The Influence of Substrate Temperature on Properties of Zinc Sulphide Thin Films Synthesized by Chemical Spray Pyrolysis

Research Article

Received: 09 November 2019

Accepted: 11 December 2019

Published: 02 January 2020

P. O. Ofor¹, S. N. Ude¹, G. M. Whyte², C. S. Obayi¹, P. S. Nnamchi¹, A. D. Omah¹, F. U. Whyte¹, S. Madu¹, U. C. Ogbuefi³, C. C. Daniel-Mkpume¹, B.O. Anyaka³, B. A. Okorie¹ & F. I. Ezema²

¹Metallurgical and Materials Engineering Department, University Nigeria, Nsukka, Nigeria.

²Crystal Growth Laboratory, Physics Department, University of Nigeria, Nsukka, Nigeria.

³Electrical Engineering Department, University Nigeria, Nsukka, Nigeria.

Corresponding Author

Author Email:

peter.offor@unn.edu.ng

Abstract: Chemical spray pyrolysis (CSP) was employed to deposit Zinc sulphide (ZnS) thin films with soda-lime glass (slg) as substrates at 300 °C, 350 °C and 400 °C using solutions made of Zinc chloride (0.1 M) and Thiourea (0.1 M). The transmittance (T) at 550 nm gave 42.35 and 87.22% while energy band gap (E_g) is between 3.63 – 4.03 eV. The refractive indices (n) of the thin films were within 1.32 to 3.84 at $\lambda = 550$ nm. The X-ray diffraction (XRD) peaks of films were identified as hexagonal and cubic structures. The sizes of the crystallites are in the range of 4.958 and 6.662 nm. Scanning electron microscopy (SEM) revealed clusters of nanoparticles and pores. The Raman and Fourier transform infrared (FTIR) results showed the presence of Zn-S vibrations while photoluminescence indicated the existence of sulphur vacancies. The film's hydrophilic surface nature was revealed by the contact angle measurement.

Keywords: Zinc Sulphide, Structure, FTIR, Band gap.

1. INTRODUCTION

Zinc sulphide films find vast applications in photoluminescent, optoelectronic and solar cells applications [1]. This has led to recent focus of research on this area of chalcogenide semiconductor materials. It is characterized by high refractive index, wide direct energy gap and high transmittance in the visible spectra [2], non-poisonous and ecofriendly [3]. The goal of good research is to improve on device performance and reliability at minimal cost. This has led researchers to deposit thin films using different techniques as CBD [4], SILAR [5], CSP [6], thermal evaporation [7] and Sol-gel [8]. In the midst of these, CSP is more advantageous because it is economical and useful for deposition of uniform and coherent thin films on large area surfaces at moderate operating temperatures [9].

Thin films are very important materials for device fabrications [10]. As pointed out earlier, the goal of profitable and result oriented research is to improve on device performance and reliability at minimal cost. Such devices are expected to operate at faster speed with reduced power consumption, reduced weight, enhanced reliability, reduced size and more economically worthwhile. The investigation of the properties of such thin film materials is of utmost importance to properly understand the specific area of application of any deposited thin film for the production of suitable devices with improved properties. Though research on ZnS films deposition by CSP has been ongoing yet a more detailed work is still required in the inquiry into the properties of spray-formed ZnS thin films [11] for probable device application. The impact of substrate temperature on the structure, optical and surface morphology of spray-formed ZnS thin films is investigated in this study.

2. EXPERIMENTAL PROCEDURE

The soda-lime glass substrates used in this work were thoroughly treated with double distilled water (DDW) and detergent. Then, they were boiled in chromic acid for 1 hour and allowed for 5 hours in the acid. The cleaning

process was continued with the substrates being washed again in DDL after they were removed from the chromic acid. They were cleaned ultrasonically for 1 hour and allowed to dry and lastly cleaned with acetone in readiness for CSP deposition.

The precursor solutions were made of Thiourea ($\text{CS}(\text{NH}_2)_2$) AR and zinc chloride (ZnCl_2) (dry) AR. Zn^{2+} was made available by ZnCl_2 while S^{2-} was made available by $\text{CS}(\text{NH}_2)_2$. 0.1 M ZnCl_2 solution and 0.1 M ($\text{CS}(\text{NH}_2)_2$) solution were prepared in DDW. The solution quantity used as final spray solution was 30 ml. The solution quantity comprised 15 ml of 0.1 M ZnCl_2 solution and 15 ml of 0.1 M of ($\text{CS}(\text{NH}_2)_2$) solution and sprayed on substrates at 300 °C, 350 °C and 400 °C to form the ZnS thin films.

