The Study of Copper Zinc Sulphide (CuZnS$_2$) Thin Films

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Abstract

Thin films of CuZnS$_2$ 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$_2$ 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 ultrasonification 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$_2$ 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

$$\alpha h f = A(\alpha h f - E_g)^n \tag{1}$$

and for indirect transitions

$$\alpha h f = B(\alpha h f - E_g)^n \tag{2}$$

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 $(\alpha h f)^n$ as function of hf is extrapolated to $\alpha = 0$, the intercept gives the transition band gaps. For semiconductors and insulators (where $k^2 << n^2$), there exists a relation between R and n given by [11, 36]

$$R = (n-1)^2/(n+1)^2. \tag{3}$$

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

$$K = \alpha\lambda/4\sqcap \tag{4}$$

where α is the absorption coefficient of the film and λ is the wavelength of electromagnetic wave. The relationship between dielectric constant ε and the extinction coefficient k is given by [35]

$$\varepsilon = (n+ik)^2 \tag{5}$$

where $\varepsilon = \varepsilon_r + \varepsilon_i,$ $\varepsilon_{r=}n^2 - k^2$ and $\varepsilon_i = 2ink$, ε_r and ε_i are the real and imaginary parts of the dielectric constant, respectively. Optical conductivity σ_o is given by [35]
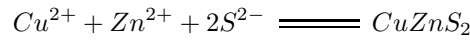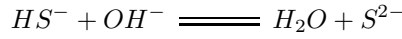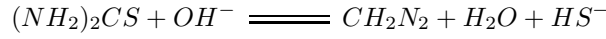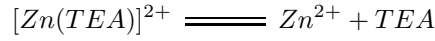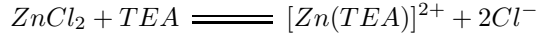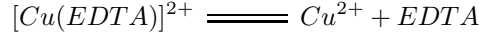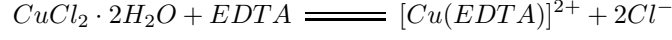
$$\sigma_o = \alpha n c/4\sqcap \tag{6}$$

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 $CuCl_2 \cdot 2H_2O$, 5 ml of 0.1 M EDTA, 5 ml of $ZnCl_2$, 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 Spectrrophotometer and the photomicrograph was carried out using Olympus PMG. The optical properties studied included the absorbance $\underline{A}$, transmittance T and reflectance R. These were used to estimate the other properties such as refractive index n, extinction coefficient k, dielectric constant ε and optical conductivity σ_o. The reaction is shown as follows:

$$CuCl_2 \cdot 2H_2O + EDTA \Longrightarrow [Cu(EDTA)]^{2+} + 2Cl^-$$

$$[Cu(EDTA)]^{2+} \Longrightarrow Cu^{2+} + EDTA$$

$$ZnCl_2 + TEA \Longrightarrow [Zn(TEA)]^{2+} + 2Cl^-$$

$$[Zn(TEA)]^{2+} \Longrightarrow Zn^{2+} + TEA$$

$$(NH_2)_2CS + OH^- \Longrightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \Longrightarrow H_2O + S^{2-}$$

