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SOLID STATE PROPERTIES OF COPPER-SILVER- SULPHIDE ($CuAg_2S_2$) THIN FILMS DEPOSITED BY SOLUTION GROWTH TECHNIQUE

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Abstract
Chemical bath deposited Copper Silver Sulphide ($CuAg_2S_2$) thin films on glass substrates were studied for its optical properties using spectrophotometer. Some of the optical properties studied include absorbance, transmittance, reflectance, refractive index, optical conductivity, absorption coefficient, dielectric constant and extinction coefficient. The direct band gap obtained is 2.3eV and the indirect band gap is 1.1eV. Some of the possible applications of the film are mentioned.

Keywords: Chemical bath deposition, $CuAg_2S_2$ thin film, optical properties and band gap energy.

INTRODUCTION
Interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in solar cells light emitting diodes and non-linear optical devices [Ortega-lopez *et al.* 2003] has been increasing in the recent years.
Ternary compounds are found to be promising materials for optoelectronic device applications such as green emitting devices and are suggested to be possible material for window layer of solar cells [Woon-Jo and Gye-choon 2003]. Some of them have been investigated for specific applications to super ionic conducting materials [Sasaki *et al.* 2003]. These ternary compounds are increasingly being studied for efficient solar energy conversion through photo-electrochemical solar cells [Padam and Rao 1986, Estrella Veronica *et al*. 2003], and have become potential candidates for such applications [Pawar *et al*. 1986, Jae-Hyeong *et al.* 2003]. Although, the deposition of ternary thin films have been reported using advanced technologies, the low cost and simple solution growth technique seems to be much better [Padam and Rao 1986].
This paper reports the investigation of optical properties of copper silver sulphide thin film, which was deposited using solution growth technique. The optical properties investigated include absorbance (A), transmittance (T) and reflectance (R), which were then used to calculate other parameters such as refractive index

(n), extinction coefficient (k), dielectric constant (ε) and optical conductivity (σ_o). The determination of these optical properties and the band-gap energy of these films was based on equations found in the literature [Pankove 1971, Ezema and Okeke 2003].

THEORY

For a weakly absorbing thin film on a non- absorbing substrate, the transmittance (T) can be expressed as [Theye 1985]

$$T = (1-R^2) \exp(-\alpha t) \quad (1)$$

Or $$t = (1/\alpha) \ln \{(1- R^2)/ T\} \quad (2)$$

where R is the reflectance, α is absorption coefficient and t is thickness of the film. Eq. (2) can be used to calculate the thickness of films where the absorbance (A) is in the range of $0.1 \leq A \leq 0.9$ [Pentia *et al*. 2004, Salam 2002, Majumdar *et al*. 2003, Quijada *et al*. 1998, Ramesh *et al*. 2003, Shwarsctein *et al*. 2006] for semiconductors and insulators, where the extinction coefficient (k) and refractive index (n) are related as $k^2 \ll n^2$, the relationship between R and n is given by [Ezema 2004, Rodrigo *et al*. 2002],

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

also, k and α are related by

$$k = \alpha\lambda/4n \quad (4)$$

where λ is the wavelength of the electromagnetic radiation. The relationship between dielectric constant (ε) and k is

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

where ε_r and ε_i are real and imaginary parts *of* E respectively. The optical conductivity (σ_o) is expressed as given by [Quijada *et al*. 1998]

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

where c is the velocity *of* light. In high absorption region under photon energy, the relation between absorption coefficient and photon energy is [Chen *et al*. 2003, Mitsuaki *et al*. 2003]

$$\alpha h f = A (\alpha h f - E_g)^n \ldots\ldots \text{for direct transitions} \quad (7)$$

where f is the frequency of incident photon, h is Planck's constant, A is constant that characterizes crystalline semiconductor and B is constant that characterizes many amorphous semiconductors, E_g is optical energy gap and n is number which characterizes the optical processes (n =1/2 for direct allowed transition, 3/2 for forbidden direct allowed transition and 2 for indirect allowed transition). When the straight portion of the plot of $(\alpha h f)^n$ against (h f) is extrapolated to $\alpha^2 = 0$, the intercept gives value of the transition band gap.

MATERIALS AND METHODS

The chemical deposition of the thin film onto the glass substrate was carried out by using a mixture of 1m copper chloride, 0.1m Ethylenediaminetelraacetate (EDTA), 0.1m silver nitrate 7.4m Triethanolamine (TEA), 14m ammonia, 1m Thiourea, distilled water microscopic glass slide and beaker.

