

1-1-2008

## The Study of Copper Zinc Sulphide (CuZnS<sub>2</sub>) Thin Films

CHIDI CHUKWUEMEKA UHUEGBU

ELISHA BAMIDELE BABATUNDE

CORNELIUS O. OLUWAFEMI

Follow this and additional works at: <https://journals.tubitak.gov.tr/physics>



Part of the [Physics Commons](#)

---

### Recommended Citation

UHUEGBU, CHIDI CHUKWUEMEKA; BABATUNDE, ELISHA BAMIDELE; and OLUWAFEMI, CORNELIUS O. (2008) "The Study of Copper Zinc Sulphide (CuZnS<sub>2</sub>) Thin Films," *Turkish Journal of Physics*: Vol. 32: No. 1, Article 6. Available at: <https://journals.tubitak.gov.tr/physics/vol32/iss1/6>

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Physics by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact [academic.publications@tubitak.gov.tr](mailto:academic.publications@tubitak.gov.tr).

# The Study of Copper Zinc Sulphide (CuZnS<sub>2</sub>) Thin Films

**Chidi Chukwuemeka UHUEGBU, Elisha Bamidele BABATUNDE,  
Cornelius Olufunmilayo OLUWAFEMI**

*Department of Physics, Covenant University, Ota, Ogun State, NIGERIA  
e-mail: cuhuegbu@yahoo.co.uk, ebbabatunde@yahoo.com, corneliusoluwafemi@yahoo.com*

Received 26.04.2007

## Abstract

Thin films of CuZnS<sub>2</sub> were successfully deposited on glass substrates from aqueous solution of copper chloride in which EDTA and TEA were used as complexing agents. The optical and solid state properties were studied include: absorbance, transmittance, reflectance, extinction coefficient, refractive index, absorption coefficient, optical conductivity, dielectric constants. The direct and indirect band gaps obtained ranges from 2.2 eV to 2.4 eV for direct band gap and 0.4 eV to 0.9 eV for indirect band gap. The possible applications were also mentioned.

**Key Words:** Solution growth technique, characterization, CuZnS<sub>2</sub> thin film, band gap.

## 1. Introduction

The process of thin film deposition involves the deposition of material atom-by-atom, molecule-by-molecule, ion-by-ion or cluster of species by cluster of species condensation [1]. This methodology is applied extensively in the manufacture of photocells and is being used in optical coating, microelectronics, surface science engineering and other technologies [2].

The technique of chemically depositing thin films has the advantage of being a low cost and applicable to the production of large area devices [3, 4]. Various aspects of chemically deposited thin films have been reported [2, 4–24]. The effect of solar radiation and ultrasonication on the various properties of thin films has been reported [2, 8]. More over, the effect of varying growth parameters, such as deposition rate, bath composition and bath temperature on the various properties of thin films have also been reported by several workers [3, 15–17, 25–33]. This paper reports the solution growth technique of CuZnS<sub>2</sub> thin film that would be adequate for solar and industrial applications and are characterized using optical methods. Optical studies using transmittance and reflectance data from samples prepared using solution growth technique have been reported [11, 18–24].

## 2. Theoretical Consideration and calculation

In both crystalline and amorphous semiconductors, the absorption coefficient near the fundamental absorption edge is dependent on photon energy. In the high absorption region, the absorption coefficient takes

on the following more general form as a function of photon energy [34, 35]. For direct transitions

$$\alpha hf = A(\alpha hf - E_g)^n \quad (1)$$

and for indirect transitions

$$\alpha hf = B(\alpha hf - E_g)^n \quad (2)$$

where  $f$  is the frequency of the incident photon,  $h$  is the planck constant,  $A$  and  $B$  are constants,  $E_g$  is the band gap optical energy and  $n$  is the number which characterizes the optical processes.  $n$  has the value of  $1/2$  for the direct allowed transition,  $3/2$  for a forbidden direct allowed transition and  $2$  for the indirect allowed transition. When the linear portion of  $(\alpha hf)^n$  as function of  $hf$  is extrapolated to  $\alpha = 0$ , the intercept gives the transition band gaps. For semiconductors and insulators (where  $k^2 \ll n^2$ ), there exists a relation between  $R$  and  $n$  given by [11, 36]

$$R = (n - 1)^2 / (n + 1)^2. \quad (3)$$

Here,  $k$  is the extinction coefficient,  $n$  is the refractive index and  $R$  is the reflectance. There is also a relationship between  $k$  and  $\alpha$  given by [35]

$$K = \alpha \lambda / 4 \quad (4)$$

where  $\alpha$  is the absorption coefficient of the film and  $\lambda$  is the wavelength of electromagnetic wave. The relationship between dielectric constant  $\varepsilon$  and the extinction coefficient  $k$  is given by [35]