The equation for the reaction is as follows:

The spray parameters are: the spray rate is 4 ml/min, air was used as the carrier gas of flow rate of 6 ml/min, the pressure of carrier gas is maintained between 25 - 50 kg/cm², the distance of spray nozzle from the substrate is 20 cm, the volume of the solution used is 30 ml and the speed of spray head rotation is 25 mm/min.

The XRD, SEM, Raman spectroscopy, optical properties, photoluminescence and contact angle were measured as reported in an earlier study [1].

3. RESULTS AND DISCUSSION

3.1 Structural Studies

Figure 1 reveals the diffraction patterns of CSP deposited ZnS films. The presence of multiple and broad peaks is an indication that the ZnS thin films are both polycrystalline and nanocrystalline in nature as reported in the literature [12]. The observed values of the 2θ angles and d-spacing for films synthesized at 300 °C exhibited peaks consistent with JCPDS Card No. 00-080-0080 cubic ZnS structure; at 350 °C: JCPDS Card No. 00-001-0677 wurtzite ZnS structure and at 400 °C: JCPDS Card No. 00-080-0080 cubic spharelite ZnS structure. Results are presented in Table 1.

Figure 1: Diffraction patterns of films at (a) 300 °C (b) 350 °C and (c) 400 °C

The thin films deposited at 350 °C had hexagonal wurtzite ZnS structure whereas films at 300 °C and 400 °C had cubic structure. The hexagonal wurtzite structure of ZnS films with plane oriented along (002) have been reported to possess good match to CuInS₂ (112) orientation plane [13]. Hence, they are good for the production of suitable lattice matched CuInS₂/ZnS heterojunction in solar cells [13]. Generally, it has been observed that ZnS thin films are profitably used in photovoltaic devices [14]. The d-values, grain size (G), dislocation density (δ) and microstrain (ε) were estimated using the following equations:

$$2d \sin \theta = n\lambda \quad [1, 10],$$

$$G = \frac{k\lambda}{\beta \cos \theta} \quad [1, 12],$$

$$\delta = \frac{1}{G^2} \quad [10, 12],$$

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad [10, 12]$$

Where all variables retain their usual meaning.

Table 1: Lattice parameters of films at varying temperatures

Sample	Observed 2θ	Standard 2θ	Obs. d-space (Å)	Std. d-space (Å)	FWHM (β)	(hkl)	Grain size (G) (nm)	Dislocation density (δ) (Lines/m ²) x10 ¹⁵	Micro strain (ε) x10 ⁻³
Z300	28.876	28.910	3.089	3.086	0.050	111	6.662	22.532	6.884
	48.111	48.111	1.890	1.890	0.023	220	6.662	22.532	6.884
	57.052	57.107	1.613	1.612	0.015	311	6.662	22.532	6.884
Z350	28.732	28.681	3.105	3.110	0.037	002	4.983	40.273	7.247
	47.847	47.835	1.900	1.900	0.032	110	4.983	40.273	7.247
	57.982	57.955	1.589	1.590	0.025	201	4.983	40.273	7.247
Z400	28.987	28.910	3.078	3.086	0.022	111	4.958	40.681	7.430
	48.188	48.111	1.887	1.890	0.032	220	4.958	40.681	7.430
	57.108	57.107	1.612	1.612	0.044	311	4.958	40.681	7.430

The parameters presented in Table 1 indicates that the average δ- and ε-values increased with temperature while the mean crystalline size decreased with temperature.

The FT-Raman spectrum of films deposited without complexing agent by CSP is shown in Figure 2.

Figure 2: Raman shift of ZnS thin film deposited without a complexing agent.

The Raman spectral assignment of the ZnS thin films is given in Table 2 showing phonon modes whose wave numbers agree well with reference values for ZnS thin films.