$$Cu^{2+} + Zn^{2+} + 2S^{2-} \Longrightarrow CuZnS_2$$

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 $CuZnS_3$, 0.52 at 280 nm for $CuZnS_1$ and 0.72 at 280 nm for $CuZnS_2$ and then decreased sharply to 0.16 at 560 nm for $CuZnS_1$ and $CuZnS_3$ before decreasing gently with wavelength. That of $CuZnS_2$ decreased to a minimum value of 0.2 at 600 nm before increasing with wavelength. The transmittance also vary the same manner for $CuZnS_1$ and $CuZnS_2$, decreasing from a value of about 59.0% at 280 nm to various minimum values of 38.0% at 280 nm for $CuZnS_3$, 30.0% at 280 nm for $CuZnS_1$ and 20.0% at 280 nm for $CuZnS_2$, before increasing to a maximum value of 62.0% at 580 nm and decreased gently wavelength for $CuZnS_2$ while that $CuZnS_1$ and $CuZnS_3$ increased with wavelength as shown in Figure 2. In Figure 3, the reflectance of $CuZnS_1$ and $CuZnS_3$ vary in similar manner, increasing from various value of 18.0% at 280 nm for $CuZnS_1$, 19.0% at 280 nm for $CuZnS_3$ to maximum value of about 20.0% at 340 nm before decreasing sharply to 12% at 720 nm for $CuZnS_3$ and 13.0% at 720 nm and then decreased gently with wavelength. That of $CuZnS_2$ 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.
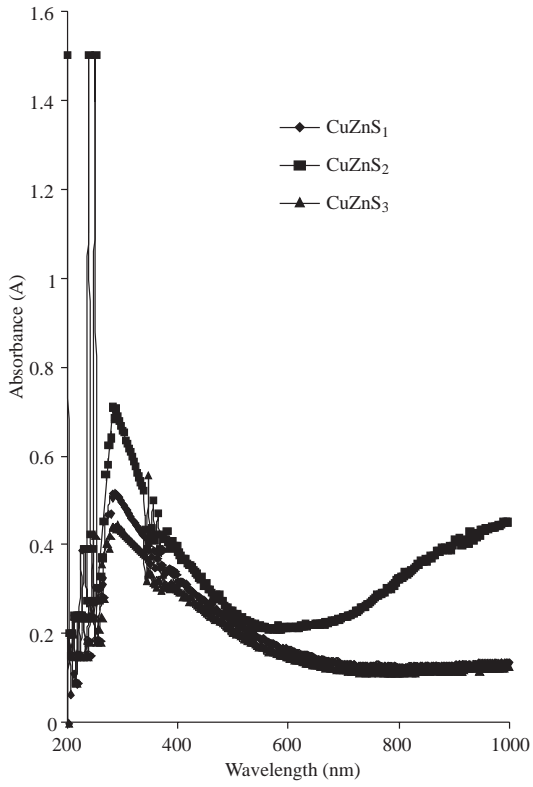
Figure 1. Absorbance A as function of wavelength λ for CuZnS thin film.
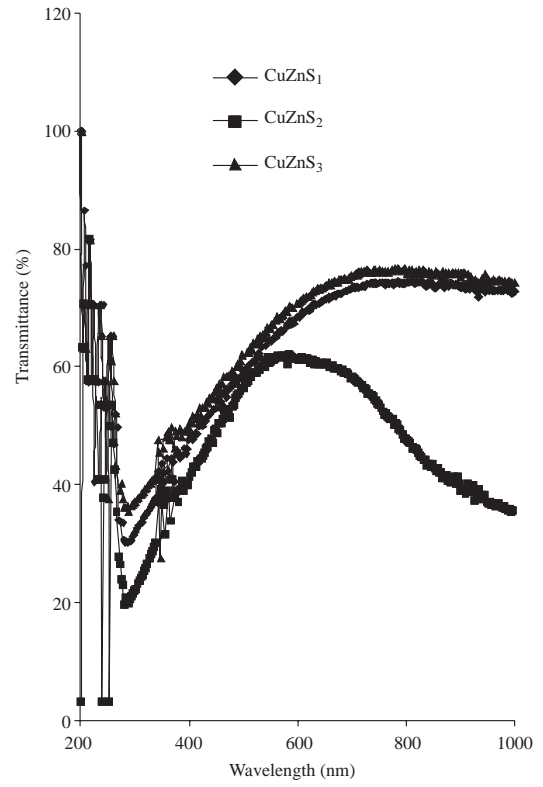
Figure 2. Transmittance T as function of wavelength λ for CuZnS thin film.
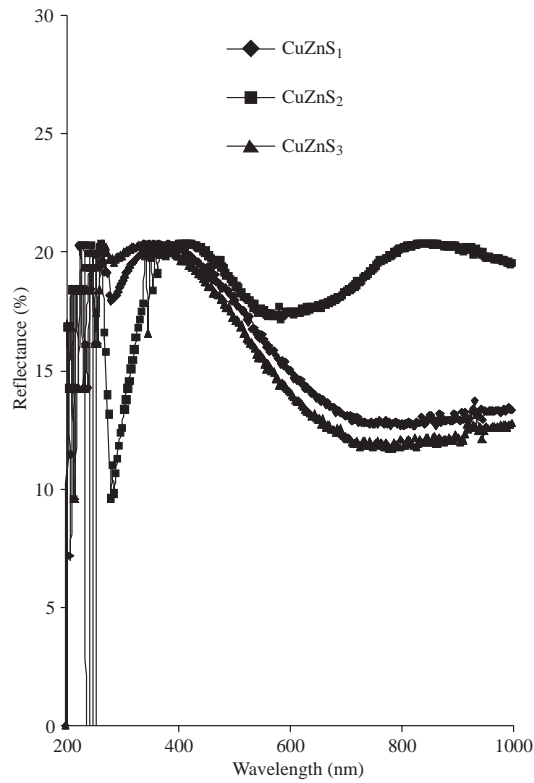
Figure 3. Reflectance R as function of wavelength λ for CuZnS thin film.