$$\varepsilon = (n + ik)^2 \quad (5)$$

where  $\varepsilon = \varepsilon_r + \varepsilon_i$ ,  $\varepsilon_r = n^2 - k^2$  and  $\varepsilon_i = 2nk$ ,  $\varepsilon_r$  and  $\varepsilon_i$  are the real and imaginary parts of the dielectric constant, respectively. Optical conductivity  $\sigma_o$  is given by [35]

$$\sigma_o = \alpha nc / 4 \quad (6)$$

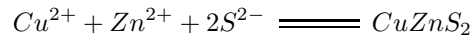
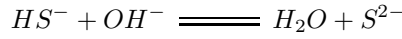
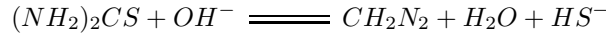
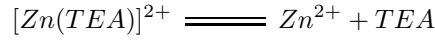
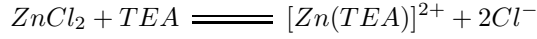
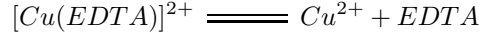
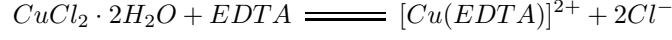
where  $c$  is the velocity of light. Optical method as discussed by Theye [37] and Ezema [38] was used to estimate the thickness of the film.

### 3. Experimental Detail and Material

Deposition of copper zinc sulphide film was based on the reaction between copper chloride zinc chloride, ethylenediaminetetra acetic (EDTA), Triethanolamine (TEA), ammonia, thiourea and microscopic glass slides. The film growth reaction bath was composed from 5 ml of 1 M  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 5 ml of 0.1 M EDTA, 5 ml of  $\text{ZnCl}_2$ , 3 ml of 7.4 M TEA, 3 ml of concentrated ammonia, 10 ml of 1 M thiourea and 20 ml of distilled water.

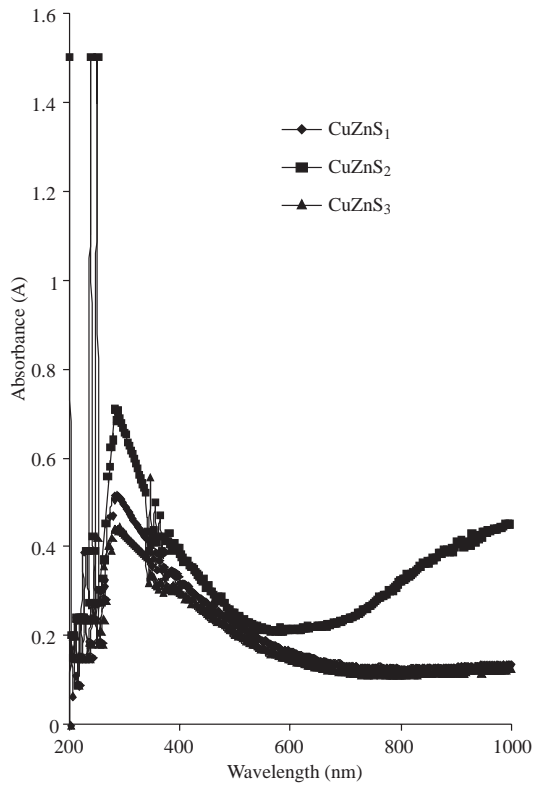
These solutions were successfully combined into 50 ml beaker. The mixture was stirred thoroughly using a glass rod to obtain homogenous mixed solution. The glass slide previously degreased in nitric acid for 48 hours, cleaned with detergent and rinsed with distilled water was dipped vertically into the beaker. After some hours, the substrate with the film was taken out, rinsed with distilled water and dried in air.

The film was characterized by measuring the absorbance and transmittance using a UNICO UV-2102 PC Spectrophotometer and the photomicrograph was carried out using Olympus PMG. The optical properties studied included the absorbance  $A$ , transmittance  $T$  and reflectance  $R$ . These were used to estimate the other properties such as refractive index  $n$ , extinction coefficient  $k$ , dielectric constant  $\varepsilon$  and optical conductivity  $\sigma_o$ . The reaction is shown as follows:

