Trends in

Applied Sciences Research

ISSN 1819-3579

Academic
Journals Inc.

www.academicjournals.com

Trends in Applied Sciences Research 1 (5): 467-476, 2006
ISSN 1819-3579

Optical Properties of CuS Thin Films Deposited by Chemical Bath Deposition Technique and Their Applications

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Abstract: CuS thin films of average thickness between 0.498 and 0.548 μm were grown on glass substrates at 300 K by chemical bath deposition technique and annealed at various temperatures. The optical constants (index of refraction n, extinction coefficient k and absorption coefficient α) were determined using the absorbance and transmission measurement from a Unico UV-2102 PC spectrophotometer, at normal incidence of light in the wavelength range of 200-1000 nm. The films have high absorption of greater than 90% in the UV region but with moderate transmission of which is greater than 30% but less than 65% throughout the entire VIS-NIR spectrum. The average refractive index (n) is between 2.07 and 2.26 while the average extinction coefficient is between 0.049 and 0.063. The refractive index greater than 2.0 makes the material a good candidate for protective coatings. The plot of $(ahv)^2$ against (hv) showed that the material has a direct band gap between 1.60 eV and 2.40 eV while the plot of $(ahv)^{½}$ against (hv) has an indirect band gap between 1.20 eV and 1.60 eV. The band gap study show a transition of from a direct Cu_2S to an indirect CuS thin film. The high absorbance of the films made them good materials for large area selective coatings for photothermal conversion of solar energy.

Key words: Optical properties, copper sulphide, thin films, semiconducting device

Introduction

In the past few decades, there has been an increasing interest in semiconducting chalcogenide thin films, which has been as a result of their wide applications in various fields of science and technology. The implication has resulted in a drastic cut in the cost of production of semiconductor devices. Binary semiconductors are considered important technological materials because of their potential applications in optoelectronic devices, solar cells, IR detectors and lasers (Hodes, 1995; Pandey *et al*., 1996). Metal chalcogenide films have been extensively studied because of their promise in electronic, optical and superconductor devices as well as in solar energy conversions (Kaur *et al*., 1980; Nair *et al*., 1989; 1990; Rai, 1993; Estrella *et al*., 2003; Ezema and Okeke, 2003a, b; Ezema, 2004).

Chemical bath deposition technique for preparation of thin films from aqueous solution is a promising technique because of its simplicity; by this method a large area of thin film can be deposited without sophisticated instruments. The properties of the deposited material can be varied and controlled by proper optimization of the chemical baths and deposition conditions.

Researchers are working on various methods to prepare good quality films as thin film semiconducting materials are now being widely used. This study reports on the preparation and optical properties of copper sulphide thin films that could be used as a semiconducting device.

The basic principle behind chemical bath-deposition is that in order to precipitate of a certain compound from a solution its Ionic Product (IP) must exceed the Solubility Product (SP). A compound that is weakly soluble in water easily satisfies this condition. However, spontaneous precipitation

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should be eliminated in order for a thin film to form. This can be achieved by using an appropriate complexing agent, which can produce stable complex of the metallic ions in the solution. The complexing agent slowly releases the metal ions on dissociation, resulting in slow precipitation of the compound in the chemical bath by ion-ion reaction. The compound can form on substrates or on the sides of the chemical bath as thin films by this method. For a metal M and complexing agent A, the existence of free metal ions in the solution can be explained by the equilibrium reaction

$$M(A)^{2+} \rightleftharpoons M^{2+} + A$$

The concentration of metal ions present in the solution can be controlled by the concentration and temperature of an appropriate complexing agent, thereby controlling the deposition rate. It is also possible that the concentration of the chalcogen ions present locally may be high enough in the chemical bath solution such that the SP may exceed the IP, which leads to localize spontaneous precipitation of chalcogenide. To overcome this, chalcogen ions are generated slowly and uniformly throughout the solution from compound yielding these ions in basic medium such that rate of release can be controlled by the pH value. For example:

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

$$HS^- + OH^- \rightleftharpoons H_2O + S^{2-} \text{ (for } S^- \text{ ions)}$$

$$Na_2SeSO_3 + 2OH \rightleftharpoons Na_2\,SO_4 + Se^{2-} \text{ (for } Se^- \text{ ions)}$$