From Figure 4 the absorption coefficient increases from various values of 0.26×10^6 m^{-1} at 1.7 eV for CuZnS$_3$, 0.30×10^6 m^{-1} at 1.7 eV for CuZnS$_1$, while that of CuZnS$_2$ decreased sharply to a minimum value of 0.44×10^6 m^{-1} at 2.1 eV. Thereafter it increases with photon energy before fluctuation sets in. The refractive index of CuZnS$_1$ and CuZnS$_3$ vary in similar manner, increasing from various values of 1.52 at 1.8 eV for CuZnS$_3$ and 1.53 at 1.8 eV to various maximum values of 2.3 at 3.2 eV for CuZnS$_1$ and 2.3 at 3.6 eV for CuZnS$_3$ before decreasing to undefined minimum at 4.4 eV for CuZnS$_1$ and CuZnS$_3$. That of CuZnS$_2$ 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.
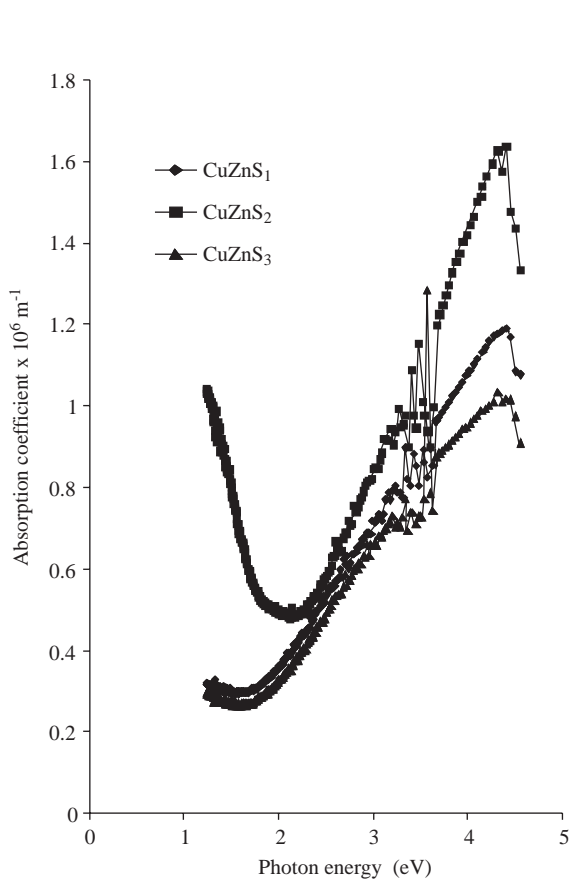