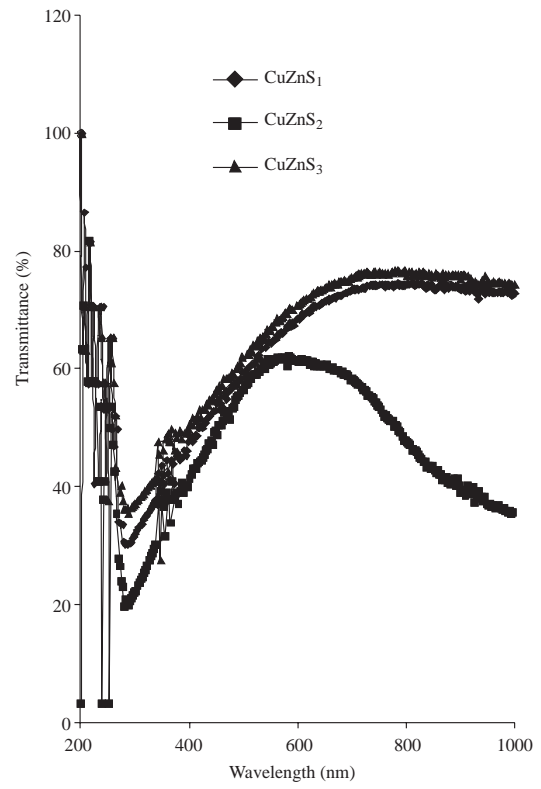


## 4. Results and Discussion

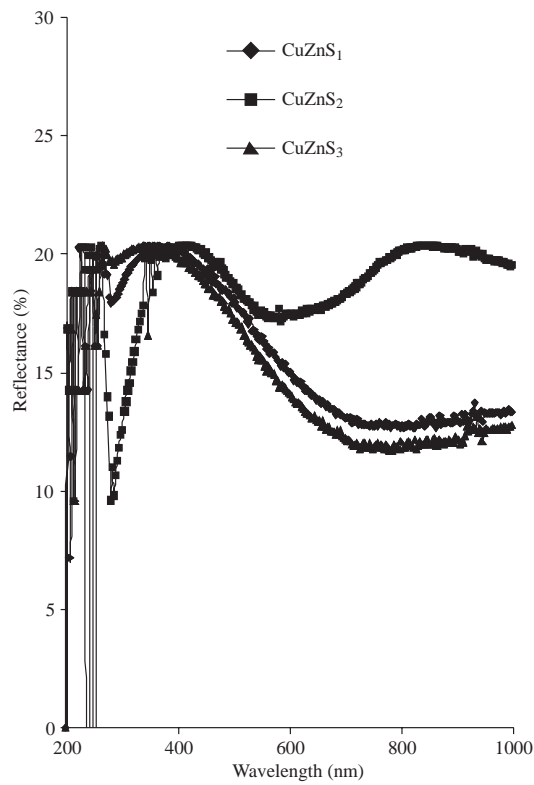
Optical properties: The spectral absorbance of copper zinc sulphide thin films, shown in Figure 1, vary with wavelength in similar manner, increasing rapidly from a value of about 0.24 at 260 nm to various maximum values of 0.44 at 300 nm for CuZnS<sub>3</sub>, 0.52 at 280 nm for CuZnS<sub>1</sub> and 0.72 at 280 nm for CuZnS<sub>2</sub> and then decreased sharply to 0.16 at 560 nm for CuZnS<sub>1</sub> and CuZnS<sub>3</sub> before decreasing gently with wavelength. That of CuZnS<sub>2</sub> decreased to a minimum value of 0.2 at 600 nm before increasing with wavelength. The transmittance also vary the same manner for CuZnS<sub>1</sub> and CuZnS<sub>2</sub>, decreasing from a value of about 59.0% at 280 nm to various minimum values of 38.0% at 280 nm for CuZnS<sub>3</sub>, 30.0% at 280 nm for CuZnS<sub>1</sub> and 20.0% at 280 nm for CuZnS<sub>2</sub>, before increasing to a maximum value of 62.0% at 580 nm and decreased gently wavelength for CuZnS<sub>2</sub> while that CuZnS<sub>1</sub> and CuZnS<sub>3</sub> increased with wavelength as shown in Figure 2. In Figure 3, the reflectance of CuZnS<sub>1</sub> and CuZnS<sub>3</sub> vary in similar manner, increasing from various value of 18.0% at 280 nm for CuZnS<sub>1</sub>, 19.0% at 280 nm for CuZnS<sub>3</sub> to maximum value of about 20.0% at 340 nm before decreasing sharply to 12% at 720 nm for CuZnS<sub>3</sub> and 13.0% at 720 nm and then decreased gently with wavelength. That of CuZnS<sub>2</sub> increased from a value of 10.0% at 280 nm to a maximum value of about 20.5% at 440 nm and then decreased to a minimum value of 17.0% at 580 nm. Thereafter it increased to another maximum value of 20.5% at 840 nm before decreasing with wavelength.