Materials and Methods

Thin films of CuS are deposited using chemical baths in which thiosulphate, thioacetamide, thiourea, dimethylthiourea are used as different sources sulphide ions (Nair *et al*., 2003; Estrella *et al*., 2003). To deposit CuS thin films on glass substrates the chemical bath was constituted as below. To prepare a volume of 100 mL of the chemical bath solution 10 mL of 1M $CuCI_2$ was taken in beaker to which the sequential additions of 8 mL of 50% TEA, 8 mL of 30% NH_3, 10 mL of 1M NaOH, 10 mL of 1 M thiourea and 54 mL distilled water. The resulting solution was well stirred and the substrate, which was previously decreased in HCl, introduced into the solution. The chemical bath was maintained at room temperature for 4 h. The slides were removed rinsed in distilled water and dried in air (300 K). The films were then annealed in an oven (373 K) and heated in an open red-hot filament (393 K).

For optical absorption measurement of the films deposited on glass slides, a similar blank slide was used as reference in a Unico UV-2102 PC spectrophotometer at the scan intervals of 6 nm. Optical band gaps were calculated knowing their absorption edge extrapolated from the absorption spectra.

Results and Discussion

The spectral Absorbance of copper sulphide films prepared at 300 K and annealed at 373 K and 393 K is displayed in Fig. 1. The film Samples absorb heavily in the UV and partly VIS regions but moderately in the remaining VIS and NIR regions.

The absorbance of the thin films were observed to decrease with wavelength through UV-VIS regions but showed a rising with wavelength at NIR regions except for the film annealed for 393 K. It is found that this film decreased rapidly initial in the UV region but slowly and constantly in the VIS-NIR regions. The annealing of the film deposited at 300 to 373 K in oven, when compared together shows that the absorbance at 300 K is higher in the UV-VIS regions but is lower at the NIR region. This showed better absorbance spectra for the film and resembles the absorbance spectra for 300 K1. The annealing of the film deposited at 300 to 393 K in hot plate when compared to 300 K shows

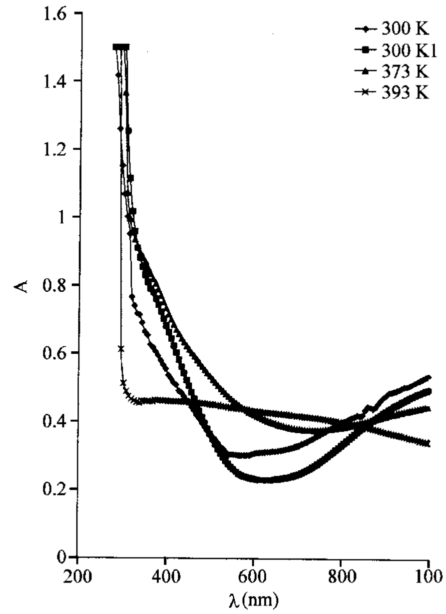


Fig. 1: Absorbance (A) as a function of wavelength (λ) under for CuS thin film under various thermal treatment

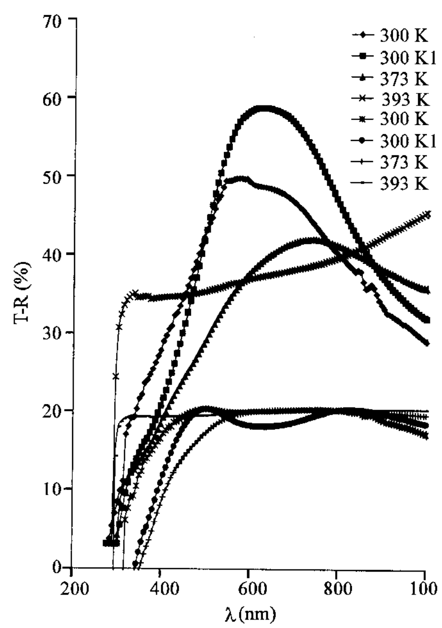


Fig. 2: Transmittance (T) and reflectance (R) as function of wavelength (λ) under for CuS thin film under various thermal treatment

the absorbance at 393 K is lower in the UV and up to 458 nm in the VIS regions and is higher from 458 nm up to 800 nm in the NIR region from where it becomes lower.