Figure 4. A Plot of absorption coefficient αs a function of photon energy hf for CuZnS thin film.
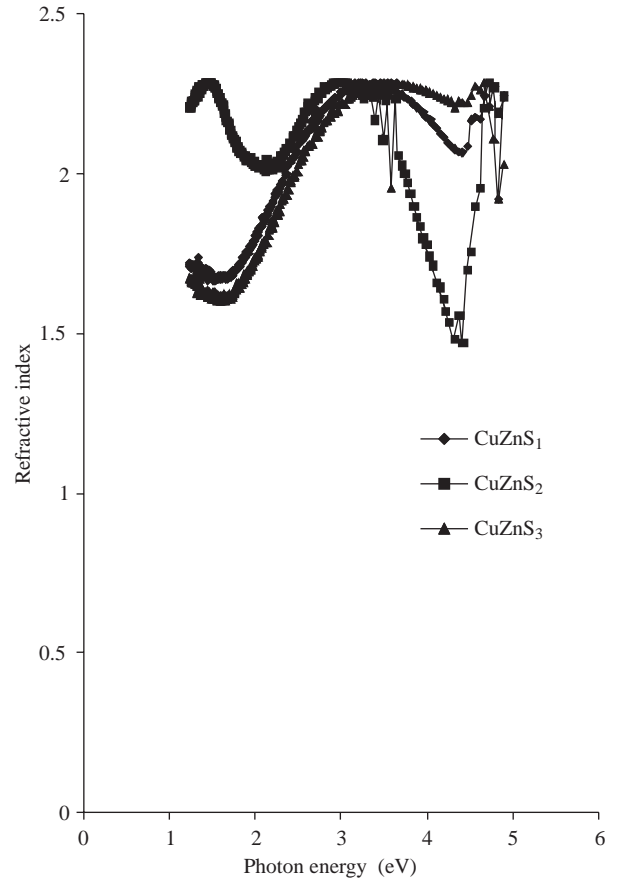
Figure 5. Refractive index n as function of photon energy hf for CuZnS thin film.

The optical conductivity of CuZnS$_1$ and CuZnS$_3$ increased from various values of 0.12×10^{14} s^{-1} at 1.6 eV for CuZnS$_1$ and 0.10×10^{14} s^{-1} at 1.8 eV for CuZnS$_3$. While that of CuZnS$_2$ decreased sharply from a value of 0.54×10^{14} s^{-1} at 1.2 eV to a minimum value of 0.23×10^{14} 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 24×10^{-3} at 1.2 eV for CuZnS$_1$ and CuZnS$_3$, 82×10^{-3} at 1.2 eV for CuZnS$_2$ to various minimum values of 17×10^{-3} at 1.8 eV for CuZnS$_1$, 15×10^{-3} at 1.8 eV for CuZnS$_3$ and 21×10^{-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$_1$ and CuZnS$_3$ vary in similar manner, increasing from various values of 2.8 at 1.6 eV for CuZnS$_1$ 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$_2$ 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 60×10^{-3} at 1.7 eV for $CuZnS_1$, 50×0^{-3} at 1.7 eV for $CuZnS_3$, 85×10^{-3} at 2.2 eV for $CuZnS_2$ from various value of 90×10^{-3} at 1.2 eV for $CuZnS_1$, 80×10^{-3} at 1.2 eV for $CuZnS_3$ and 365×10^{-3} at 1.2 eV before increasing with photon energy as shown in Figure 11.
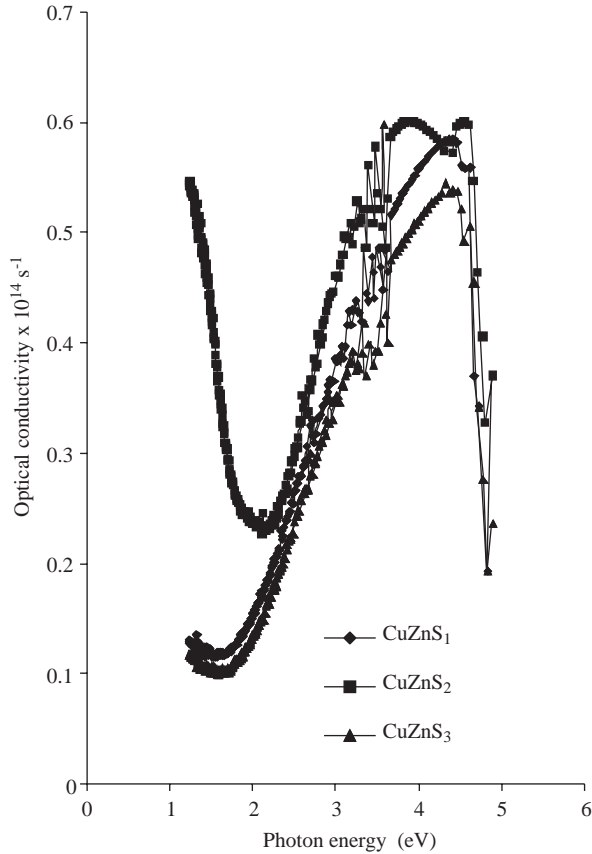

Figure 6. Optical conductivity σ_w as function of photon energy hf for CuZnS thin film.