**Figure 1.** Absorbance  $A$  as function of wavelength  $\lambda$  for CuZnS thin film.

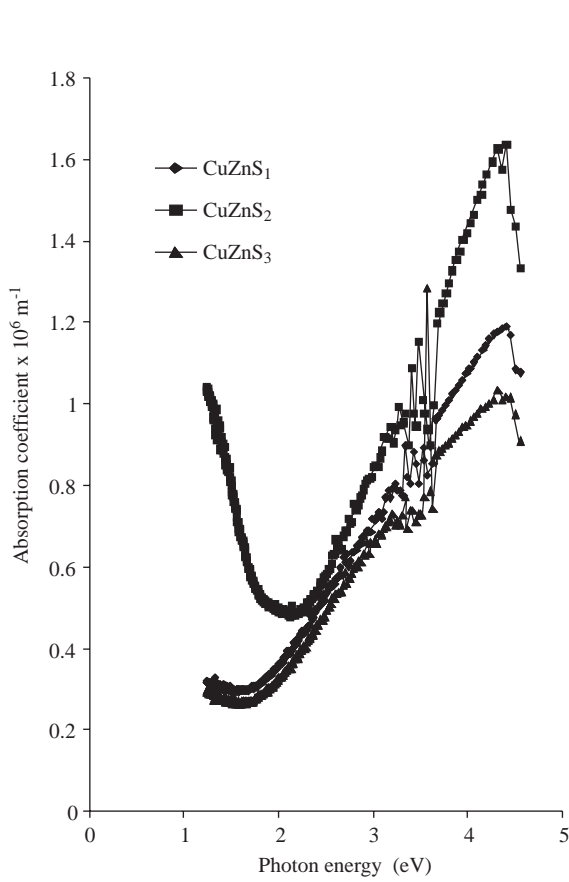


**Figure 2.** Transmittance  $T$  as function of wavelength  $\lambda$  for CuZnS thin film.

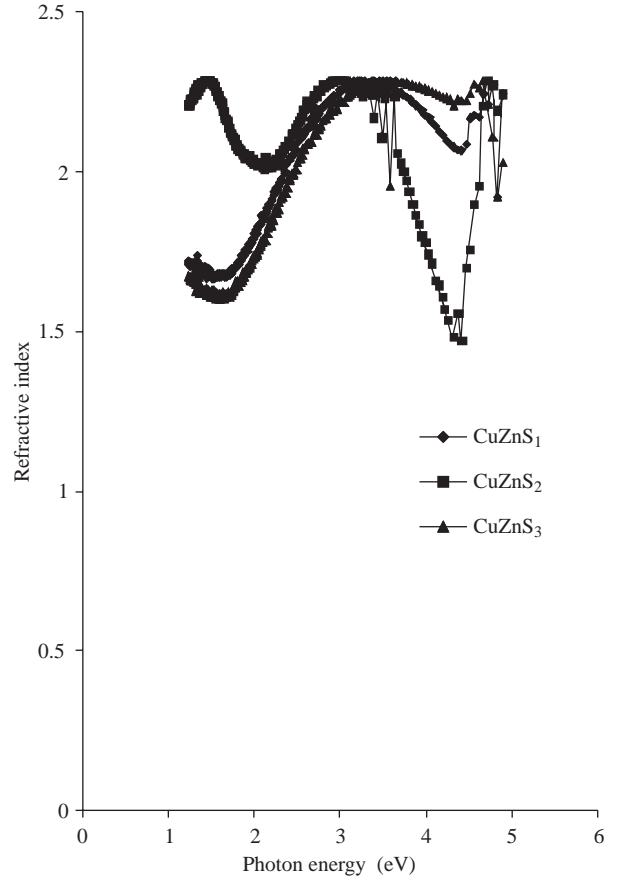


**Figure 3.** Reflectance  $R$  as function of wavelength  $\lambda$  for CuZnS thin film.

From Figure 4 the absorption coefficient increases from various values of  $0.26 \times 10^6 \text{ m}^{-1}$  at 1.7 eV for CuZnS<sub>3</sub>,  $0.30 \times 10^6 \text{ m}^{-1}$  at 1.7 eV for CuZnS<sub>1</sub>, while that of CuZnS<sub>2</sub> decreased sharply to a minimum value of  $0.44 \times 10^6 \text{ m}^{-1}$  at 2.1 eV. Thereafter it increases with photon energy before fluctuation sets in. The refractive index of CuZnS<sub>1</sub> and CuZnS<sub>3</sub> vary in similar manner, increasing from various values of 1.52 at 1.8 eV for CuZnS<sub>3</sub> and 1.53 at 1.8 eV to various maximum values of 2.3 at 3.2 eV for CuZnS<sub>1</sub> and 2.3 at 3.6 eV for CuZnS<sub>3</sub> before decreasing to undefined minimum at 4.4 eV for CuZnS<sub>1</sub> and CuZnS<sub>3</sub>. That of CuZnS<sub>2</sub> increased to a maximum value of 2.3 at 1.5 eV and decreased to a minimum value of 2 at 2.1 eV before increasing to another maximum value of 2.3 at 3.0 eV. Thereafter, it decreased to an undefined minimum at 4.4 eV before fluctuating as shown in Figure 5.



