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Optical and Electrical Properties of Copper Sulfide Films of Variable Composition

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Four kinds of copper sulfides of different chemical compositions were chemically deposited and examined for their optical and electrical characteristics. Electroless chemical deposition from aqueous copper thiosulfate baths in acidic media was used to deposit thin films of Cu_2S, $Cu_{1.8}S$, $Cu_{1.4}S$, and CuS on glass, polyester, or metal substrates. Rutherford back scattering analysis was used to determine the chemical composition of the films. The optical characteristics of the films were studied in the UV–VIS–NIR region, between 0.3 and 2.5 μm. Cu_2S films were found to be highly transmissive throughout the spectral region 0.5–2.5 μm. The transmission in the near-infrared region (0.8–2.5 μm) decreased as the chemical composition approached the stoichiometry of CuS, which was found to be highly absorptive for the near-infrared radiation. All films displayed high electrical conductivity, with the CuS film being the most conductive and conductivity decreasing toward the copper-rich phase, Cu_2S. All films were found to be *p*-type semiconductors. The optical energy band gaps of the films were also studied and it is shown that the values can differ, depending on the method of determination. Some practical applications of these films are also discussed. © 1995 Academic Press, Inc.

1. INTRODUCTION

Since the historic discovery of the photovoltaic properties of Cu_xS thin films in contact with CdS films (1), the copper–sulfur systems have received particular attention. It is well known that copper and sulfur form a number of phases at least four of which are known to be stable at room temperature: covellite (CuS), in the "sulfur-rich region," and chalcocite (Cu_2S), djurlite ($Cu_{1.95}S$) and anilite ($Cu_{1.75}S$), in the "copper-rich region."

Chemical bath deposition has been an extensively used technique for depositing copper sulfide films, usually denoted Cu_xS films. Yamamoto *et al.* (2) and Gadave and Lokhande (3) have used thiosulfate baths in acidic media. A few authors have reported Cu_xS film depositions from uncomplexed as well as from complexed copper ions in alkaline media (4–8). However, none of the above works have dealt with characterization of the different species of copper sulfide. The purpose of this work was therefore to examine and report on the optical and electrical properties of copper sulfide films as a function of chemical composition.

Copper sulfides as thin films have a wide range of well-established and prospective applications, such as photothermal conversion applications (9, 10), photovoltaic applications (11, 12), electroconductive electrodes (13, 14), microwave shielding coatings (2, 14), and solar control coatings (4). The optical and electrical properties of the Cu_xS films play a crucial role in these applications.

2. EXPERIMENTAL DETAILS

2.1. Film Preparation

Copper(I) and copper(II) sulfides can be precipitated instantaneously from aqueous solutions of the corresponding salts by addition of Na_2S. These reactions, however, are inconvenient for film depositions. Retarded reactions are used for film depositions, and for that purpose copper ions are usually complexed by a suitable complexing agent, such as triethanolamine, citric acid, or EDTA. Another agent, such as thiourea or thiosulfate, is used as the sulfiding agent.

For our investigations, the copper sulfide films were deposited by a simple electroless chemical deposition

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technique from copper thiosulfate baths, similar to those used in (2, 3), except that the molar ratio of thiosulfate to copper was varied from 1 : 1 to 1 : 3. The thiosulfate plays a double role in this system: (i) it is a complexing agent for the copper ions, and (ii) it is a sulfide generating agent when it undergoes hydrolytic decomposition. In this way, thiosulfate was found to ideally fulfill the two essential roles needed for film deposition. A typical chemical bath was composed of a fixed amount (10 ml) of a 1.0 mol/liter water solution of copper(II) sulfate or copper(II) nitrate and a variable amount of 1.0 mol/liter aqueous solution of sodium thiosulfate to make a variety of copper to thiosulfate molar ratios of 1 : 1, 1 : 2, 1 : 2.5, and 1 : 3 in 100-mL beakers. The pH in all the baths was ~5, adjusted by diluted acetic acid. The temperature of the baths was maintained at 50°C. The substrates used were standard microscope glass slides (75 × 26 × 1.0 mm), transparent polyester films, and metal sheets. The glass and polyester substrates were first ultrasonically cleaned, then soaked for a few minutes in a 0.03% aqueous solution of $SnCl_2$, rinsed with distilled water, dried in air, heated in an oven for 15 min at 250°C in air, and cooled to room temperature before usage. Metal substrates were dipped for a few minutes in chromic acid, rinsed with distilled water, and dried in air before use. Copper(II) and sodium thiosulfate solutions were mixed in a beaker, and the substrates were vertically supported by the walls of the beaker. No stirring was applied. Films were grown in the baths for about 30 min after precipitation began, then taken out, rinsed with distilled water, dried in air, and preserved for investigation. Depending on the bath composition, Cu_2S, $Cu_{1.8}S$, $Cu_{1.4}S$, and CuS films of different colors were obtained, as summarized in Table 1.