The chemical bath deposition technique was used to prepare the $CUAg_2S_2$ thin film on glass substrate (slide) which had been previously degreased in concentrated nitric acid HNO_3 for 48hours, cleaned in cold water with detergent,

rinsed with distilled water and dried in air. The degreased-cleaned surface provide nucleation centre for growth of the film, hence yielding highly adhesive and uniformly deposited films.

The mixture was thoroughly stirred with a glass rod before the glass slide was vertically introduced into the beaker.

During deposition, cations and anions in the deposition solution reacted to become neutral atoms, which either precipitated spontaneously or vary slowly. Fast precipitation implied that thin films could not form on the substrate immersed in the solution. However, with the addition of TEA and EDTA, the reaction slowed down for thin film of neutral atom to be formed on the substrate. The complexing agents slowed down the precipitation action for formation of $CuAg_2S_2$, while the NH_3 solution served to stabilize PH of the mixture. Sulphide ions were released by hydrolysis of thiourea, but Cu and Ag ions formed cuprous-ethylenedia metetraacetic complex and silver triethanolamine complex ions by combining with EDTA and TEA, respectively. [Cu (EDTA and [Ag (TEA)] complexes adsorbed onto the glass substrate when heterogeneous nucleation and growth took place by ionic exchange reaction of S^{2-} ions. By the process of ion-by-ion exchange, $CuAg_2S_2$ was deposited on the glass substrate in the form of transparent, uniform and adherent film.

The thin film was characterized using UNICO UV-2102 PC spectrophotometer to determine the spectra absorbance and Transmittance of the film on the glass substrate with blank substrate is a reference glass slide. Eq. (2) was used to estimate the film thickness. The other parameters such as refractive index, extinction coefficient, dielectric constant, optical conductivity and energy band gap were determined using Eqs. (3)-(7). The energy band gap was obtained by plotting $(\alpha hf)^2$ against hf according to Eq. (7) and extrapolated upto $(\alpha hf)^2 = 0$.

Equations of reaction are as follows:

$CuCl_2.2H_2O + EDTA$ ===➔ $[Cu\ (EDTA)]^{2+} + 2Cl^-$

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

$AgNO_3 + TEA$ ===➔ $[Ag\ (TEA)^+ + NO_3$

$[Ag\ (TEA)^+$ ===➔ $Ag+ + TEA$

$(NH_2)_2\ CS + OH^-$ ===➔ $CH_2\ N_2 + H_2O + HS^-$

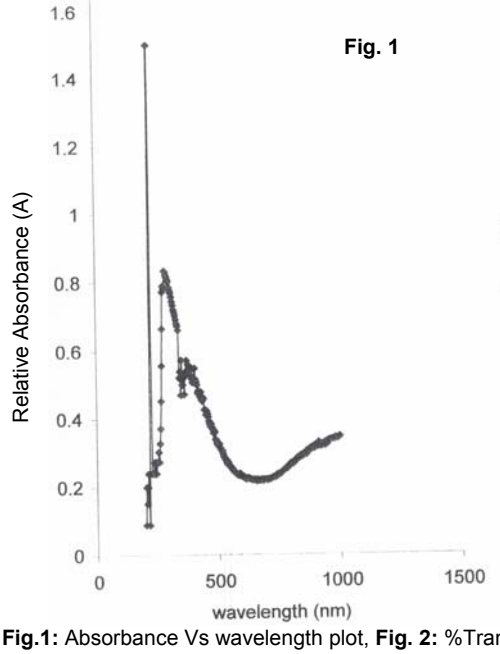
$HS^- + OH^-$ ===➔ $H_2O + S^{2-}$

$Cu^{2+} + 2Ag^+ + 2S^{2-}$ ===➔ $Cu\ Ag_2\ S_2$

RESULT AND DISCUSSION

The optical and solid state properties of copper- silver-sulphide studied include the following: the graph of spectral absorbance against wavelength as presented in Fig.1, increased sharply to a maximum value of 0.82 at 300nm from a value of 0.04 at 200nm and then decreased sharply to a minimum value of 0.21 at 650nm and thereafter increased with wavelength. The transmittance against wavelength in Fig.2 shows an increase to a maximum value of 61% at 660nm from a value of about 29% at 380nm and thereafter decreased rather sharply with wavelength. The graph of reflectance against wavelength presented in Fig.3 increased to a maximum value of 21% at 480nm from a value of 17.5% at 360nm, it then decreased to a minimum value of 17.5% at 680nm and thereafter increased steadily with wavelength. The absorption coefficient against photon energy is presented in Fig. 4. It decreased sharply from 0.8 $x10^6$ at 1.2eV to a minimum