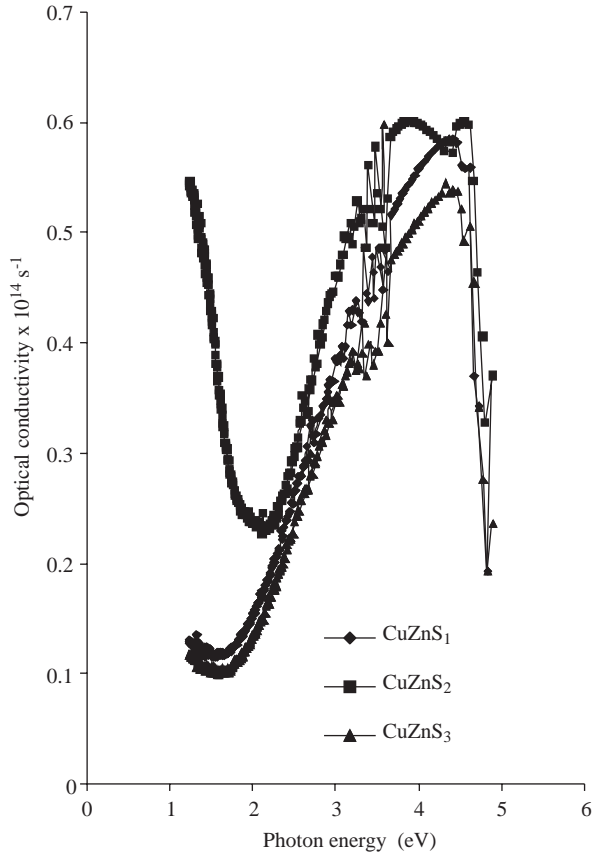
**Figure 4.** A Plot of absorption coefficient  $\alpha$  as a function of photon energy  $hf$  for CuZnS thin film.



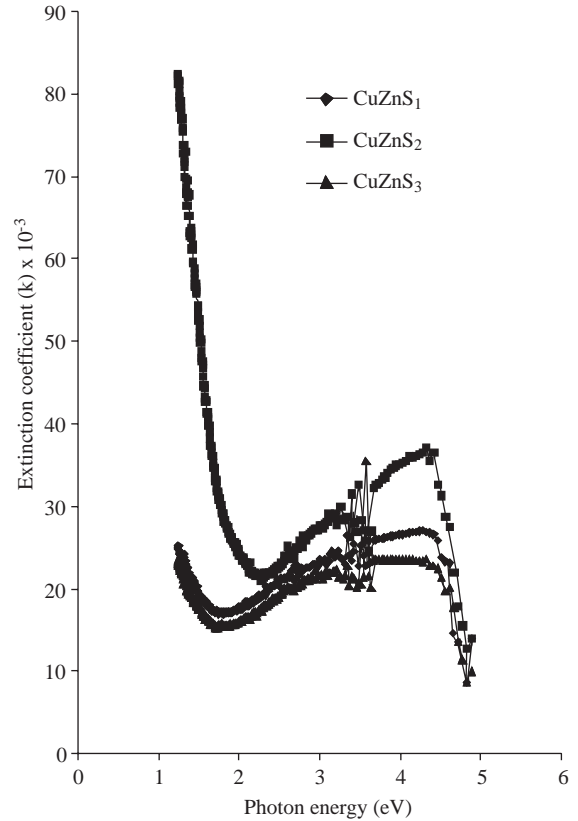
**Figure 5.** Refractive index  $n$  as function of photon energy  $hf$  for CuZnS thin film.

The optical conductivity of CuZnS<sub>1</sub> and CuZnS<sub>3</sub> increased from various values of  $0.12 \times 10^{14} \text{ s}^{-1}$  at 1.6 eV for CuZnS<sub>1</sub> and  $0.10 \times 10^{14} \text{ s}^{-1}$  at 1.8 eV for CuZnS<sub>3</sub>. While that of CuZnS<sub>2</sub> decreased sharply from a value of  $0.54 \times 10^{14} \text{ s}^{-1}$  at 1.2 eV to a minimum value of  $0.23 \times 10^{14} \text{ s}^{-1}$  at 2.1 eV as shown in Figure 6. From Figure 7, the extinction coefficient vary in similar manner, decreasing sharply from various values of  $24 \times 10^{-3}$  at 1.2 eV for CuZnS<sub>1</sub> and CuZnS<sub>3</sub>,  $82 \times 10^{-3}$  at 1.2 eV for CuZnS<sub>2</sub> to various minimum values of  $17 \times 10^{-3}$  at 1.8 eV for CuZnS<sub>1</sub>,  $15 \times 10^{-3}$  at 1.8 eV for CuZnS<sub>3</sub> and  $21 \times 10^{-3}$  at 2.2 eV. The extrapolated direct and indirect band gap are 2.2 eV, 2.3 eV, 2.4 eV and 0.4 eV, 0.6 eV and 0.9 eV respectively as shown in Figure 8 and Figure 9. In Figure 10, the real part of the dielectric constant of CuZnS<sub>1</sub> and CuZnS<sub>3</sub> vary in similar manner, increasing from various values of 2.8 at 1.6 eV for CuZnS<sub>1</sub> and 2.6 at 1.6 eV to maximum value of 5.2 at 3.6 eV before decreasing sharply to an undefined minimum at 4.4 eV. That of CuZnS<sub>2</sub> increased