2.2. *Characterization of the Films*

The chemical composition of the films was determined by Rutherford back scattering (RBS) analysis. X-ray studies were carried out using nickel filtered Cu$K\alpha$ radiation at 50 kV and 30 mA, on a Phillips X-ray diffractometer. The texture of the films was studied by a Jeol S840 scanning electron microscope. The thickness of the films was determined by ellipsometry. Transmission spectra of the films were taken on a CARY 5 UV–VIS–NIR spectrophotometer. The sheet resistance of the films was determined by the two-probe method, using 1.0-mm-wide gold-pasted electrodes, 1.0 cm in length and 1.0 cm apart. Annealing of the films was performed in air at 130 and 200°C.

TABLE 1
Basic Characteristics of Cu_xS Films

Compound deposited (formula)	Bath composition (Cu : thiosulfate)	Appearance in trans./refl. daylight	Thickness (μm)
Cu_2S	1 : 2	Yellow/golden	0.08
$Cu_{1.8}S$	1 : 1	Yellow/purple	0.12
$Cu_{1.4}S$	1 : 2.5	Neutral/green	0.10
CuS	1 : 3	Yellow-green/dark green	0.09

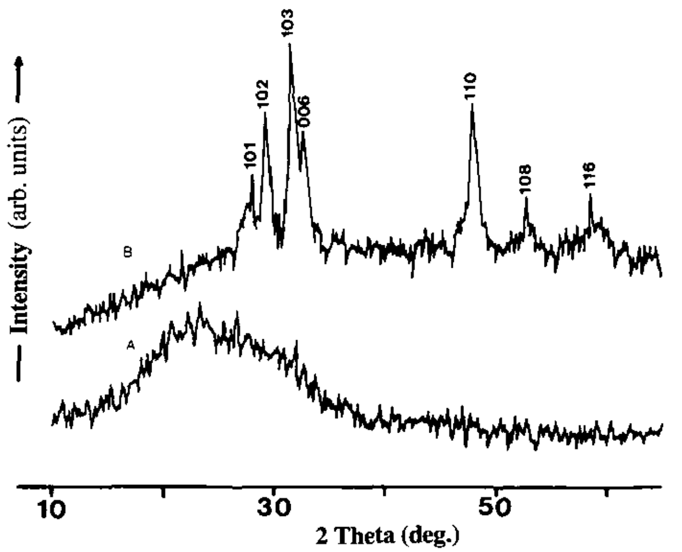

FIG. 1. X-ray diffraction patterns produced from (A) Cu_2S and (B) CuS films on glass substrates.

3. RESULTS AND DISCUSSION

The deposition process used for film growth in this work is based on hydrolytic decomposition of the consecutive copper thiosulfate complexes in acidic media. The chemistry of the deposition process has been described previously (14).

3.1. *Structural Considerations*

X-ray diffraction patterns (XRD) were recorded for all of the films. However, most of the deposited materials failed to produce sufficiently strong reflections to identify them, except for the films grown in baths with a copper to thiosulfate ratio of 1 : 3. After comparison against the standard JCPDS–ICCD diffraction patterns, from PDF-2 Sets 1–43 Database, file No. 6-464, the deposited material was identified as polycrystalline covellite (CuS). Figure 1 shows the diffraction patterns of the two chain members, Cu_2S and CuS. Not even after several days of annealing at 150°C could any reflections be observed for Cu_2S or any other films except CuS. Small grain size may be the reason, as indicated by SEM studies.