Table 2: FT-Raman frequencies of films

Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹) [Reference]
263	Zn-S	261 [15]
341	w [combined longitudinal & transverse polarized modes]	345 [15]
371	LA + TO	386, 388 [16], 0-400 [17]
455	LA + LO	458 [17]
561	2TO	546, 561 [18]
698	LO + TO	600-700 [19], [18]
773	2LO	778 [18]
854	ν(CC)	841, 844 [20]
1081	3LO	1082 [18]

3.3 FTIR Studies

FTIR spectrum of zinc sulphide thin films deposited without a complexant by CSP is presented in figure 3.

Figure 3: FTIR spectrum of the film

Table 3: FTIR frequencies of ZnS films

Wave number (cm ⁻¹)	Assignment	Wave number (cm ⁻¹) [Reference]
621	Zn-S vibration	620 [21]
647	Zn-OH stretching peak	648 [22]
828	Resonance interaction between S ²⁻ vibrational modes	851 [23]
1042	C-O stretching mode	1000-1282 [23]
1538	C=S stretching mode	1500 – 1650 [24]
2904	C-H Stretching vibration	2820-3050 [25]
3331	N-H Stretching	3300-3395 [26]

3.4. Surface morphology

The scanning electron micrographs of films at 300°C, 350°C, and 400°C are presented in Figure 4.

Figure 4: SEM images of films at (a) 300°C (b) 350°C and (c) 400°C

The micrographs revealed that the films contain some clusters of non-uniformly dispersed nanoparticles over the substrate's surface. Some nanodot-like and rectangular shaped nanorod-like particles and clusters are evident in the films deposited at 400°C and 300°C. The film deposited at 350°C appears relatively smooth with very tiny nanoparticles.

3.5. Optical properties

The optical parameters of films at 300°C, 350°C, and 400°C by spray pyrolysis technique are shown in Table 4 and in figures 5 – 14.

3.5.1 Absorbance (A)

Fig. 6 shows the absorbance plot for ZnS thin films synthesized at 300 °C, 350 °C and 400 °C.

Figure 5: The absorption spectra of ZnS thin films as a function of Wavelength.

Figure 5 shows that the absorbance increased abruptly with wavelength nearby the edge of absorption. Figure 5 shows that films of high absorbance at low wavelengths which decreased with increasing wavelength. The absorbance of films synthesized at 300 °C and 350 °C are lower and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has higher absorbance. The energy consistent with the edge of absorption is very critical because its significant contribution in deciding the value of the band gap of ZnS semiconductor thin films [1]. The transfer of electrons from valence band to the conduction band commences once the photon energy corresponds with the band gap of the thin films [1, 27]. Sharp absorption edge is normally displayed by thin films that have low density of defects near the band-edge which implies that the thin film synthesized at 300 °C and 350 °C near the band edge, possesses minimal defect density [1, 28, 29].

3.5.2 Transmittance (T)

Figure 6 shows the *T* plot for films synthesized at 300 °C, 350 °C and 400 °C. A close look at the Figure reveals decreasing values of *T* with wavelength. The values are displayed in Table 4. The *T* of the films synthesized at 300 °C and 350 °C are higher and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has lower transmittance. Films with high *T* in the NIR region are suitable for infrared photoelectric detection and selective coating for solar cells [30 - 32].

Figure 6: Transmittance plots of films.

3.5.3 Reflectance (*R*)

Figure 7 shows the *R* plot for the films synthesized at 300 °C, 350 °C and 400 °C. The *R* of films was computed by the common equation [27]:

$$R + T + A = 1 \quad (2)$$

Figure 7: The Reflectance spectra of the films.

The values of *R* at 550 nm are exhibited in Table 4.

3.5.4 Absorption coefficient (*α*)

Figure 8 shows the *α* plot for films synthesized at 300 °C, 350 °C and 400 °C.

α was computed using equation 6 [31]:

$$\alpha = 2.303A/t \quad (6)$$

It is vividly seen that the *α* increased with temperature. The *α* of the films are given in Table 4. Figure 8 shows that *α* reduced with decrease in photon energy as reported in [27].

Figure 8: Absorption coefficient of ZnS films

3.5.5 Band gap energy (E_g)

Fig. 9 shows the energy band gap plot for ZnS thin films synthesized at 300 °C, 350 °C and 400 °C.

Figure 9: Optical energy gap of films

The well-known Tauc relation was used to determine the E_g of the films [33, 34]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (7)$$

The E_g for the films are presented in Table 4. The E_g of films are in good agreement with reported values [18, 35]. The increase in E_g will lead to the enhancement of short circuit current of solar cell which will make it possible for the films to be expediently utilized as window layer in heterojunction solar cells as reported in the literature [14].

