo.futa.edu.ng

Abstract: Semiconducting Zinc Sulphide (ZnS) thin films were deposited on glass substrate using relatively simple Chemical Bath Deposition (CBD) technique. Nano crystalline ZnS thin films were fabricated in the study. Optical characterization of the films showed that the materials are transparent to visible light, opaque to ultraviolet radiation and near infra red radiation. The electrical conductivity decreases as the energy increases while the optical conductivity increases gradually over an energy range, and then sharply afterward. The XRD pattern showed that the deposited ZnS had distinct peaks at 31.59, 32.21, 44.76 and 46.73^{o} respectively with 101, 110 and 111 preferred orientations. The energy band gap of ZnS film was found to be between 3.20–3.70eV with a direct band gap transition. These properties make ZnS thin films find useful applications as cover plates for solar energy panels and materials in the fabrication of semiconductor devices. In addition, the films were found to exhibit switching potentials.

Keywords: Electrical, Optical, Solid state properties, ZnS.

1. INTRODUCTION

Nano crystalline materials have been noted to attract considerable attention due to their unique properties that are rare in macroscopic materials, attributed mainly to the sizes and surface effects of the materials. Such important and attractive technological applications of nano materials can be found in their optical, electronic, magnetic, chemical and structural properties [1].

Nano materials are often developed through various techniques on suitable substrates, hence, researchers have shown that the properties of the resulting thin film materials are to a large extent dependent on the technique of deposition. Such deposition techniques have also improved the efficiency of the materials and their utilization as sources of alternative energy to compliment the already depleting conventional energy resources, which are limited in terms of deposit and geographical location all over the world [2-4].

Thin films play significant roles in virtually all electronic and optical devices. Thin films had been used as anti-reflection coatings on window glass, video screen, camera lenses and other optoeletronic devices. These films are less than 100 nm thick and are usually made from electric transparent materials that have refractive indices less than that of the substrate [5]. Attentions are gradually being shifted to ferromagnetic and ferroelectric thin films for possible usage as computer memory as well as pharmaceutical applications especially during drug delivery [6, 7].

Deposition techniques and methods of growing thin films rage from very simple and cheap to complex and expensive. Various forms of thin films have been developed for solar radiation absorption and glassing which are used for photo-thermal-devices. Scientists are currently occupied with research into possible ways of improving the performance of solar energy devices to provide comfort in buildings and automobiles [8]. ZnS has been adjudged as a potentially important material for antireflection coating for heterojuction solar cell light emmiting diode, photovoltaic cells, etc [9, 10]. ZnS materials could also be used in radio frequency field spattered films such as CdZnS and modified ZnS/CdS [11, 12]. Research had shown that ZnS are transpament to visible light, opague to ultraviolet radiation and near infra-red radiations [13, 14].

In this work, attention is focused on the study of the optical, electrical and solid state properties of nanocrystalline ZnS through the Chemical Bath Deposition (CBD) Technique.

2. MATERIALS AND METHOD

In the deposition of ZnS thin films, glass side of dimension 75mm x 25mm x 1mm were used as substrates. The glass slides were thoroughly degreased by soaking them in a concentrated Hydrochloric (HCl) acid for about twenty four (24) hours, followed by thorough wash in a detergent, rinsed in plenty of distilled water and dried in a dust free environment. The materials used are; 1m solution of Zinc Chloride ($ZnCl_2$) which provides Zn^{2+} ions, 1m solution of Thiourea [$CS(NH_2)_2$] as S^{2-} ions source, 1M solution of Ammonia (NH_3) which is the complexing agent and 1m solution of Sodium Hydroxide (NaOH) which provides the basic medium. Five different reaction bath

Table 1: Different volume composition and time for the preparation of ZnS thin films.

