

1-1-2010

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EYA, D. D. O. (2010) "Chemical bath deposition and characterization of Cu<sub>20</sub>-Cu<sub>x</sub>S thin films," *Turkish Journal of Physics*: Vol. 34: No. 1, Article 6. <https://doi.org/10.3906/fiz-0905-18>  
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# Chemical bath deposition and characterization of $\text{Cu}_2\text{O}-\text{Cu}_x\text{S}$ thin films

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Received .2009

## Abstract

$\text{Cu}_2\text{O}-\text{Cu}_x\text{S}$  thin films have been deposited on glass substrate by chemical bath deposition technique. The films were obtained by depositing Copper Sulphide ( $\text{Cu}_x\text{S}$ ) on Copper (I) Oxide ( $\text{Cu}_2\text{O}$ ) and then  $\text{Cu}_2\text{O}$  on  $\text{Cu}_x\text{S}$ .

The peak solar transmittance across the thin films were found to be  $< 40\%$  and as low as  $10\%$ , and falls with energy into the infra-red region. The absorbance is higher near the UV and IR regions. Reflectance is  $< 20\%$ . The band gap of both respective combinations is in the range of  $2.19-2.32$  eV and with film thickness  $0.54 \mu\text{m}-1.30 \mu\text{m}$ . The extinction coefficient and refractive index are in the ranges of  $5.41 \times 10^{-2} - 20.11 \times 10^{-2}$  and  $1.60-2.60$ , respectively.

Since the absorbance increases as one goes towards the IR region, the films could be useful in solar control (providing cool interior) in tropical regions.

**Key Words:** Chemical bath, optical properties, transmittance, energy band gap, solar control, Copper (I) Sulphide, annealing

## 1. Introduction

Preparation and use of  $\text{Cu}_x\text{S}$  thin films in solar control have been extensively reported in [1–3]. Solar control coatings refer to selective solar radiation filters required for glazing applications in warm climates and heat mirror coatings refer to those required for applications in cold climates. Ideally, solar control coatings must enable controlled optical transmittance ( $\sim 10-50\%$ ) and low reflectance ( $< 10\%$ ) in the visible region ( $0.4-0.7 \mu\text{m}$ ) and high reflectance ( $\sim 90\%$ ) for longer wavelength ( $> 0.7 \mu\text{m}$ ) radiation. Such characteristics will provide adequate natural illumination of the interior of a building while rejecting much of the incident radiation which might cause an undesirable increase in interior temperature of the building and thereby increase the cooling cost in locations with warm climates.

In contrast, ideal heat mirror coatings must possess a high transmittance ( $\sim 90\%$ ) in the entire solar spectrum (up to a wavelength  $\sim 2.5 \mu\text{m}$ ) but high reflectance ( $\sim 90\%$ ) for thermal radiation. Thermal radiation causes temperature to rise in buildings in colder locations thereby reducing heating cost [1].

To take care of the unstable nature of  $\text{Cu}_x\text{S}$  films, it was suggested in [1] that polymer coating be applied over the films to enhance the stability of the coatings and ensure further protection against any possible toxicity.

In this paper, the deposition of  $\text{Cu}_x\text{S}$  on  $\text{Cu}_2\text{O}$  on glass substrate and the effect on the properties of the films are reported.

The deposition of  $\text{Cu}_x\text{S}$  on  $\text{Cu}_2\text{O}$  improves the stability of resulting films and also moderates the properties of the precombination of individual films since the choice of substrate can strongly affect the film morphology, structure and optical properties [4].

## 2. Experimental details

A detailed deposition procedure for  $\text{Cu}_2\text{O}$  has been reported in our paper [5], and P. K. Nair and M. T. S. Nair reported for  $\text{Cu}_x\text{S}$  in [1, 2].

In the present work, chemical baths for the deposition of  $\text{Cu}_2\text{O}$  were constituted with 0.1 M solution of Copper Nitrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ] and 0.1 M solution of Hydrazine ( $\text{NH}_2 \cdot \text{NH}_2$ ) mixed in equal volumes in 50 ml beakers with 1 M Triethanolamine (TEA) used as complexing agent. On the other hand, the baths for the deposition of  $\text{Cu}_x\text{S}$  were constituted with 0.5 M solution of Copper Nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), 1 M solution of thiourea, 25% Ammonia (aqueous, as supplied) and 1 M solution of TEA used as complexing agent.