The transmittance and reflectance spectra (Fig. 2) estimated from absorbance spectra showed that all the films have transmittance between 3 and 59% in the UV-VIS-NIR regions.

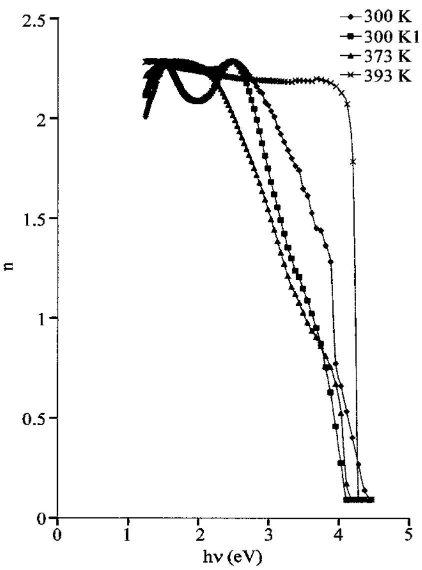


Fig. 3: Refractive index (n) as function of with photon energy (hν) for CuS thin film under various thermal treatment

The transmittance of the films increased with wavelength from the UV regions to the VIS regions but decreased with wavelength at the NIR regions except the film annealed to 393 K, which increased rapidly in the UV region but increased slowly and constantly towards NIR regions. The films have reflectance that increased with wavelength in the UV and part of VIS regions but became constant with wavelength in the remaining VIS and NIR regions. The samples showed average transmittances of greater than 17% throughout UV-VIS-NIR regions. We consider architectural use of these films as spectrally selective window coatings. They are of two types; solar control and low thermal emittance or heat mirror coating (Granquist, 1987). The former is transparent only in the visible region of the solar spectrum (300-700 nm) while the infrared part (above 800 nm) is reflected so that the interior of the building is kept cool. They are therefore suitable in warm countries and saves energy spent on conventional air conditioners. The latter is suitable in cold climates. These coatings are transparent to visible and NIR radiation (300-3000 nm) to minimize heat loss and have low thermal emittance (high reflectance) above 300 nm.

The spectral transmittances of 300 K, 300 K1 and 373 K show that the films are capable of fairly suppressing UV and IR radiations while transmitting the VIS radiations. Films 300 K, 300 K1 and 373 K are suitable for solar control coatings. Human eye is sensitive only in the range 400-700 nm and is peaked at 500 nm (photopic vision). This is an important factor in window coatings and is fairly met in these films.

Film annealed at 393 K suppressed transmittance of UV radiation while fairly transmitting the VIS and IR radiations. This property make the film annealed to 393 K a good material for thermal control coatings and for screening off UV portion of electromagnetic radiation, which is dangerous to human health and as well harmful to domestic animals. The film can be used for coating eyeglasses for protection from sunburn caused by UV radiations. Since it shows moderately high transmittance of VIS and NIR radiations it can be used for coating of poultry roofs and walls. This will ensure that young chicks, which have not developed protective thick feather, are protected from UV radiations while the heating portion of the electromagnetic spectrum maintains the heating of the poultry house and as well there is admittance of VIS light in the house.

The variation of n with hν for the samples of CuS thin films is shown in Fig. 3. The average refractive indexes for samples are within the range of 2.07 and 2.27 while the maximum occurred at 2.28 but different photon energies.