Sample	Time (Hours)	1M $ZnCl_2$ (ml)	1M TU (ml)	1M NaOH (ml)	1M NH_3 (ml)	H_2O (ml)
A	6.00	10.00	10.00	10.00	10.00	10.00
B	8.00	10.00	10.00	10.00	10.00	10.00
C	6.00	15.00	15.00	5.00	5.00	10.00
D	8.00	15.00	15.00	5.00	5.00	10.00
E	8.00	15.00	15.00	10.00	5.00	5.00

compositions were made in a 50 ml. The resulting solution was thoroughly stirred with the aid of a glass rod stirrer for about sixty seconds, to obtain a homogenous solution. The chemical equations for the reactions are as follows;

$$ZnCl_2 + 2NH_3 \longrightarrow Zn(NH_3)_2Cl_2 \quad (1)$$

$$CS(NH_2)_2 + OH^- \longrightarrow CH_2N_2 + H_2O + SH^- \quad (2)$$

$$SH^- + OH^- \longrightarrow H_2O + S^{2-} \quad (3)$$

$$Zn(NH_3)_2Cl_3 + CS(NH_2)_2 + 2OH \longrightarrow ZnS + CH_2N_2 + 2NH_3 + 2H_2O + Cl \quad (4)$$

The chemical slides were clamped vertically in the reaction bath with the aid of a synthetic cover, which also helps to screen off dust particles and other impurities from getting into the reaction bath. The volume composition of the reaction bath and the deposition time were varied to get the optimum conditions for the deposition of ZnS thin films. The volume composition and the deposition period are shown in Table 1. The structural analysis was carried out using the PW 3204 X' Port Pro M D Diffractometer at the Sheda Science and Technology Village, Abuja, Nigeria while the optical analysis was examined using the UV-6045 Jenwey Spectrometer at the Engineering and Materials Research Institute (EMDI), Akure, Nigeria.

3. THEORETICAL CONSIDERATION

The calculations of the optical and electrical properties of the deposited films were done based on the theory in literatures [15, 16].

The structural and solid state properties of the films were determined from the XRD analysis. Using the Scherre's formula. The Grain Size (D) was calculated using the relation;

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (5)$$

where λ is the wavelength of X-Ray, β is the Full Width at Half Maximum (FWHM), θ is the diffraction angle and K is 0.9 which varies with (hkl) and crystalline shape.

The lattice constant (a) is calculated as;

$$a^2 = \left(\frac{\lambda^2}{4\sin^2\theta}\right)\left(h^2 + k^2 + l^2\right) \quad (6)$$

The dislocation density is given as

$$\rho = aD \quad (7)$$

while the Micro Strain

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (8)$$

4. RESULTS AND DISCUSSION

4.1 X-Ray Diffraction Study

The XRD diffraction pattern of ZnS thin films deposited for 6 hours is shown in Fig. 1. Distinct peaks of the thin films were observed at 31.59^0, 32.21^0, 44.76^0 and 46.73^0 corresponding to structures of lattice constant (a) 8.49Å, 8.33Å, 10.51Å and 11.37Å with (101), (110) and (111) preferred orientations. The broad lump on the displayed pattern could be associated with the amorphous glass substrate and some amorphous phase present in the ZnS thin films. The small values of the dislocation density and micro strain recorded indicate the formation of high quality ZnS thin films.

4.2 Optical Properties

Transmission measurements were performed at normal incidence over spectral range between 290-1110 nm. The transmission spectral of ZnS thin film obtained with different volume compositions of the reaction bath deposited for 6 hours and 8 hours are shown in Fig. 2 and Fig. 3. Generally, an increase in the transmission values over the entire spectral range was recorded with decrease in film thickness. In the visible region, the transmission ranges between 41% - 65%. It was also observed that optical transmittance increases with increase in wavelength. The transmittance values obtained accounts for the suitability of ZnS thin films as a good material for solar energy collection particularly when used as surface coating on collector plate.

Fig. 4 and Fig. 5 showed the plots of optical absorbance versus wave length of ZnS thin films. The absorbance generally decreases with increase in wavelength, and has relatively low values in the infrared region of the spectra. Good absorption was observed between the wavelength range of 290–500 nm, hence, the material is suitable for application in the fabrication of solar cells.