value of 0.5 x10^6 at 1.9eV. Thereafter, it increased sharply with photon energy to a value of about 1.28 x10^6 at 3.3eV. The refractive index against photon energy is presented in Fig. 5. It decreased to a minimum value of about 2.04 at 1.9eV from a value of 2.28 at 1.2eV. Thereafter, it increased sharply to a maximum value of 2.28 at 2.6eV before falling sharply to about 1.94 at 3.3eV. The graph of optical conductivity against photon energy is presented in Fig. 6. It decreased sharply to a minimum value of 0.24 X10^{14} S^{-1} at 1.9eV from a value of about 0.43 X10^{14} S^{-1} at 1.2eV and thereafter, increased sharply with photon energy to about 0.6 X10^{14} S^{-1} at 3.3eV. The extinction coefficient against photon energy is presented in Fig. 7. It dropped sharply to a minimum value of about 25 x10^{-3} at 2.0eV from a value of about 64 x10^{-3} at 1.4eV before it increased rather steadily with photon energy to a value of about 39 x10^{-3} at 3.2eV. The direct band gap was extrapolated at $(\alpha\ h\ f)^2 = 0$ to be 2.3eV as shown in Fig. 8 and that of the indirect band gap is extrapolated at $(\alpha\ hf)^{1/2} = 0$ giving the value of 1.1 eV as presented in Fig. 9. The graph of real part of the dielectric constant is presented in Fig. 10. It decreased to a minimum value of about 4.2 at 1.9eV from a value of about 5.2 at 1.2eV. Thereafter, it increased steadily to a maximum value of 5.2 at 2.6eV before decreasing to about 3.8 at 3.3eV. The graph of imaginary part of the dielectric constant is presented in Fig. 11. It decreased sharply to a minimum value of 100 x10^{-3} at 2.0eV from a value of 290x10^{-3} at 1.2eV. Thereafter, it increased to a maximum value of 160 x10^{-3} at 2.8eV before decreasing with photon energy. It was observed that absorbance heavy in the UV-region and poor in the VIS-NIR-regions, the transmittance was less in UV-region and more in VIS-NIR regions and reflectance is in the UV-region and more in the VIS-NIR-region. These properties make the material good for thermal control coatings for cold climates, antireflection coatings and solar cell materials. Generally the films could find applications in agricultural, architectural, car and electronics industries.



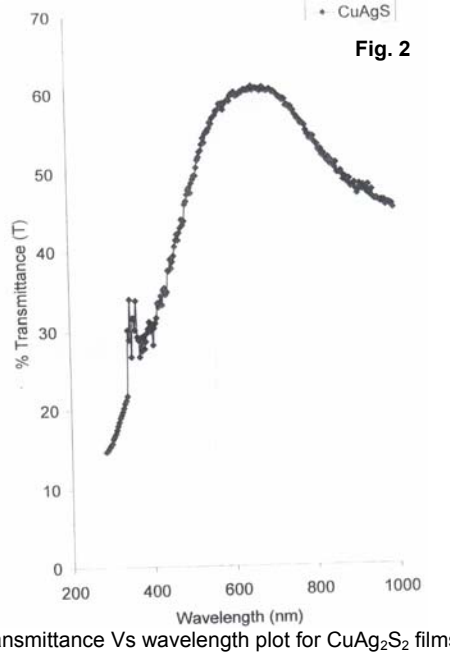


Fig.1: Absorbance Vs wavelength plot, **Fig. 2:** %Transmittance Vs wavelength plot for $CuAg_2S_2$ films.