to a maximum value of 4 at 2.1 eV before increasing to another maximum value of 5.2 at 3 eV. Thereafter, it decreased to an undefined minimum at 4.4 eV. The imaginary part of the dielectric constant vary in the same manner, decreasing to various minimum values of  $60 \times 10^{-3}$  at 1.7 eV for CuZnS<sub>1</sub>,  $50 \times 10^{-3}$  at 1.7 eV for CuZnS<sub>3</sub>,  $85 \times 10^{-3}$  at 2.2 eV for CuZnS<sub>2</sub> from various value of  $90 \times 10^{-3}$  at 1.2 eV for CuZnS<sub>1</sub>,  $80 \times 10^{-3}$  at 1.2 eV for CuZnS<sub>3</sub> and  $365 \times 10^{-3}$  at 1.2 eV before increasing with photon energy as shown in Figure 11.



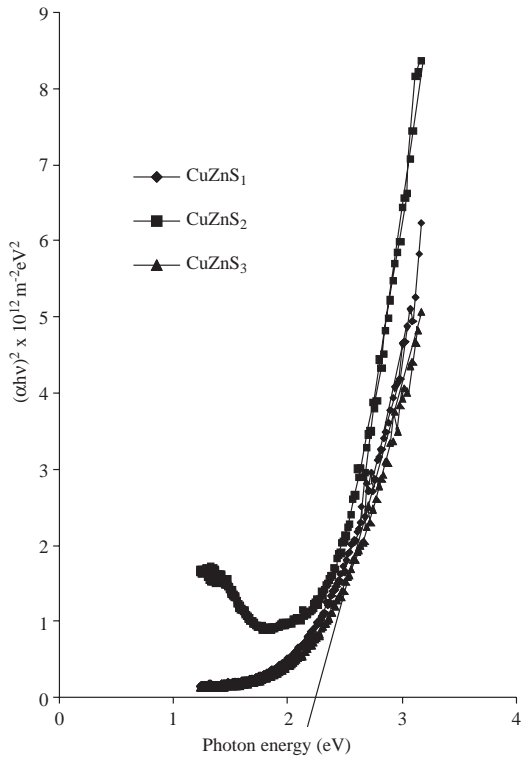
**Figure 6.** Optical conductivity  $\sigma_w$  as function of photon energy  $hf$  for CuZnS thin film.



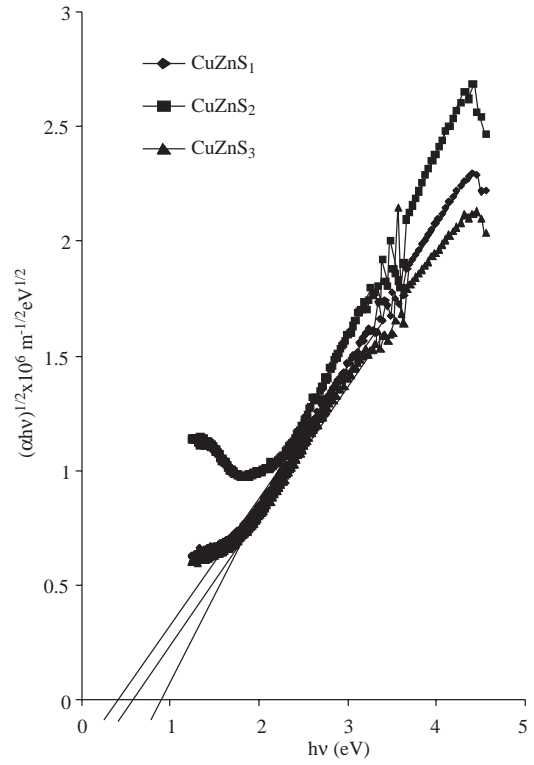
**Figure 7.** Extinction coefficient  $k$  as function of photon energy  $hf$  for CuZnS thin film.

The computed thickness varies from  $0.048 \mu\text{m}$  to  $0.627 \mu\text{m}$ . Figure 12 is the photomicrograph which reveals the crystalline nature of the films.