Fig. 6 and Fig. 7 show the plots of optical reflections and wavelength for ZnS thin film. All the films show low

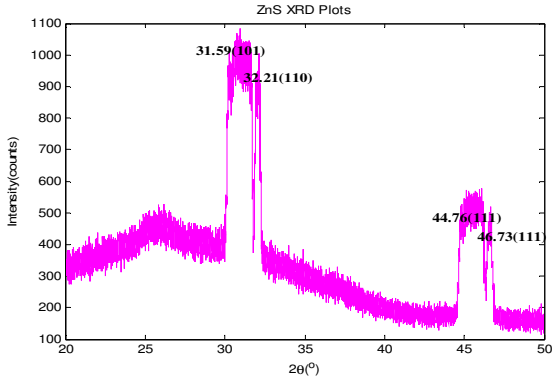

Fig. 1: X-Ray Diffraction pattern for ZnS thin film.

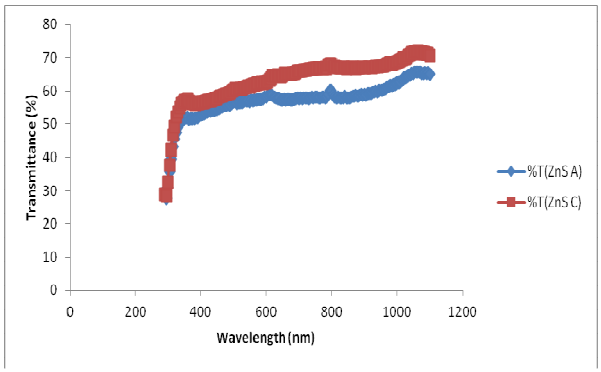

Fig. 2: Transmittance as a function of wavelength for different volumes of precursors of ZnS thin films deposition for 6 hours.

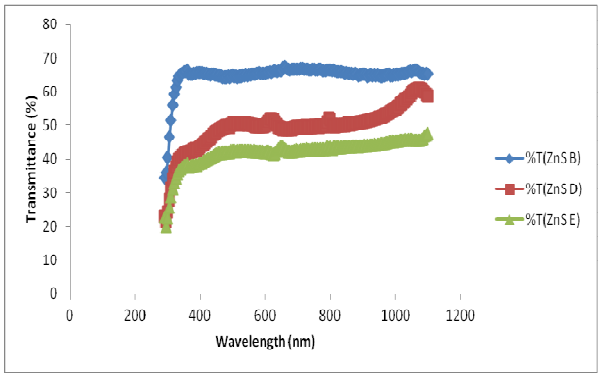

Fig. 3: Transmittance as a function of wavelength for different volumes of precursors of ZnS thin films deposited for 8 hours.

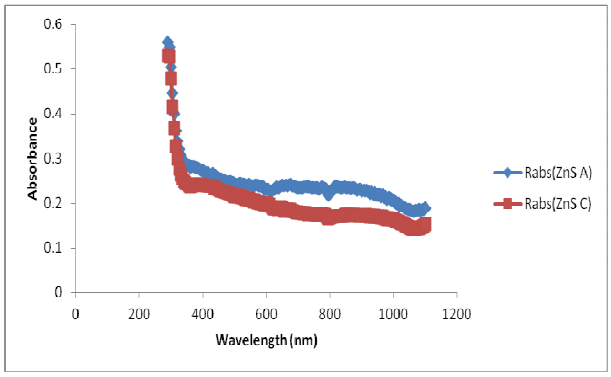

Fig. 4: Absorbance as a function of wavelength for different volumes of precursors of ZnS thin films deposited for 6 hours.