3.5.6 Refractive index (n)

Fig. 10 shows the n plot for ZnS thin films synthesized at 300 °C, 350 °C and 400 °C.

n of the films was evaluated using: $n = (1 + R + R^{1/2}) / (1 - R)$ [12, 31].

Figure 10: The refractive index of the films.

Fig. 10 shows that the n decreases with increase in the wavelength. The n of the films synthesized at 300 °C and 350 °C are lower and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has higher n . The effects of biaxial stresses on the n of thin films have been reported in the literature [14]. The literature indicated that the n increases with decrease in biaxial tensile stress. This may be attributed to the fact that the synthesized ZnS films might have experienced change in their crystalline network during the spray process. This may have led to the profound change observed in the values of n of the synthesized ZnS thin films in this research work. The n of the films is shown in Table 4.

3.5.7 Extinction coefficient (k)

Fig. 11 shows the k plot for the films synthesized at 300 °C, 350 °C and 400 °C. k was evaluated by equation:

$$k = \frac{\alpha\lambda}{4\pi} \quad [36].$$

Figure 11: Extinction coefficient plot of the films.

Fig. 11 shows that the k of the films decreases with rise in wavelength as earlier reported [1, 37]. The k of the films synthesized at 300 °C and 350 °C are lower and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has higher extinction coefficient. The k of the films is given in Table 4.

3.5.8. Real dielectric constant (ϵ_r)

Fig. 12 shows the ϵ_r plot for the films synthesized at 300 °C, 350 °C and 400 °C.

Figure 12: The Real dielectric constant of the films.

The ϵ_r was calculated by equation: $\epsilon_r = n^2 - k^2$ [27]

It is observed that ϵ_r of the films decrease with rise in wavelength. The ϵ_r of the films synthesized at 300 °C and 350 °C are lower and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has higher real dielectric constant. The ϵ_r are shown in Table 4.

3.5.9. Imaginary dielectric constant (ϵ_i)

Fig. 13 shows the imaginary dielectric constant plot for ZnS thin films synthesized at 300 °C, 350 °C and 400 °C.

Figure 13: The imaginary dielectric

The imaginary parts of dielectric constant were estimated using: $\epsilon_i = 2nk$ [27]. The figure shows that ϵ_i of the films decreased with rise in wavelength. The ϵ_i of the films synthesized at 300 °C and 350 °C are lower and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has higher imaginary dielectric constant. The ϵ_i of the films are given in Table 4.

3.5.10. Optical conductivity (σ)

Fig. 14 shows the σ plot for the films synthesized at 300 °C, 350 °C and 400 °C.

Figure 14: σ plot for the films synthesized at 300 °C, 350 °C and 400 °C

The σ is obtained from: $\sigma = \frac{\alpha nc}{4\pi}$ [12] where the optical variables retain their usual meaning.

Fig. 14 shows clearly that σ of the ZnS thin films increases with photon energy. The deposited films have high absorbance in the region of high photon energy. The observed increase in σ is attributed to excitation of electrons by incident photon energy [38]. Moreover, it is shown that the σ of the films synthesized at 300 °C and 350 °C are lower and relatively constant in the visible portion of the electromagnetic wave while the one synthesized at 400 °C has higher optical conductivity. The σ values are presented in Table 4.

Table 4. Optical parameters of deposited ZnS films [at $\lambda = 550$ nm for T, R, n, k, ϵ_r and ϵ_i and at 3.0 eV for α and σ].

Sample	T (%)	R (%)	$\alpha \times 10^4$ (cm) ⁻¹	E _g (eV)	N	K $\times 10^{-2}$	ϵ_r	$\epsilon_i \times 10^{-2}$	$\sigma \times 10^{12}$ (s ⁻¹)
Z300	87.22	12.41	0.41	3.63	1.32	0.52	1.75	2.05	0.398
Z350	87.04	12.90	1.46	3.78	1.35	0.51	1.87	3.62	0.682
Z400	42.35	57.60	16.79	4.03	3.84	15.73	14.86	120.66	38.897

3.6. Photoluminescence (PL)

PL spectrum of the films spray-formed at 400 °C is displayed in Figure 15. Figure 15 shows peaks at 379 and 413 nm emission wavelengths. The peaks at 379 and 413 nm revealed excitonic near band edge emission and the presence of sulphur vacancies respectively. The extension of broadened peak might have been produced by the amorphous glass substrate as highlighted by [38].