The SEM micrographs of the two chain members of the copper sulfides are shown in Fig. 2. These reveal that the substrates are well covered with the deposited

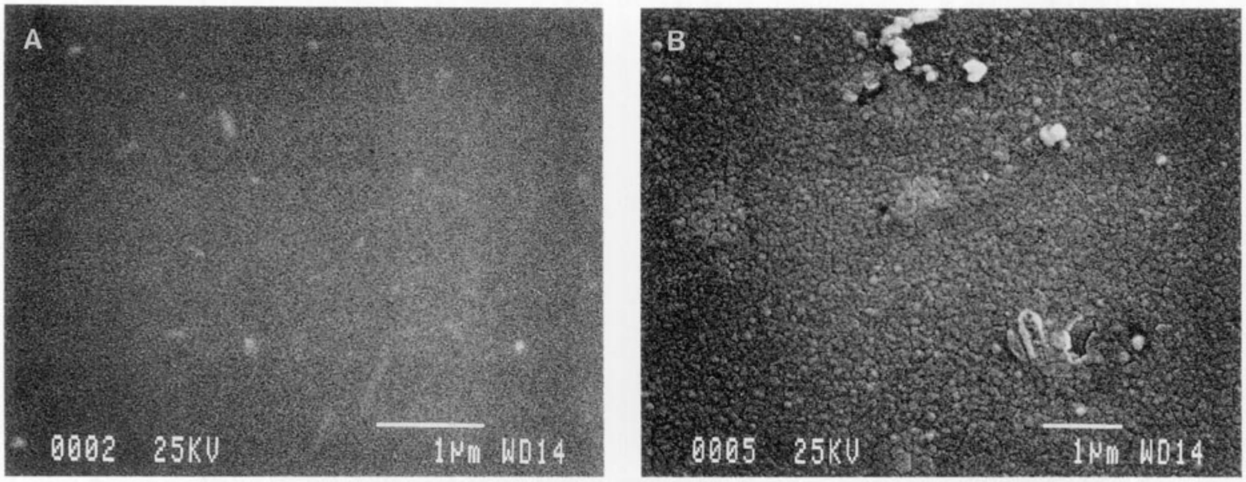

FIG. 2. SEM micrographs of (A) Cu_2S and (B) CuS films on glass substrates.

material. It is also easy to see that the Cu_2S films are made of very small grains, unlike CuS. With this in mind, it is not surprising that CuS films produced some reflections by XRD, while Cu_2S and the other two films which also had small-grain texture did not. However, it is hard to explain the difference in the grain size, since all of the films were grown at the same temperature and same pH.

3.2. Optical Considerations

The VIS–NIR absorption and transmission spectra of each of the copper sulfide films were recorded in the spectral region 0.3 to 2.5 μm and are presented in Figs. 3–6. It can be seen that the crossover terminal points of absorption and transmission change with the composition of the films. Two crossover terminal points of absorption and transmission are observed with $Cu_{1.4}S$ and CuS films. Extrapolations of the absorption spectra to the wavelength axis are also shown, for preliminary estimation of the optical energy band gaps of each film compound. For the sake of more convenient comparison, the transmission spectra of each kind of film in the spectral region 0.3–2.5 μm are also given in Fig. 7. As can be seen, a sharp rise in transmittance for all films is observed at the beginning of the visible region (about 0.4 μm). However, there is a patterned difference in transmission with further increase of wavelength. While the Cu_2S films maintain a high transmission throughout the rest of the electromagnetic spectrum (Fig. 7, curve A), the situation changes as the chemical composition approaches CuS; i.e., the films exhibit increased absorption in the NIR region of the spectrum. The CuS films of just 0.1-μm thickness exhibit remarkable absorption of up to 75% of the near-infrared radiation between 0.8 and 0.25 μm (Fig. 7, curve D). The transmission in the shorter wavelength region is probably due to interband transitions from the valence toward the conduction band, while transmission in the higher wavelength may be attributed to free carriers.