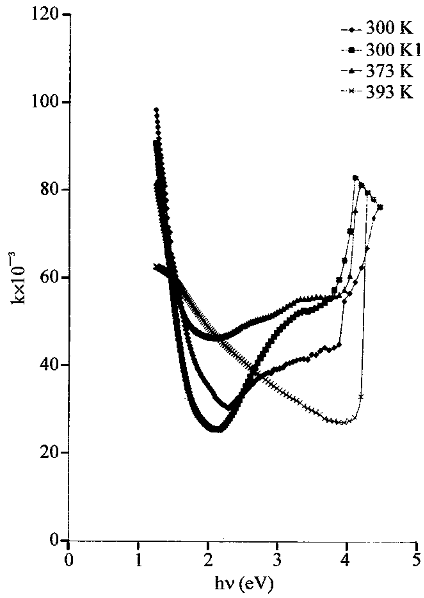


Fig. 4: Variation of extinction coefficient (k) with photon energy (hν) for CuS thin film under various thermal treatment

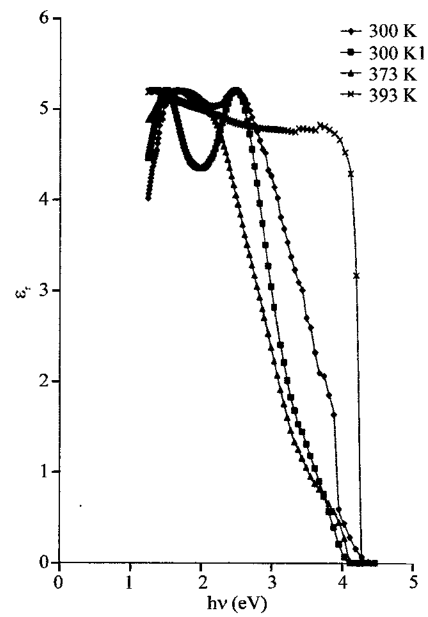


Fig. 5: Real dielectric constant (ε_r) as function of with photon energy (hν) for CuS thin film under various thermal treatment

The variation of k with hν for the samples of CuS thin films is shown in Fig. 4. The maximum k values for the samples range between 6.25×10^{-2} and 9.83×10^{-2} with average values in the range between 4.91×10^{-2} and 6.35×10^{-2}.

The plots of ε_r and ε_i against hν are shown in Fig. 5 and 6, respectively. From minimum values that ranged between 0.003 and 0.02 at the high-energy region, ε_r rises to maximum values that ranged

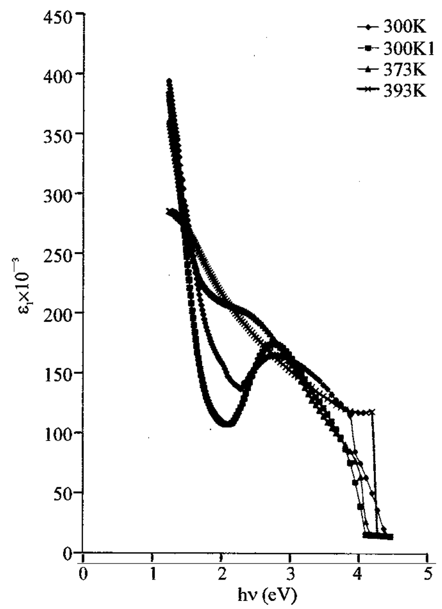


Fig. 6: Imaginary dielectric (ε_r) as function of with photon energy (hν) for CuS thin film under various thermal treatment

between 5.19 and 5.20. On the hand from minimum values that ranged between 1.43×10^{-3} and 1.55×10^{-3} at the high-energy region, ε_i rises to maximum values that ranged between 2.85 and 3.94. Two prominent minima were observed by samples 300 K and 300 K1 which were films deposited at ambient temperature, which were observed to disappear on annealing to 373 and 393 K.

A plot of optical conductivity σ_o against hν is shown in Fig. 7. The average values range between $0.42\times10^{14}S^{-1}$ and $0.50\times10^{14}S^{-1}$ for all the samples while maximum values occur $0.60\times10^{14}S^{-1}$. The films deposited at ambient temperature and annealed to 373 K observed prominent peaks and minima which disappeared on annealing to 393 K.

The plots of α against hν are shown in Fig. 8. The region of higher values of α that is $\alpha>10^4cm^{-1}$ correspond to transition between extended state in both valence and conduction bands while the lower values that is $\alpha\leq10^4cm^{-1}$ is the region where absorption present a rough exponential behavior (Kotkata *et al*., 1994).