Figure 15: Photoluminescence spectra of the film.

3.7. Contact angle

The only sample which contact angle was measured is the film formed at 400°C. Its contact angle is shown in Figure 16.

Figure 16: The Contact angle of the ZnS film

Figure 16 shows contact angle of 69.3° which implies that the surface is hydrophilic, that's why it can practically find application for the production of charge storage devices [11, 39]. The surface free energy is 42.15 MJ/m².

4. CONCLUSIONS

Chemical Spray Pyrolysis was employed in depositing ZnS films at 300°C, 350°C and 400°C using solutions made of Zinc chloride (0.1 M) and Thiourea (0.1 M). The transmittance is between 42.35 - 87.22 %. The energy band gaps of the films are between 3.63 – 4.03 eV. The thin films' refractive indexes are from 1.32 to 3.84 at 550 nm. The XRD show films of cubic and hexagonal structures. The grain size is between 4.958 and 6.662 nm whereas the surface morphology contains clusters of nanoparticles and pores. Raman spectroscopy and the FTIR spectroscopy exhibited Zn-S vibrations while photoluminescence indicated the existence of sulphur vacancies. The hydrophilic surface nature of films was revealed by the contact angle analysis.

The assistance from MOU between the University of Nigeria, Nsukka, Nigeria and Shivaji University, Kolhapur is acknowledged by the authors.

REFERENCES

- [1] Offor P. O., Nwanya A. C., Omah A. D., Daniel-Mkpume C. C., Malik M., Okorie B. A., Ezema F. I. (2017) Chemical spray pyrolysis deposition of zinc sulphide thin films using ethylenediaminetetraacetic acid disodium salt complexant. *J Solid State Electrochem* 21:2687– 2697. <https://doi.org/10.1007/s10008-017-3668-2>
- [2] P.A. Luque, A. Castro-Beltran, A.R. Vilchis-Nestor, M.A. Quevedo-Lopez and A. Olivas (2015): Influence of pH on Properties of ZnS Thin Films Deposited on SiO₂ Substrate by Chemical Bath Deposition, *Materials Letters* 140, 148–150
- [3] A. Derbali, A. Attaf, H. Saidi, H. Benamra, M. Nouadji, M.S. Aida, N. Attaf and H. Ezzaouia (2018): Investigation of Structural, Optical and Electrical Properties of ZnS Thin Films Prepared by Ultrasonic Spray Technique for Photovoltaic Applications, *Optik* 154, 286–293
- [4] B. A. Ezekoye, P. O. Offor, V. A. Ezekoye, F. I. Ezema (2013): Chemical Bath Deposition Technique of Thin Films: A Review, *International Journal of Scientific Research*, Volume: 2/Issue: 8, pp. 452 – 456.
- [5] Haneefa, M.M., Kandasamy, S., Suldanmohideen, S.F., Mohideen, M.G.K. and Jeyaraj, D.R. (2015): Structural Properties of Zinc Sulphide Thin Films Deposited by SILAR Method, *Journal of Chemical and Pharmaceutical Research*, 7 (10 S), pp. 141 – 145.
- [6] K. Ben Bacha, N. Bitri and H. Bouzouita (2016): Effect of Annealing Parameters on Structural and Morphological Properties of Sprayed ZnS Thin Films, *Optik* 127, 3100–3104
- [6] S. Mahmoud and Z. S. El Mandouh (1987): Structure and Optical Properties of Vacuum-Deposited Scandium Films on Crystalline Substrates, *Journal of Material Science*, 22, 651 – 656
- [7] Yow-Jon Lin W-S (2016): Effects of sulfide treatment on the electrical, photoluminescent and structural properties of ZnS films. *J. Lumin* 172, 286–289.
- [8] Tatjana D., Inga, G., Malle, K., Valdek, M., Maarja, G., Ilmo, S., Kathriin, U., Risto, V., and Tarmo, U. (2015): Spray Pyrolysis Deposition and Characterization of Highly C-Axis Oriented Hexagonal ZnS Nanorod Crystals, *Cryst. Res. Technol.* 50, No. 1, pp. 85–92.
- [9] P. O. Offor, B. A. Okorie, F. I. Ezema, V. S. Aigbodion, C. C. Daniel-Mkpume and A. D. Omah (2015): Synthesis and Characterization of Nanocrystalline Zinc Sulphide Thin Films by Chemical Spray Pyrolysis, *Journal of Alloys and Compounds*, 650, pp. 381 – 385.
- [10] A. Derbali, A. Attafa, H. Saidi, H. Benamra, M. Nouadji, M.S. Aida, N. Attaf and H. Ezzaouia (2018): Investigation of Structural, Optical and Electrical Properties of ZnS Thin Films Prepared by Ultrasonic Spray Technique for Photovoltaic Applications, *Optik* 154, 286–293.
- [11] Offor P. O., Okorie B. A., Lokhande C. D., Patil P. S., Ezema F. I., Omah A. D., Aigbodion, V. S. Ezekoye B. A. and Ezema I. C. (2017): The Properties of Spray-Deposited Zinc Sulphide Thin Films using Trisodium Citrate