In each case, both films were deposited on commercial glass slides ( $76 \times 26 \times 1 \text{ mm}^3$ ) degreased in aqua regia, washed in detergent and rinsed in distilled water. At the end of the deposition period (4 1/2 and 4 hours, respectively), the films were rinsed in distilled water and dried in air.

Later,  $\text{Cu}_x\text{S}$  was deposited on  $\text{Cu}_2\text{O}$  ( $\text{Cu}_2\text{O-Cu}_x\text{S}$ ) films and then  $\text{Cu}_2\text{O}$  on  $\text{Cu}_x\text{S}$  ( $\text{Cu}_x\text{S-Cu}_2\text{O}$ ) films. Some samples of the films were annealed at temperature of 423 K.

Measurements for the analysis of the optical properties of the films were made using an UNICAM Helios  $\alpha$  Spectrophotometer. The compositions of the films were analyzed using energy dispersive X-ray fluorescence (EDXRF). The source uses Silver (Ag) X-ray tube (2.6–20.0 KeV) as the excitation source.

## 3. Results and discussion

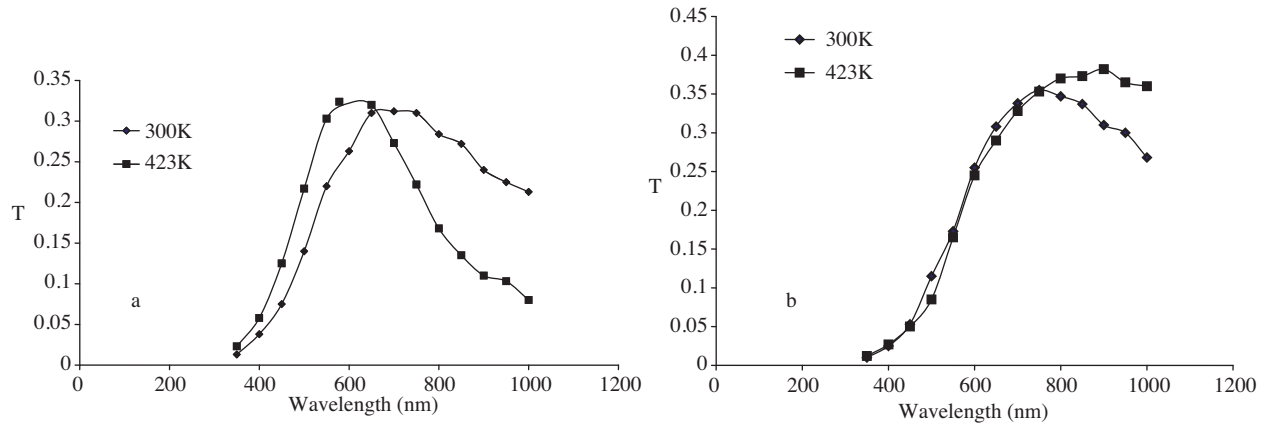
$\text{Cu}_2\text{O}$  and  $\text{Cu}_x\text{S}$  individually degrade with time even though the rate appears to be slower in  $\text{Cu}_x\text{S}$  than in  $\text{Cu}_2\text{O}$ . In [1], polymer coating on  $\text{Cu}_x\text{S}$  films was applied to enhance its stability. However, it is observed here that the rate of degradation of the films having  $\text{Cu}_x\text{S}$  on  $\text{Cu}_2\text{O}$  is very much slower than for  $\text{Cu}_x\text{S}$  or  $\text{Cu}_2\text{O}$  films separately.

The percentage transmittance of  $\text{Cu}_2\text{O}$  can be as high as 80–90% in visible-infrared regions (VIS-IR) while reflectance is 5–20%. Even though  $\text{Cu}_x\text{S}$  has peak transmittance in visible region [1–3, 6], it is not as high as the former case. The peak for the as-grown samples is 68% while for the samples annealed at 423 K the peak transmittance is 41%.