Crystals of Cu_xS are reported to show a direct band gap value of 1.7 eV and indirect band gap values of 1.05-1.21 eV when x is 2 (chalcocite) and 1.3 eV when x is in the range of 1.935-1.955 (djurleite) (Nair *et al*., 1998).

A plot of $(\alpha h\nu)^2$ against hν for CuS films are shown in Fig. 9. These reveal band gap between 1.60 eV and 2.40 eV. The band gap 1.60 eV for the film annealed at 393 K was found to be close to the band gap for Cu_2S reported to be 1.70 eV (Nair *et al*., 1998), 1.72 eV (Osuji, 1994) while the band gap of 2.40 eV for film deposited at ambient temperature is found to be within range 1.95-2.60 eV (Udeajah, 1996).

A plots of $(\alpha h\nu)^{1/2}$ against hν for CuS films are shown in Fig. 10. These reveal band gaps between 1.20 eV for annealed at 373 K, 1.55 eV for film at 300 K1 and 1.80 eV for film at 300 K. The indirect band gap for 300 K1 agrees fairly well with 1.55 eV (Nair *et al*., 1998) reported for indirect for CuS thin films. These band gaps of film together with the high absorbance within the solar spectrum make them good material for fabrication of solar cell.

The average solid-state properties of the film under various heat treatments are presented in Table 1.

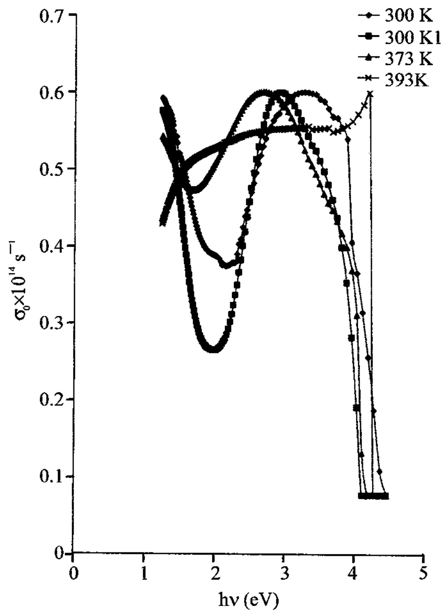


Fig. 7: Plots of optical conductivity (σ_0) as function of with photon energy (hν) for CuS thin film under various thermal treatment

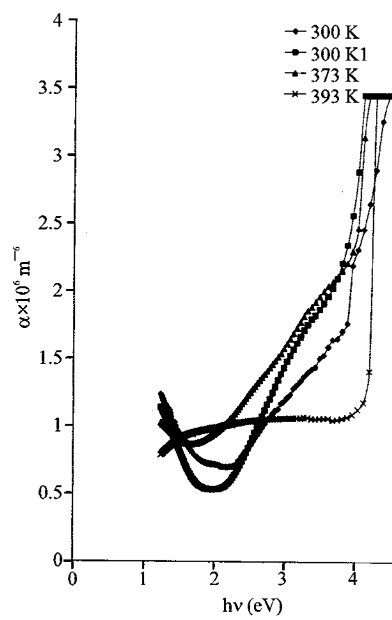


Fig. 8: Plots of absorption coefficient (α) as function of with photon energy (hν) for CuS thin film under various thermal treatment

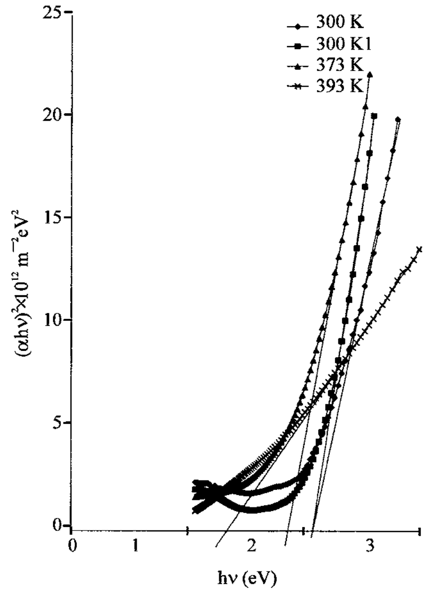


Fig. 9: A plot of $(\alpha h\nu)^2$ as function of with photon energy (hν) for CuS thin film under various thermal treatment