- [12] Daranf, W., Aida, M.S., Hafdallah, A. and Lekiket, H. (2009): Substrate Temperature Influence on ZnS Thin Films Prepared by Ultrasonic Spray, *Thin Solid Films* 518, pp. 1082–1084.
- [13] Derbali A., Attaf A., Saidi H., Benamra H., Nouadji M., Aida M.S., Attaf N. and Ezzaouia H. (2018): Investigation of Structural, Optical and Electrical Properties of ZnS Thin Films Prepared by Ultrasonic Spray Technique for Photovoltaic Applications, *Optik* 154, pp. 286–293
- [14] Pillai, S., Seery, M., Synnott, D., Colreavy, J. and Hinder, S. (2013), Novel Microwave Assisted Synthesis of ZnS Nanomaterials, *Nanotechnology*, 24, pp. doi: 10.1088/0957-4484/24/4/045704.
- [15] Cheng, Y. C., Jin, C. Q., Gao, F., Wu, X. L., Zhong, W., Li, S. H. and Chu, P.K. (2009): Raman scattering study of zinc blende and wurtzite ZnS, *Journal of Applied Physics* 106, pp. 123505-1 - 123505-5.
- [16] Díaz-Reyes, J., Castillo-Ojeda, R., Martínez-Juárez, J., Zaca-Moran, O., Flores-Mena, J. E. and Galván-Arellano, M. (2014), Growth and Characterization of ZnS Nanofilms Grown by Rf Magnetron Sputtering on GaAs, *International Journal of Circuits, Systems and Signal Processing*, 8, pp. 15 – 21.
- [17] Gode, F. (2011): Annealing Temperature Effect on the Structural, Optical and Electrical Properties of ZnS Thin Films, *Physica B* 406, pp. 1653–1659.
- [18] Yung-Tang, N. and In-Gann, C. (2006), Raman Scattering and Electroluminescence of ZnS:Cu,Cl Phosphor Powder, *Applied Physics Letters* 89, pp. 261906-1 - 261906-3.
- [19] Kim, S-Y., Hwang, C-S., (2010), Syntheses and Optical Characterizations of ZnS:Mn Nanocrystals Capped by Polyethylene Oxide Molecules of Varying Molecular Weights, *Bull. Korean Chem. Soc.* Vol. 31, No. 12, pp. 3834 – 3837.
- [20] Ummartyotin, S., Bunnak, N., Juntaro, J., Sain, M. and Manuspiya, H. (2012), Hybrid Organic–Inorganic of ZnS Embedded Pvp Nanocomposite Film for Photoluminescent Application, *C. R. Physique* 13, pp. 994–1000.
- [21] Dhanma, M. and Kavitha, B. (2009): Influence of TEA (Complexing Agent) on the Structural Properties of CBD ZnS Thin films, *Chalcogenide Letters*, Vol. 6, No. 7, pp. 299 – 307.
- [22] Nagamani, K., Revathi, N., Prathap, P., Lingappa, Y., Reddy, K.T.R. (2012), Al-Doped ZnS Layers Synthesized by Solution Growth Method, *Current Applied Physics* 12, pp. 380-384.
- [23] Huang, W. H., Chan, S.W., Lee, Y.C. (2015): Optical Properties of Zinc Sulphide Thin Movies Prepared by Spray Pyrolysis, *Fabrics Journal*, Volume 4, No.2, pp. 35-40.
- [24] Agarwal, S., Patidar, D. and Saxena, N.S. (2011), Effect of ZnS Nanofiller and Temperature on Mechanical Properties of Poly(methyl methacrylate), *Journal of Applied Polymer Science*, Vol. 123, pp. 2431–2438.
- [25] Changli, L., Zhanchen, C., Zuo, L., Bai, Y. and Jiacong, S. (2003), High Refractive Index Thin Films of ZnS/Polythiourethane Nanocomposites, *J. Mater. Chem.*, 13, 526–530.
- [26] Saeed NM (2011) Structural and Optical Properties of ZnS Thin Films Prepared by Spray Pyrolysis Technique. *Journal of Al-Nahrain University*, 14:86-92.