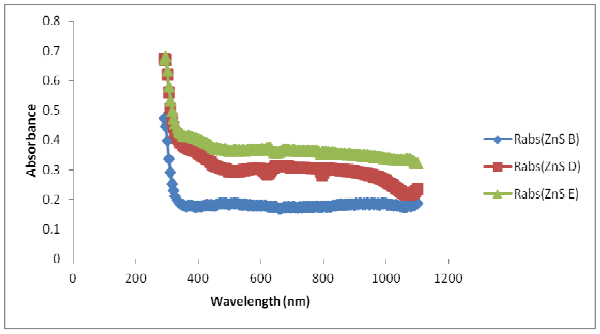

Fig. 5: Absorbance as a function of wavelength for different volumes of precursors of ZnS thin films deposited for 8 hours.

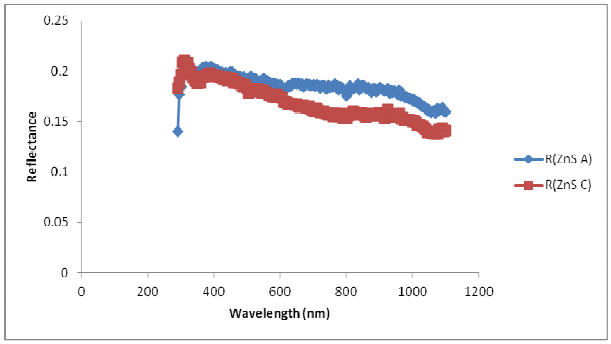

Fig. 6: Reflectance as a function of wavelength for different volumes of precursors of ZnS thin films deposited for 8 hours.

reflectance throughout the spectra region. The low values recorded confirm ZnS thin films as very good materials for anti–reflection coating [17]. The optical properties of the films are contained in Table 2.

4.3 Absorption Coefficient and Optical Band Gap

The absorption coefficient (α) was determined from the transmission and absorption spectra. The energy at the point when (α^2) is zero represents the energy gap, E_g which can be determined by extrapolation in Fig. 8 and Fig. 9

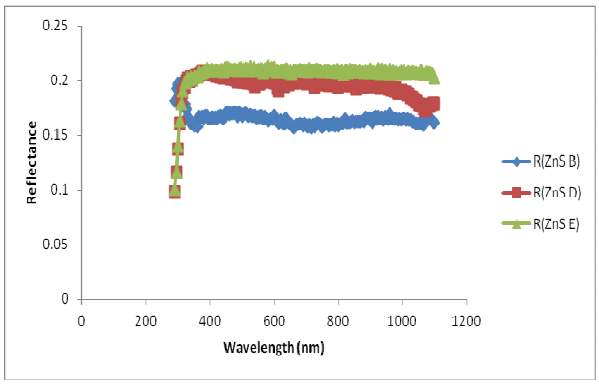

Fig. 7: Reflectance as a function of wavelength for different volumes of precursors of ZnS thin films deposited for 6 hours.

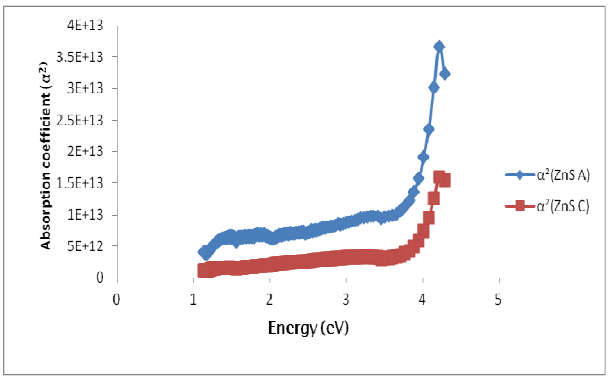

Fig. 8: Absorption coefficient (α²) as a function of energy for different volumes of precursors of ZnS thin films deposited for 8 hours.