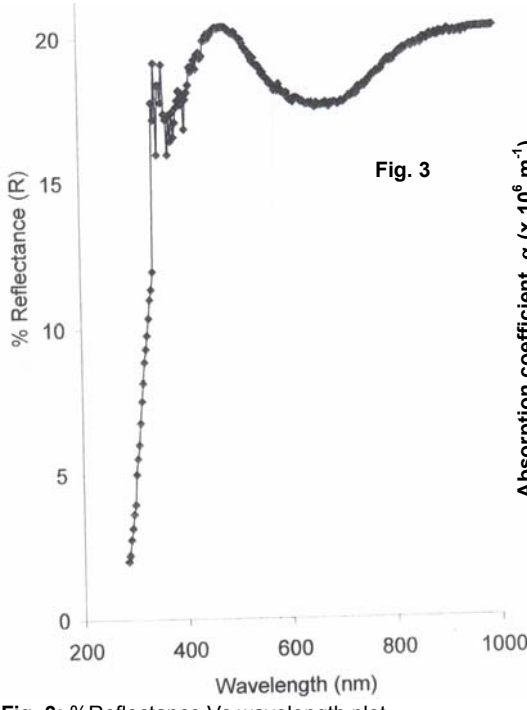


Fig. 3: %Reflectance Vs wavelength plot for $CuAg_2S_2$ thin film.

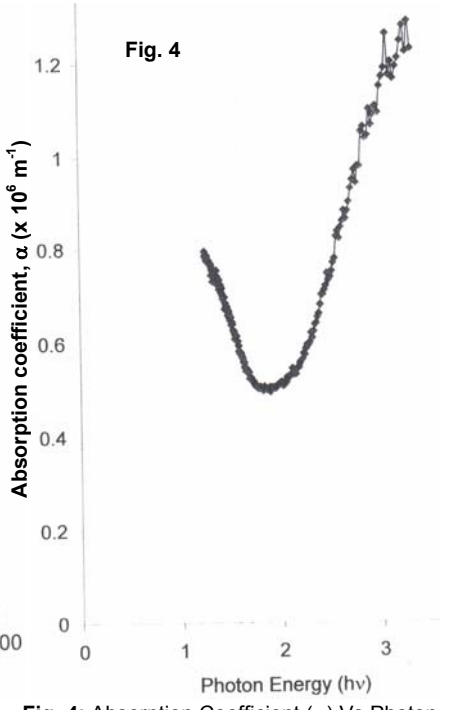


Fig. 4: Absorption Coefficient (α) Vs Photon Energy plot for $CuAg_2S_2$ thin film.

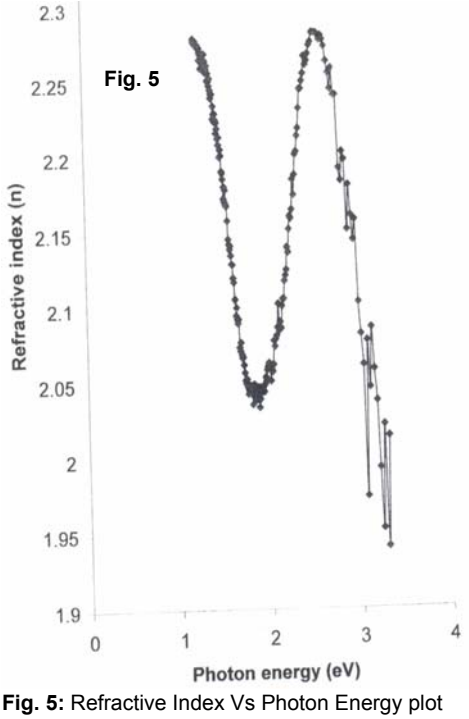


Fig. 5: Refractive Index Vs Photon Energy plot for $CuAg_2S_2$ thin film.

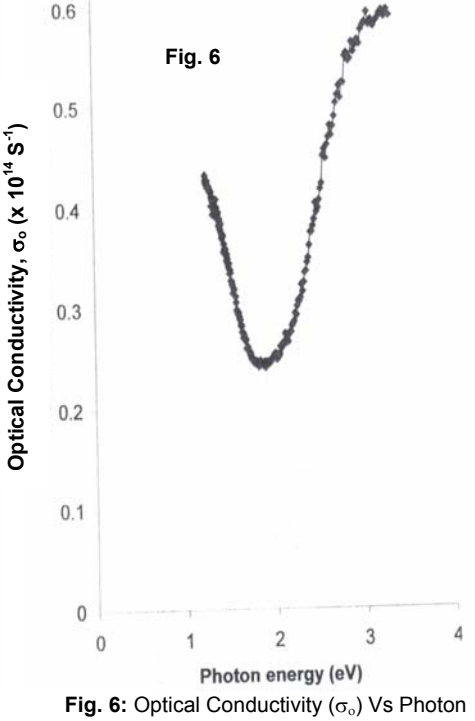


Fig. 6: Optical Conductivity (σ_o) Vs Photon Energy plot for $CuAg_2S_2$ thin film.