- [27] Mansour BA, Shaban H, Gad SA, EL-Gendy YA, Salem AM (2010) Effect of film thickness, annealing and substrate temperature on the optical and electrical properties of $\text{CuGa}_{0.25}\text{In}_{0.75}\text{Se}_2$. *Journal of Ovonic Research*, 6, 13-22..
- [28] Marquez E, Shaaban ER, Abousehly AM, (2014) Structural and optical properties of ZnS thin films. *Int. J. New. Hor. Phys.* 1, 1, 17-24.
- [29] Ezenwa IA, Elekalachi CI (2015) Transmittance Spectra of ZnS Thin Film at Varying Concentration of Zinc ion Precursor. *Physics Journal* 1:320-324.
- [30] Osuji RU (2016) *Lovely Surprises in Small Packages: Thin Film Photovoltaics*. University of Nigeria Press Ltd, Nsukka.
- [31] Lohar GM, Shinde SK, Fulari VJ (2014) Structural, Morphological, Optical And Photoluminescent Properties of Spray-Deposited ZnSe Thin Film, *J Semicond* 35:113001-113001-5.
- [32] Haneefa, M.M., Kandasamy, S., Suldanmohideen, S.F., Mohideen, M.G.K. and Jeyaraj, D.R. (2015): Structural Properties of Zinc Sulphide Thin Films Deposited by SILAR Method, *Journal of Chemical and Pharmaceutical Research*, 7 (10 S), pp. 141 – 145.
- [33] Deepa K, Preetha KC, Murali KV, Dhany AC, Ragina AJ, Remadevi TL (2014) The Effect of Various Complexing Agents on the Morphology and Optoelectronic Properties of Chemically Deposited ZnS Thin Films: A Comparative Study. *Optik* 125:5727–5732.
- [34] Pitchaimani K, Amalraj L, Muthukumaran S (2016) Microstructure, optical and structural characterization of $\text{Cd}_{0.98}\text{Fe}_{0.02}\text{S}$ thin films co-doped with Zn by chemical bath deposition method. *Physica E* 78:56–64.
- [35] Elidrissi B, Addou M, Regragui M, Bougrine A, Kachouane A, Bernède JC (2001) Structure, Composition and Optical Properties of ZnS Thin Films Prepared by Spray Pyrolysis. *Materials Chemistry and Physics* 68:175–179.
- [36] Bacha BK, Timoumi A, Bitri N, Bouzouita H, (2015) Structural, Morphological and Optical Properties of Sprayed ZnS Thin Films on Various Substrate Natures. *Optik* 126:3020–3024.
- [37] Jasib AA, Yousif AA (2015) The Effect of Thickness Nanoparticle ZnS Films on Optical Properties. *International Journal of Basic and Applied Science* 03:38-51.
- [38] Heine, J.R., Rodriguez-Viejo, J., Bawendi, M.G. and Jensen, K.F. (1998): Synthesis of CdSe Quantum – Dot – ZnS Matrix Thin Films Via Electrospray Organometallic Chemical Vapour Deposition, *Journal of Crystal Growth*, 195, pp. 564 – 568.
- [39] Ubale AU, Chipade K. S., Bhute M. V., Raut P. P. , Malpe G. P., Sakhare Y. S., Belkhedkar M. R. (2012) Structural, Optical and Electrical Properties of Nanostructured CdS:CuS Composite Thin Films Grown by CBD Method. *International Journal of Materials and Chemistry* 2:165-172.