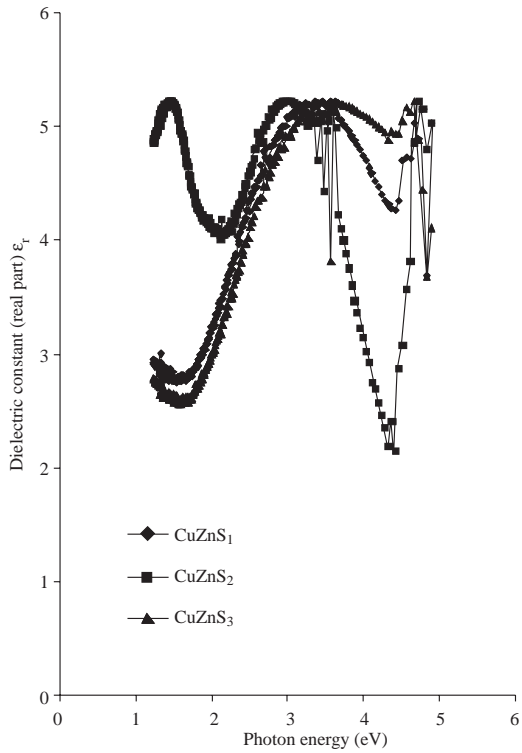
The spectral absorbance of copper-Zinc-Sulphide was observed to be heavy in UV-region but poor in VIS region as seen in Figure 1. In Figure 2, the transmittance was heavy in the VIS-NIR region and poor in the UV region and in Figure 3, reflectance was less in the UV region and more in the VIS-NIR regions. These properties make the films good materials for poultry buildings, eye glasses, solar cell, anti-reflection, thermal control and photosynthetic applications.



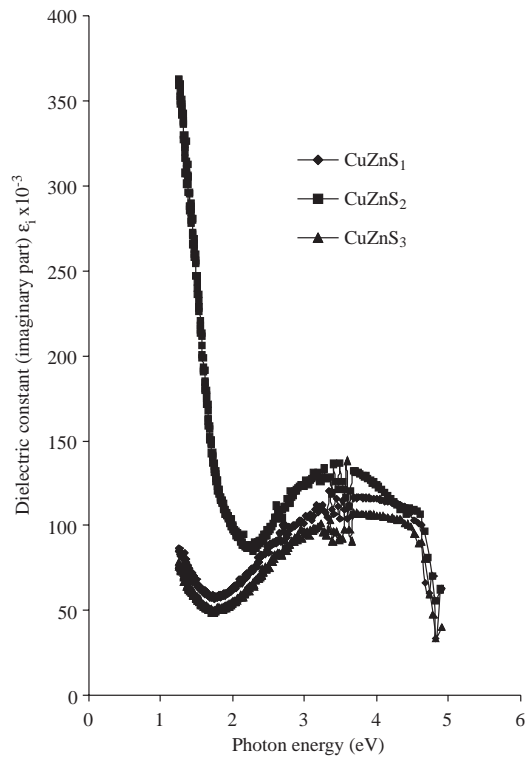
**Figure 8.** A plot of  $(\alpha h\nu)^2$  as a function of photon energy  $hf$  for CuZnS thin film.



**Figure 9.** A plot of  $(\alpha h\nu)^2$  for CuZnS thin film.

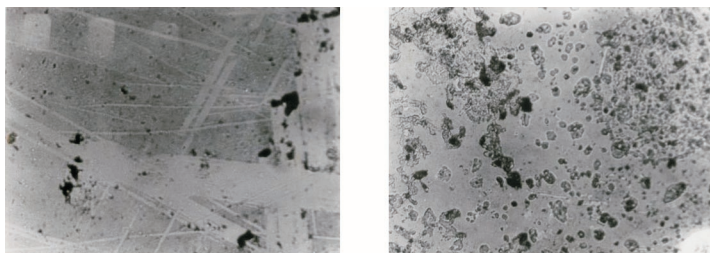


**Figure 10.** Real dielectric constant  $\epsilon_r$  as function of photon energy  $hf$  for CuZnS thin film.



**Figure 11.** Imaginary dielectric  $\epsilon_i$  as function of photon energy  $hf$  for CuZnS thin film.





**Figure 12.** Photomicrograph of the films revealing the crystalline nature.

## 5. Conclusion

We have demonstrated the possibility of depositing ternary thin films of  $\text{CuZnS}_2$  using solution growth techniques (SGT) and have successfully characterized them. Some of the applications were discussed.