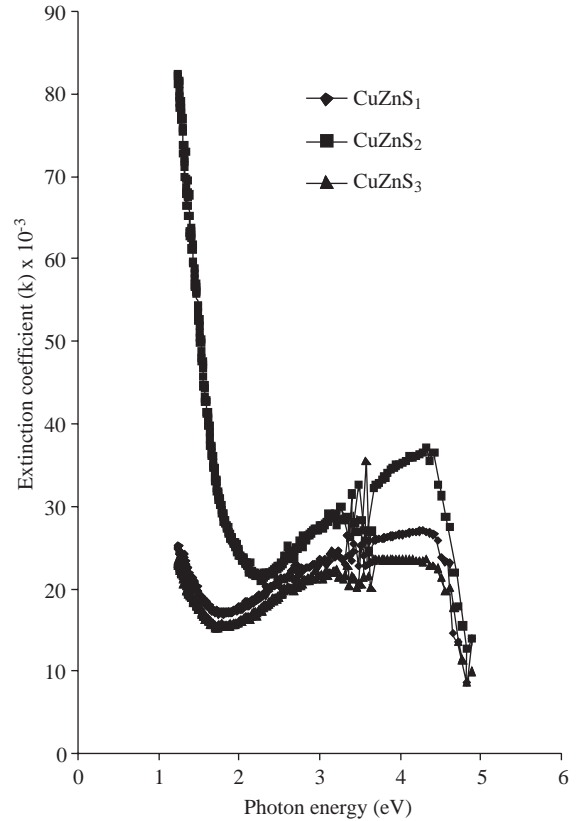**Figure 7.** Extinction coefficient k as function of photon energy hf for CuZnS thin film.

The computed thickness varies from 0.048 μm to 0.627 μm. 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.
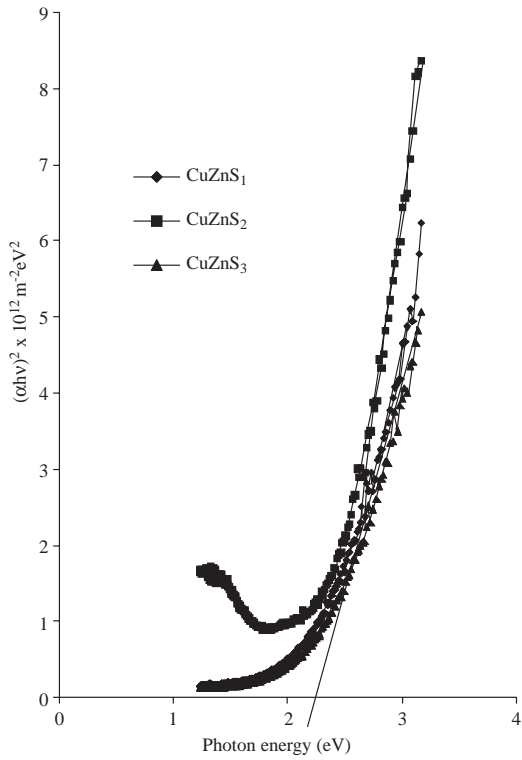
Figure 8. A plot of $(\alpha h\nu)^2$ as a function of photon energy hf for CuZnS thin film.
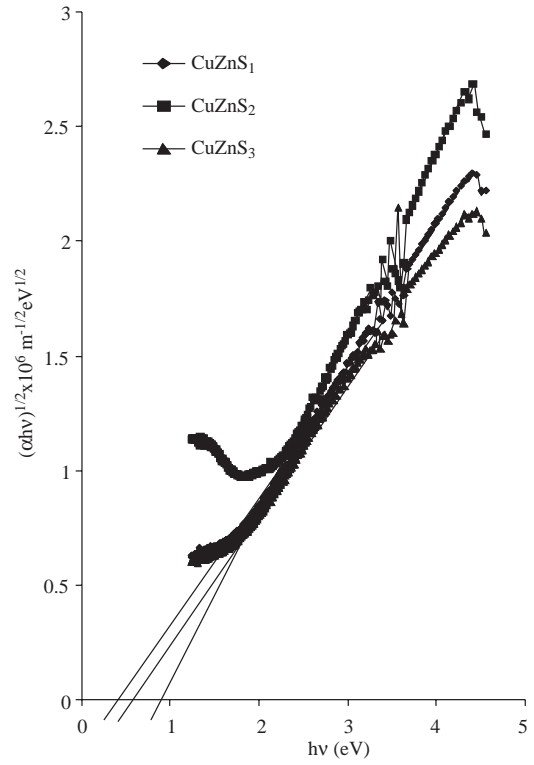
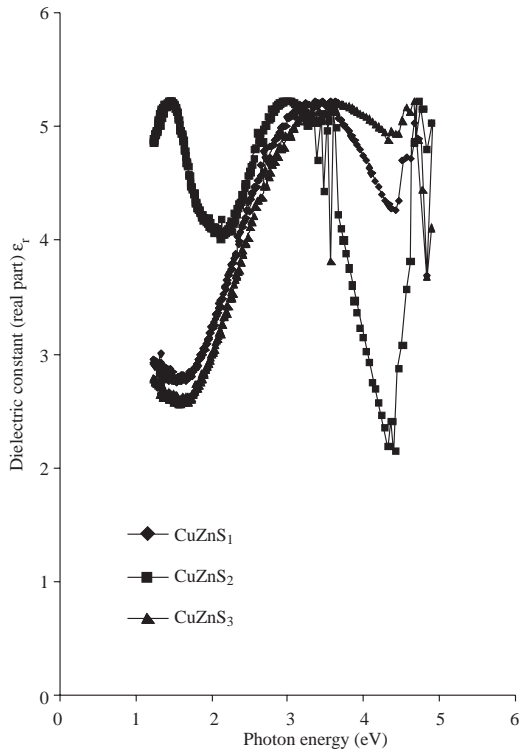**Figure 9.** A plot of $(\alpha h\nu)^2$ for CuZnS thin film.