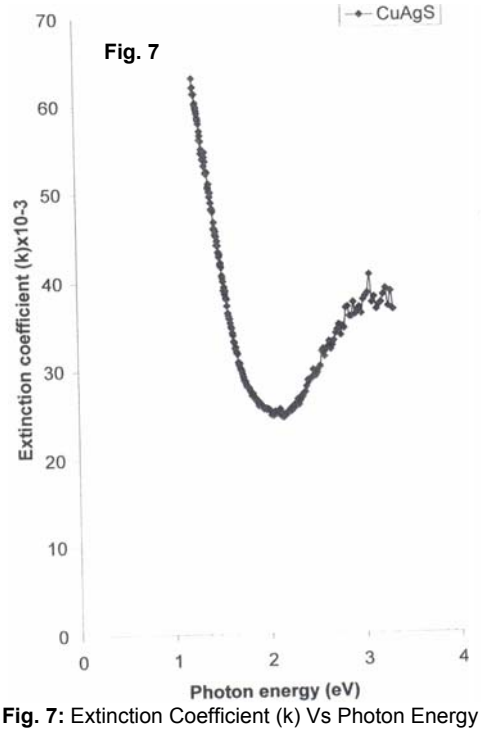


Fig. 7: Extinction Coefficient (k) Vs Photon Energy plot for $CuAg_2S_2$ thin film.

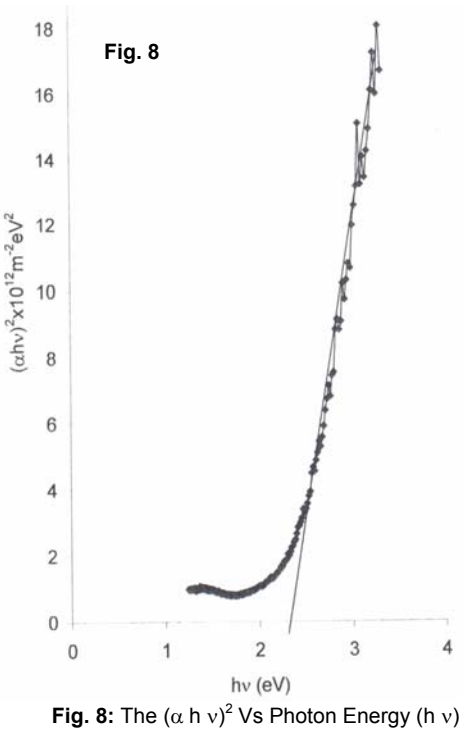


Fig. 8: The $(\alpha\ h\ \nu)^2$ Vs Photon Energy $(h\ \nu)$ plot for $CuAg_2S_2$ thin film.

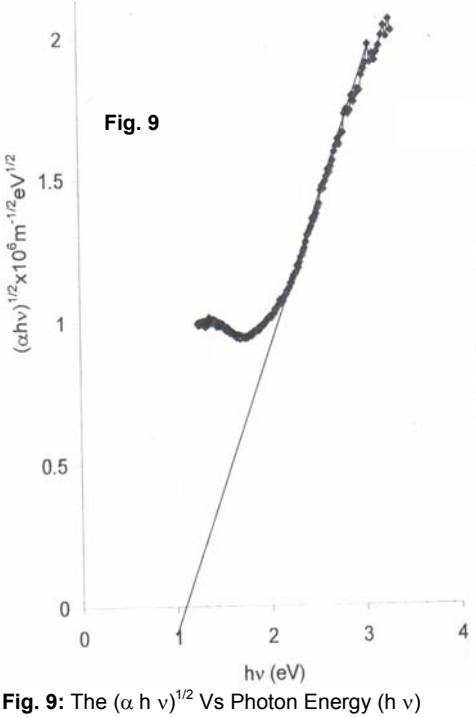


Fig. 9: The $(\alpha\ h\ \nu)^{1/2}$ Vs Photon Energy $(h\ \nu)$ plot for $CuAg_2S_2$ thin film.