## References

- [1] K. L. Chopra, and S. R. Das, *Thin Solar cells*, (Plenum press, New York, 1983).
- [2] T. Roseberg, S. Kuan and H. J. Hovel, *Physics Today*, **33**(5), (May 1980), 41, JY.
- [3] K. J. Choi, J. B. Kim Yoo and D. Kim, *Solar energy*, **64**, (1998), 41.
- [4] P. K. Nair, M. T. S. Nair, A. Fernandez and M. Ocampo, *J. Phys. D Appl. Phys.*, **22**, (1989), 829.
- [5] P. K. Nair and M. T. S. Nair, *Semicond. Sci. Technol.*, **4**, (1989), 807.
- [6] P. K. Nair and M. T. S. Nair, *Semicond. Sci. Technol.*, **7**, (1992), 239.
- [7] P. K. Nair, M. Ocampo, A. Fernandez and M.T.S. Nair, *Sol. Ener. Mater.*, **20**, (1990), 235.
- [8] P. K. Nair and M. T. S. Nair, *Sol. Ener. Mater*, **15**, (1987), 431.
- [9] M. T. S. Nair and P. K. Nair, *Semicond. Sci. Technol.*, **4**, (1989), 191.
- [10] P. K. Nair and M. T. S. Nair, *Solar Cells*, **22**, (1987), 102.
- [11] I. C. Ndukwe, *Sol. Ener. Mater. Sol. Cells*, **40**, (1996), 123.
- [12] R. Ortega-Borges and D. Lincot, *J. Electrochem. Soc.*, **140**, (1993), 3464.
- [13] G. K. Padam and S. U. M. Rao, *Sol. Ener.Mater.*, **13**, (1986), 297.
- [14] P. S. Pramanik, R. N. Bhattacharya and P. K. Basu, *Thin Solid Films*, **149**, (1987), 181.
- [15] P. J. Sabestian and H. Hu, *Adv. Mater. Opt. Electron*, **4**, (1994), 407.
- [16] K. L. Chopra, R. C. Kainthla, D. K. Pandya and A. D. Thakoor, *Physics of thin films*, vol. 12 (Academic press, New York. 1982).
- [17] I. Kaur, D. K. Pandya and K. L. Chopra, *J. Electrochem. Soc.*, **127**, (1980), 943.
- [18] F. I. Ezema and C. E. Okeke, *Nig. J. Phys.*, **14**, (2002), 48.
- [19] F. I. Ezema, and C. E. Okeke, *Nig. J. Solar Ener.*, **14**, (2003), 68.
- [20] F. I. Ezema and C. E. Okeke, *Academic Open Internet Journal*  
[http://www.acadjournal.com/2003/v9/part2/p4/chemical\\_bath\\_deposition.pdf](http://www.acadjournal.com/2003/v9/part2/p4/chemical_bath_deposition.pdf).

- [21] F. I. Ezema and C. E. Okeke, *Greenwich Journal of Science and Technology*, **3**, (2003), 90.
- [22] F. I. Ezema and P. U. Asogwa, *Pacific Journal of Science and Technology*, **5**, (2004), 33.
- [23] F. I. Ezema, *Journal of the University of Chemical Technology and Metallurgy*, **39**, (2004), 225.
- [24] F. I. Ezema, *Open internet Journal* <http://www.acadjournal.com/2004/vii/part2/p1/index.htm>.
- [25] V. S. Karande, S. H. Mane, V. B. Pujari and L. P. Deshmukh, *Turk. J. Phys.*, **27**, (2003), 559.
- [26] D. S. Sutrave, G. S. Shakane, V. B. Patil and L. P. Deshmukh, *Turk. J. Phys.*, **24**, (2000), 63.
- [27] V. B. Pujari, V. B. Gaikward, E. U. Masumdar, P. D. More and L.P. Deshmukh, *Turk. J. Phys.*, **26**, (2002), 407.
- [28] V. Estrella, M. T. S. Nair and P. K. Nair, *Semicond. Sci. Technol.*, **18**, (2003), 190.
- [29] A. Numez-Rodriguez, M. T. S. Nair and P. K. Nair, *Mater. Res. Symp. Proc.*, **730**, (2002), v5.14.1.
- [30] Y. Rodriguez-Lazcano, L. Guerrero, O. GomezDaza, M. T. S. Nair and P. K. Nair, *Superficies y vacio*, **9**, (1999), 100.
- [31] Y. Rodriguez-Lazcano, M. T. S. Nair and P. K. Nair, *J. Crystal Growth*, **23**, (2001), 399.
- [32] P. K. Nair, L. Huang, M. T. S. Nair, H. Hu, E. A. Meyers and R. A. Zingaro, *J. Mater. Res.*, **12**, (1997), 651.
- [33] N. A. Lange, *Lange's Handbook of chemistry*, 14<sup>th</sup> edn, (McGraw-Hill Book Co., New York, 1992).
- [34] I. M. Tsidilkovsk, *Band structure of semiconductors*, (Pergamon Press Oxford, 1982).
- [35] J. I. Pankove, *Optical Processes in semiconductors*, (Prentice Hall, New York, 1971).
- [36] M. Janai, D. D. Alfred, D. C. Booth and B. O. Seraphin, *Sol. Ener. Mater.*, **1**, (1979), 11.
- [37] M. Theye, *Optical Properties of Thin Films*, (edited by K.L. Chopra and L.K. Malhotra), *Thin film technology and applications*, (Tata McGraw-Hill, New Delhi, 1985).
- [38] F. I. Ezema, *Journal of University of Science and Technology*, **23**, (2003), 32.