Transmittance falls as wavelength increases from the visible region into the infrared region. In the

daylight,  $\text{Cu}_x\text{S}$  films exhibit golden or green color [7]. The match between the transmittance spectra of the  $\text{Cu}_x\text{S}$  films and the spectral sensitivity of photopic vision leaves the perception of a greenish-yellow illumination in the building interior [2].

The peak transmittance for  $\text{Cu}_2\text{O-Cu}_x\text{S}$  films in visible region is about 35% and can be below 10% in the infrared region, as shown in Figure 1(a). Even though the peak transmittance for  $\text{Cu}_x\text{S-Cu}_2\text{O}$  films in the visible region falls within the same range as in  $\text{Cu}_2\text{O-Cu}_x\text{S}$ , the transmittance in the infrared can be as high as 38%, as shown in Figure 1(b). Generally, the reflectance is very low; but in some cases, reflectance can be as high as  $< 20\%$ , as shown in Figure 2. The very high degree of absorption in the UV and IR regions produced some distortion in the transmission properties in those regions, as shown in Tables 1 and 2 and Figure 2. These



**Figure 1.** A graph of Transmittance,  $T$  versus wavelength,  $\lambda$  for (a)  $\text{Cu}_2\text{O-Cu}_x\text{S}$  and (b)  $\text{Cu}_x\text{S-Cu}_2\text{O}$  thin films.

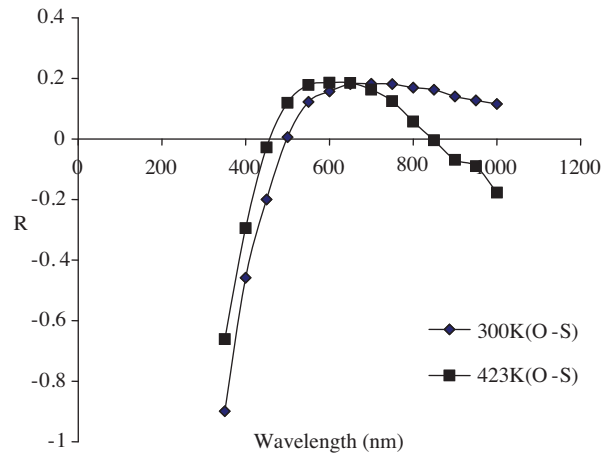
**Table 1.** Transmission data of  $\text{Cu}_x\text{S}$  thin films at 300 K (1) and 423 K (2).

Wavelength, $\lambda$	Absorption, $A_1$	Absorption, $A_2$	Transmittance, $T_1$	Transmittance, $T_2$	Reflectance, $R_1$	Reflectance, $R_2$
300	1.117	1.640	0.076	0.023	-0.193	-0.663
348	0.817	1.067	0.152	0.086	0.031	-0.153
400	0.658	0.933	0.220	0.117	0.122	-0.050
450	0.483	0.733	0.329	0.185	0.188	0.082
500	0.366	0.583	0.431	0.261	0.203	0.156
550	0.317	0.433	0.482	0.369	0.201	0.198
600	0.251	0.414	0.561	0.385	0.183	0.201
650	0.217	0.383	0.607	0.414	0.176	0.203
700	0.267	0.400	0.681	0.398	0.152	0.202
750	0.200	0.467	0.631	0.341	0.169	0.192
800	0.150	0.533	0.708	0.293	0.142	0.174
863	0.184	0.584	0.655	0.261	0.161	0.155
926	0.200	0.634	0.631	0.232	0.169	0.134
989	0.200	0.751	0.631	0.177	0.169	0.072
1052	0.217	0.784	0.607	0.164	0.176	0.062

optical characteristics match the ideal solar control characteristics. The properties of the annealed samples match those ideal characters much more. Details of the optical properties are shown in Table 1, Table 2, and Figures 1 and 2.