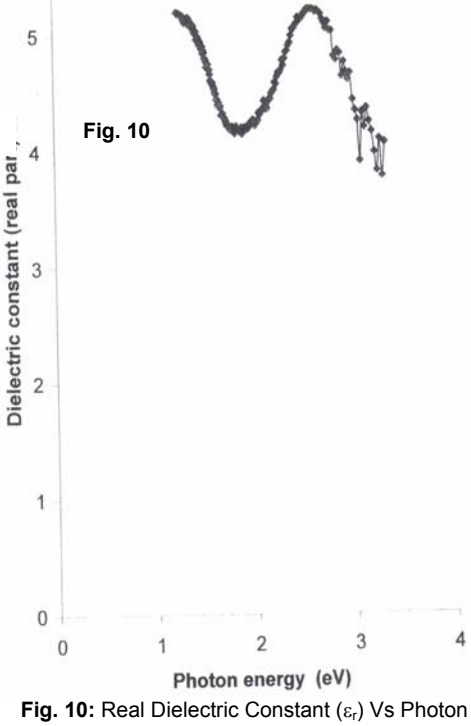


Fig. 10: Real Dielectric Constant (ε_r) Vs Photon Energy $(h\ \nu)$ plot for $CuAg_2S_2$ thin film.

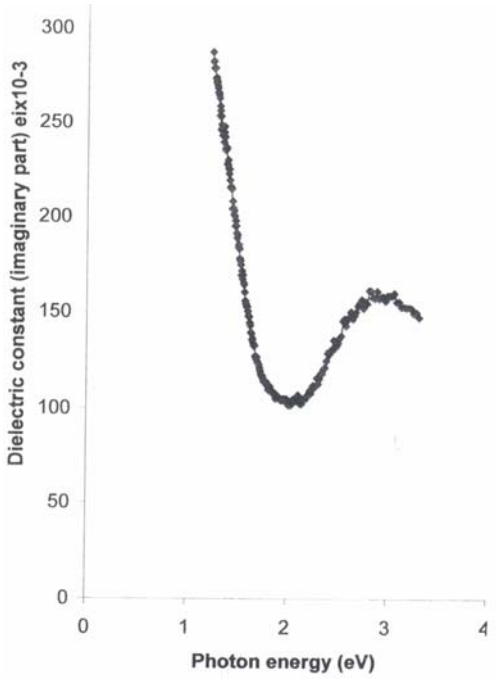


Fig. 11: Imaginary Dielectric Constant (ε_i) Vs Photon Energy plot for $CuAg_2S_2$ thin film.

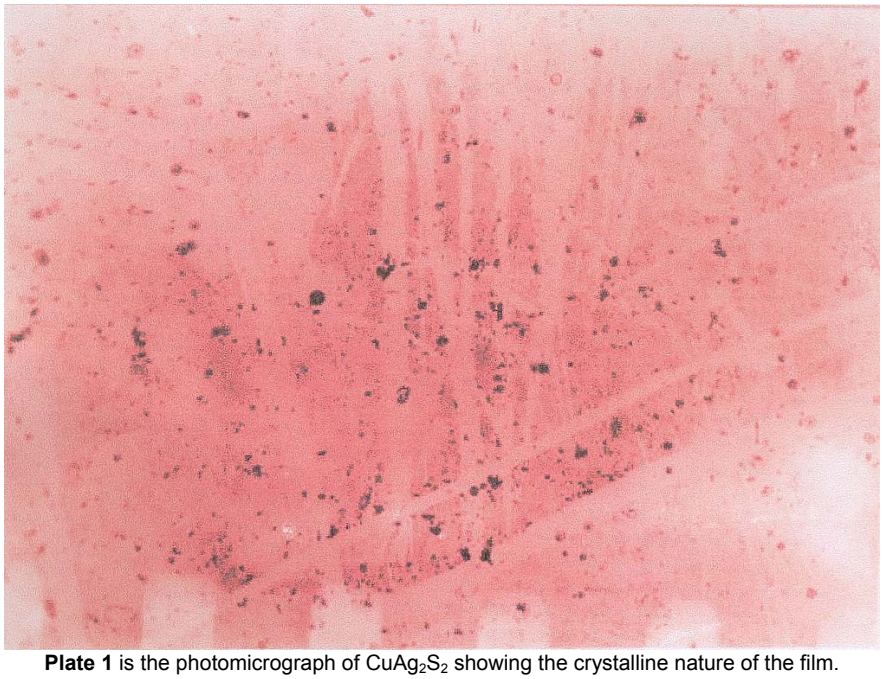


Plate 1 is the photomicrograph of $CuAg_2S_2$ showing the crystalline nature of the film.

In summary, we have demonstrated the possibility of depositing ternary films using solution growth techniques (SGT) and have successfully characterized the film. The possible applications of the film have been highlighted.

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