Figure 10. Real dielectric constant ε_r as function of photon energy hf for CuZnS thin film.
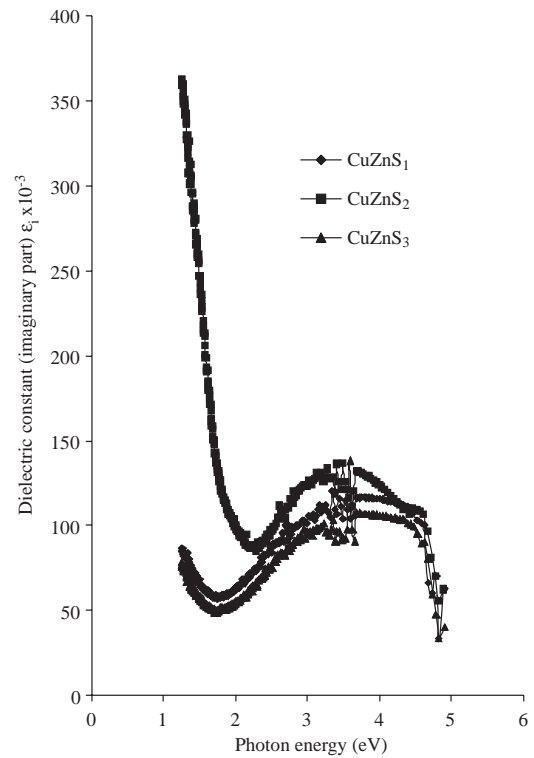
Figure 11. Imaginary dielectric ε_i as function of photon energy hf for CuZnS thin film.
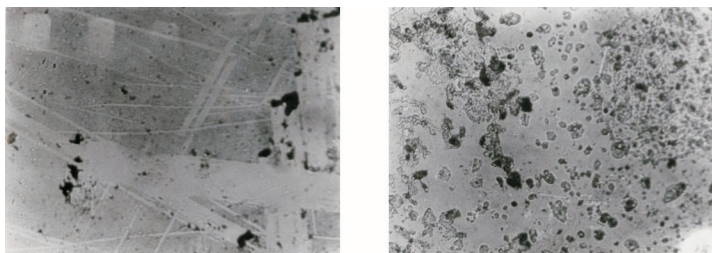
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Figure 12. Photomicrograph of the films revealing the crystalline nature.

5. Conclusion

We have demonstrated the possibility of depositing ternary thin films of $CuZnS_2$ using solution growth techniques (SGT) and have successfully characterized them. Some of the applications were discussed.

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