**Table 2.** Transmission data of  $\text{Cu}_x\text{S}-\text{Cu}_2\text{O}$  thin films at 300 K (1) and 423 K (2).

Wavelength, $\lambda$	Absorption, $A_1$	Absorption, $A_2$	Transmittance, $T_1$	Transmittance, $T_2$	Reflectivity, $R_1$	Reflectivity, $R_2$
350	1.886	1.638	0.013	0.023	-0.899	-0.661
400	1.420	1.237	0.038	0.058	-0.458	-0.295
450	1.125	0.903	0.075	0.125	-0.200	-0.028
500	0.864	0.664	0.014	0.217	0.006	0.119
550	0.638	0.519	0.220	0.303	0.122	0.178
600	0.580	0.492	0.263	0.322	0.157	0.186
650	0.509	0.495	0.310	0.320	0.181	0.185
700	0.506	0.564	0.312	0.273	0.182	0.163
750	0.509	0.664	0.310	0.221	0.181	0.124
800	0.547	0.775	0.284	0.168	0.169	0.057
850	0.565	0.870	0.272	0.135	0.163	-0.005
900	0.620	0.959	0.240	0.110	0.140	-0.069
950	0.648	0.987	0.225	0.103	0.127	-0.090
1000	0.672	1.097	0.213	0.080	0.115	-0.177

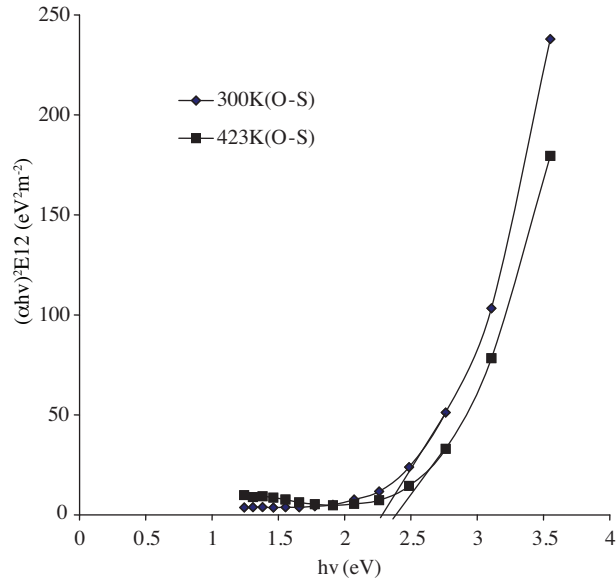


**Figure 2.** A graph of *Reflectance, R versus wavelength,  $\lambda$*  for  $\text{Cu}_x\text{S}-\text{Cu}_2\text{O}$  thin films.

The absorption coefficient  $\alpha$  of the films is related to their energy band gap  $E_g$  by the relation

$$(\alpha h\nu)^2 = h\nu - E_g. \quad (1)$$

In order to determine the energy band gap, graphs of  $(\alpha h\nu)^2$  as a function of photon energy  $h\nu$  are plotted in Figure 3. The range of values obtained is 2.19–2.32 eV. From separate analysis, the range for  $\text{Cu}_x\text{S}$  is 2.39–2.62 eV and 2.32–2.60 eV for  $\text{Cu}_2\text{O}$ . Similar ranges were obtained in [6, 8] for  $\text{Cu}_x\text{S}$  and for  $\text{Cu}_2\text{O}$  in [9].



**Figure 3.** A graph of  $(\alpha hv)^2$  versus  $hv$  for  $\text{Cu}_2\text{O-Cu}_x\text{S}$  thin films.

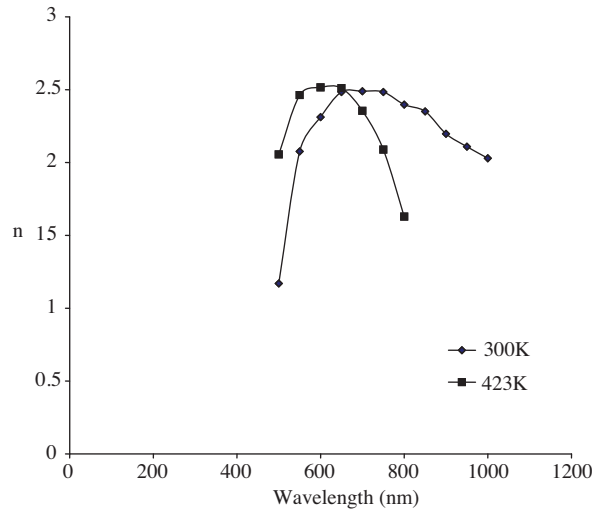
The range of thicknesses of  $\text{Cu}_2\text{O-Cu}_x\text{S}$  films is  $0.536\text{--}1.303\ \mu\text{m}$ . Ranges of values obtained for  $\text{Cu}_x\text{S}$  and  $\text{Cu}_2\text{O}$  respectively are lower than those of  $\text{Cu}_2\text{O-Cu}_x\text{S}$ . Details are shown in Table 3. The refractive index  $n$  of the films is related to their reflectance  $R$  by the relations

$$R = \frac{(n-1)^2}{(n+1)^2} \text{ or } n = \frac{1+R^{1/2}}{1-R^{1/2}}. \quad (2)$$