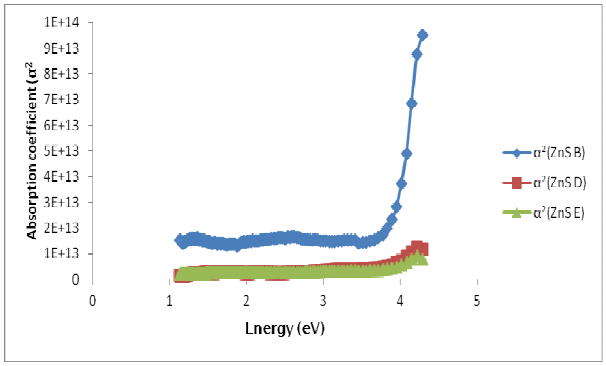

Fig. 9: Absorption coefficient (α²) as a function of energy for different volumes of precursors of ZnS thin films deposited for 6 hours.

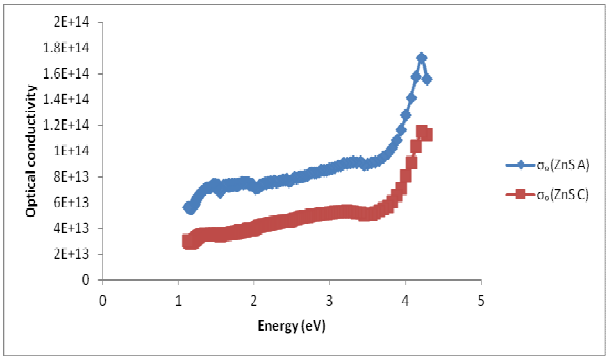

Fig. 10: Graph of optical conductivity as a function of energy for different volumes of precursors of ZnS thin films deposited for 6 hours.

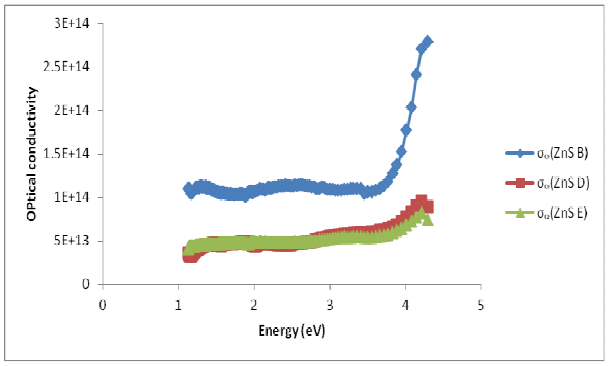

Fig. 11: Graph of optical conductivity as a function of energy for different volumes of precursors of ZnS thin films deposited for 8 hours.

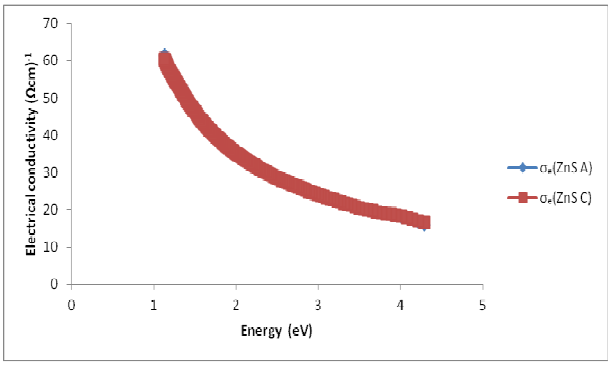

Fig. 12: Electrical conductivity as a function of energy for different volumes of precursors of ZnS thin films deposited for 6 hours.

respectively. The values of absorption coefficient (α) recorded in this study range from 1.47-3.99 x10^6 cm^{-1}. It was observed that the ZnS thin films in the study exhibit direct band gap transition as in Fig. 10 and Fig. 11 [18].