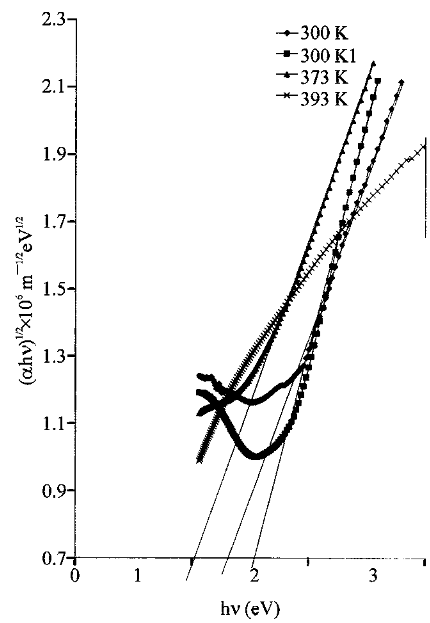
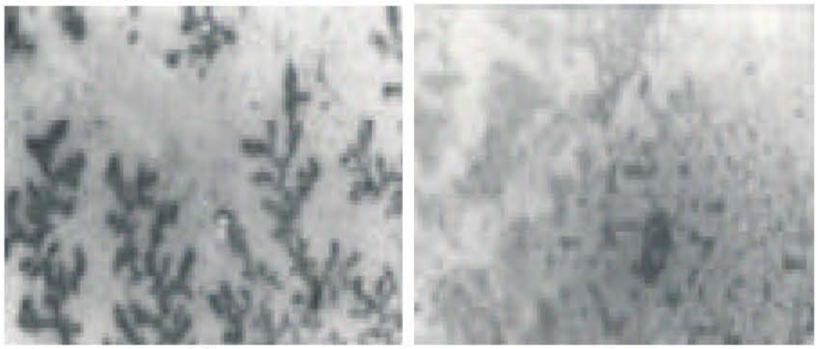


Fig. 10: A plot of $(\alpha h\nu)^{1/2}$ as function of with photon energy (hν) for CuS thin film under various thermal treatment

Table 1: Solid state properties and thickness of CuS under thermal treatment

Sample No	Aver. α (m^{-1})	Direct band gap E_g (eV)	Indirect band gap E_g (eV)	Aver. (ε_r)	Aver. (ε_i)	Thickness (μm)
300 K	0.954	2.40	1.55	4.88	0.277	0.527
373 K	0.925	2.20	1.20	5.11	0.274	0.515
393 K	0.902	1.60	-	5.13	0.264	0.498
300 K1	1.091	2.40	1.60	4.03	0.182	0.548



(a) (b)

Fig. 11a, b: Optical micrograph of CuS thin film annealed (a) at 300K and (b) at 393K

Table 1 shows that as average absorption coefficient (α) decreased other parameters such as dielectric constant both real (ε_r) and imaginary (ε_i) and thickness decreased with thermal treatment.

Figure 11(a,b) shows the optical micrograph of CuS thin film deposited at 300 K and annealed to 393 K. The optical micrographs (magnification 100x) of the as deposited films at 300 K reveal good film uniformity. The variations in the morphology of the film show that the annealing of the film affects the structure of the film and as well the absorption coefficient.

Conclusions

CuS thin films with direct energy band gaps between 1.60 and 2.40 eV and indirect band gaps between 1.20 and 1.55 eV have been successfully deposited using chemical bath deposition technique. The deductions from the spectrophotometers show estimated average values of n that range between 2.07 and 2.26, k range between 4.91×10^{-2} and 6.35×10^{-2} and that of σ_0 between $0.42\times10^{14}S^{-1}$ and $0.50\times10^{14}S^{-1}$. The percentage transmittance of the films ranged between 19 and 59% in the visible regions. The films were found to have average transmittance of about 40% in the UV-VIS-NIR regions while exhibiting average reflectance of about 20% in the same regions. Some of the films could be effective as coatings for solar control, eyeglasses, poultry houses and as well good materials for solar cell fabrication.

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