**Table 3.** Thickness of  $\text{Cu}_x\text{S-Cu}_2\text{O}$  thin films annealed at various temperatures.

Sample	Annealing Temperature (K)	Range of thicknesses ( $\mu\text{m}$ )
$\text{Cu}_x\text{S}$	300	0.335–0.979
	423	0.190–1.062
	453	0.104–0.280
	523	0.004–0.239
$\text{Cu}_2\text{O}$	300	0.005–0.069
	423	0.020–0.075
	453	0.002–0.092
$\text{Cu}_2\text{O-Cu}_x\text{S}$	300	0.655–1.300
	423	0.637–1.269
$\text{Cu}_x\text{S-Cu}_2\text{O}$	300	0.581–1.303
	423	0.536–1.298

The refractive index of the films is in the range of  $1.60\text{--}2.52$ . Graphs of refractive indices as functions of wavelength  $\lambda$  are shown in Figure 4. The refractive index rises sharply to peak value in the visible region and falls sharply into the infrared region.



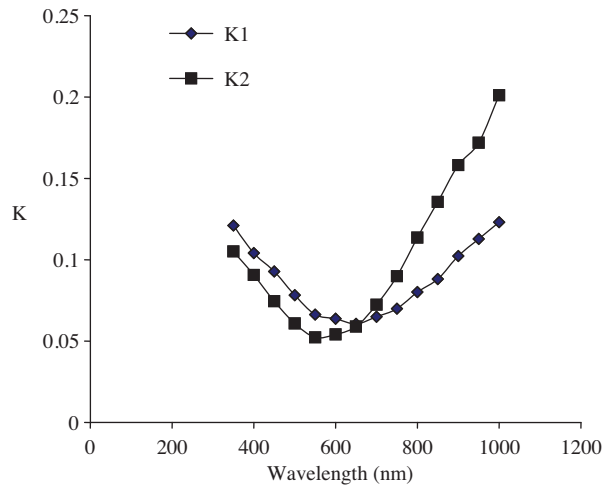
**Figure 4.** A graph of Refractive,  $n$  versus wavelength,  $\lambda$  for  $\text{Cu}_2\text{O-Cu}_x\text{S}$  thin films

The extinction coefficient  $K$  was estimated from the formula

$$K = \alpha\lambda/4\pi, \quad (3)$$

from which the value range  $K = 0.052$  to  $K = 0.201$  was obtained. Graphs of  $K$  as a function of wavelength are shown in Figure 5. The coefficient falls to a minimum from UV to VIS then rises sharply from the VIS to IR regions. This shows that the films have the least absorption in the VIS and very high rate of absorption in the UV and IR regions.

These optical properties make the  $\text{Cu}_2\text{O-Cu}_x\text{S}$  thin films nice glazing material for maintaining cool interior in buildings in warm climatic regions while still keeping the rooms well illuminated. To ensure that the thermal radiation from the warm glazing to the interior is inhibited and the thermal energy dissipated in the glazing due to absorption is predominantly transferred to the exterior by enhanced convective heat transfer of the glazing to the exterior, it was suggested in [2] that reflectance in the spectral region should be strengthened while encouraging low thermal emittance.



**Figure 5.** Extinction coefficient  $K$  as a function of wavelength  $\lambda$ .

## 4. Conclusion

$\text{Cu}_2\text{O-Cu}_x\text{S}$  thin films have been prepared by Chemical bath deposition technique. The films have peak transmittance and low reflectance in the visible region of the electromagnetic spectrum and high rate of absorption in the UV and IR regions. These make the films excellent glazing material for solar control in warm climatic regions. The range of energy band gap of the films is 2.19–2.32 eV.

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