4.4 Electrical Conductivity and Solid State Properties

Fig. 12 and Fig. 13 showed the electrical conductivity of ZnS thin films. The films were found to conduct well at low frequency, that is, the electrical conductivity decreases with increase in energy of the incident radiation. It was also observed that the materials conduct better at photon energy within the ultraviolet and infra-red electromagnetic spectrum. The electrical conductivity of ZnS thin film was

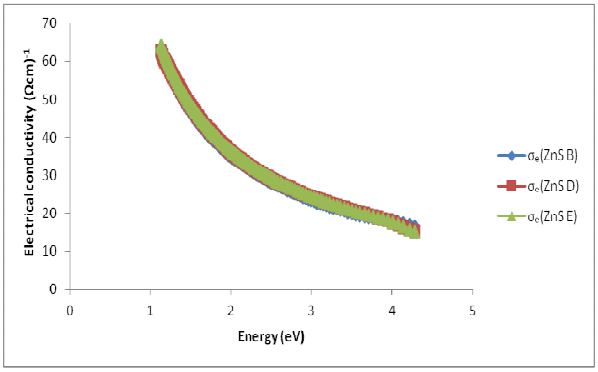

Fig. 13: Electrical conductivity as a function of energy for different volumes of precursors of ZnS thin films deposited for 8 hours.

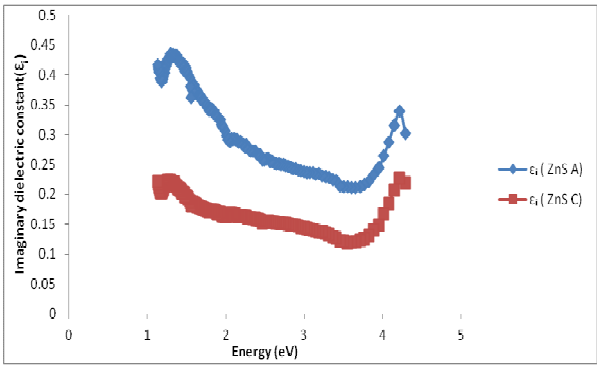

Fig. 14: Imaginary dielectric constant (ε_i)as a function of energy for different volumes of precursors of ZnS thin films deposited for 6 hours.

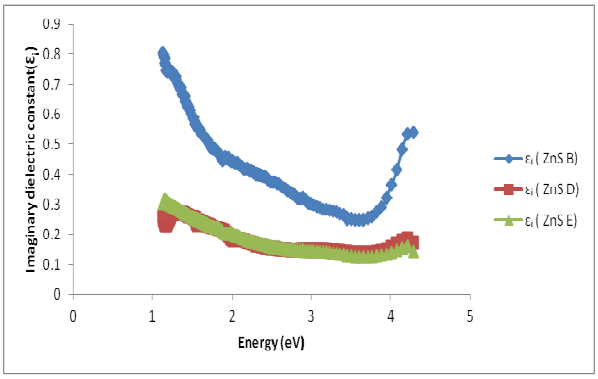

Fig. 15: Imaginary dielectric constant (ε_i) as a function of energy for different volumes of precursors of ZnS thin films deposited for 8 hours.

found to be thickness dependent as the electrical conductivity increases with increase in film thickness. The electrical conductivity of the thin film varies from 39.05 x 10^{-5}-40.85 x10^{-5} $(\Omega cm)^{-1}$. These values are within the electrical conductivity range of 10^{-12}-10^{2} $(\Omega cm)^{-1}$ for semiconductor materials. Fig. 14 – Fig. 17 show the real and imaginary dielectric constant of the thin films. The

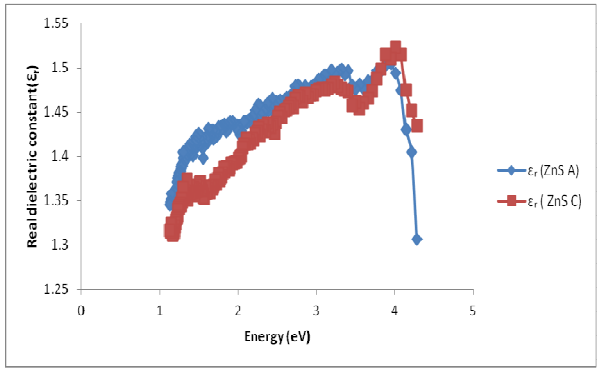

Fig. 16: Real dielectric constant (ε_r) as a function of energy for different volumes of pre cursors of ZnS thin films deposited for 6 hours.

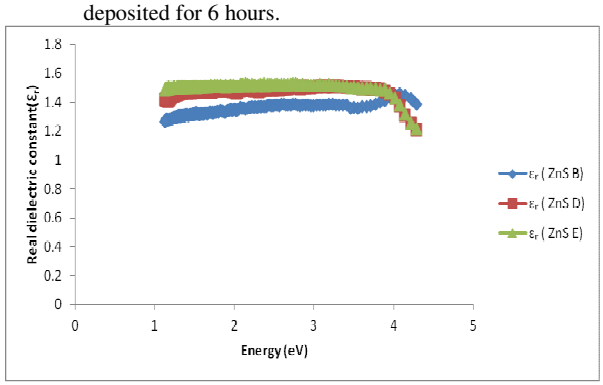

Fig. 17: Real dielectric constant (ε_r) as a function of energy for different volumes of precursors of ZnS thin films deposited for 8 hours.

imaginary dielectric constant of the materials decreases initially with increase in energy followed by a sharp increase. The reverse is the case for the real dielectric constant. This characteristic suggests a switching capability of the deposited ZnS thin film material.

Table 3 and Table 4 show the solid state and electrical properties respectively of the ZnS thin films. Nano crystalline films were fabricated with the thickness of the samples deposited for six hours given as 212.4 and 109.0 nm, while those deposited for eight hours are 315.7, 432.1 and 523.1 nm respectively. These values clearly indicate that the reaction bath had influence on the properties of the films. This also confirms recent research [14, 18].

5. CONCLUSION

Nano crystalline ZnS thin films were fabricated in the study. The electrical conductivity of ZnS thin film was found to be thickness dependent and within the electrical conductivity range of 10^{-12}-10^{2} $(\Omega cm)^{-1}$ for semiconductor materials with a direct band gap transition. The optical and solid state properties of the material affirm the suitability of the films for application in device fabrication and applications.

Table 2: Optical properties of deposited ZnS thin films.

Sample	Absorbance (A)	Transmittance (T)	Reflectance (R)	Refractive index (n)	Absorption coefficient (α) x 10^5	Extinction Coefficient (k)	Optical conductivity (σ_o) x 10^{13}
A	0.24	0.57	0.19	1.21	2.66	0.13	7.68
B	0.19	0.65	0.16	1.81	3.99	0.20	11.33
C	0.20	0.64	0.17	1.81	1.47	0.071	4.21
D	0.31	0.49	0.19	1.21	1.66	0.081	4.80
E	0.42	0.41	0.17	1.21	1.87	0.087	4.90

Table 3: Solid state properties of deposited ZnS thin films.

hkl	2θ (^{o})	d-spacing (Å)	Lattice constant, a(Å)	FWHM (β)	Grain size D (Å)	Dislocation density ρ (line/m^2)	Micro-strain (ε)
101	31.58	2.83	8.49	0.3072	4.69	0.400	0.0739
110	32.21	2.77	8.33	0.0480	0.30	0.025	0.0115
111	44.76	2.02	10.51	0.0768	0.19	0.021	0.0177
111	46.73	1.94	11.37	0.0768	0.19	0.022	0.0176

Table 4: Electrical properties of deposited ZnS thin films.

Sample	Thickness (nm)	Eg (eV)	Electrical Conductivity (σ_e)	Imaginary Dielectric (ε_i)	Real Dielectric (ε_r)
A	212.4	3.40	39.80	0.34	1.43
B	315.7	3.20	39.10	0.51	1.34
C	109.0	3.70	39.05	0.18	1.40
D	432.1	3.60	40.29	0.21	1.47

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