Annealing of the films for up to 72 hr at 130°C did not bring about any significant change in their optical characteristics. A slight shift to a yellowish color was observed with the green films ($Cu_{1.4}S$ and CuS). Annealing at 200°C in air caused a noticeable change in the color of the $Cu_{1.4}S$ and CuS films from green to yellow, while at

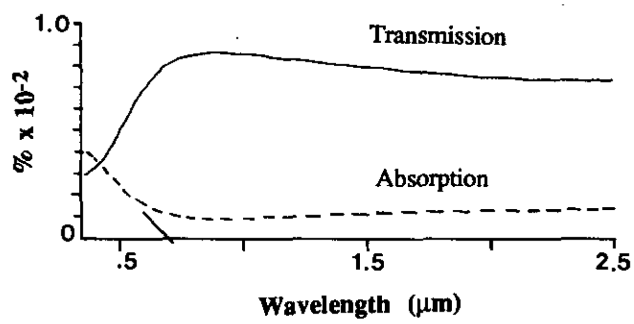

FIG. 3. Optical transmission and absorption spectrum of a Cu_2S film.

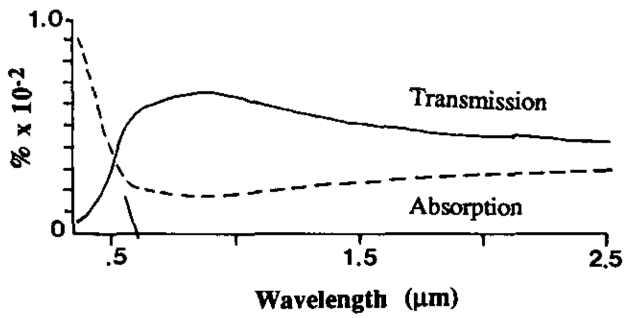

FIG. 4. Optical transmission and absorption spectrum of a $Cu_{1.8}S$ film.

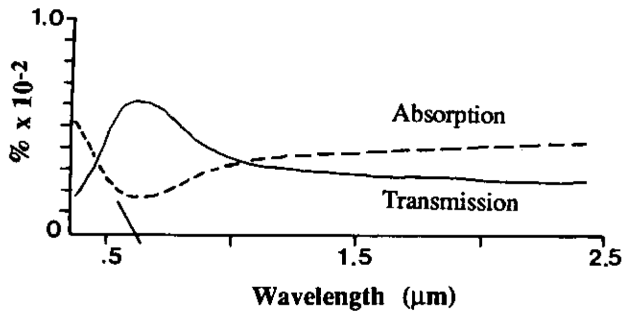

FIG. 5. Optical transmission and absorption spectrum of a $Cu_{1.4}S$ film.

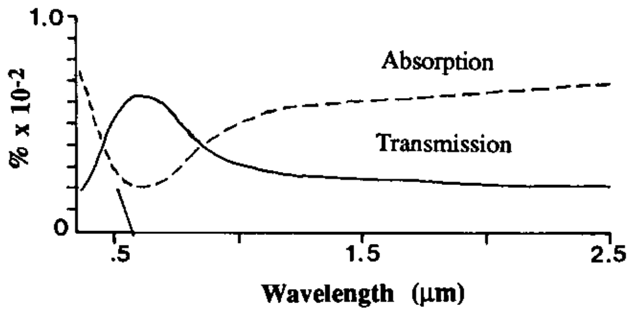

FIG. 6. Optical transmission and absorption spectrum of a CuS film.

the same time, the transmission spectra of the Cu_2S and $Cu_{1.8}S$ films changed only a little. Figure 8 shows the transmission spectra of all the samples after annealing for 1 hr at 200°C. The optical energy band gaps (E_g) of the films were also studied. Various literature references report band gaps between 1.2 and 2.6 eV for Cu_xS films (3, 5–7, 15, 16). However, a closer look at these references reveals that some authors have determined E_g as α vs $h\nu$, others as $\alpha^{1/2}$ vs $h\nu$, and still others as $(\alpha h\nu)^2$ vs $h\nu$. To illustrate the difference in the E_g values derived from a single spectrum, the three possible graphical determinations of E_g for the CuS thin films obtained in this work are presented in Fig. 9. Additionally, the E_g values were evaluated by extrapolation of the corresponding absorption spectra (Figs. 3–6). For the sake of comparison with previous literature data, the E_g values for all four kinds of copper sulfides obtained in this work were determined in four ways, and the results are given in Table 2.

3.3. Electrical Considerations

The sheet resistance of each kind of film was determined on as-deposited samples and again after annealing at 130 and 200°C. The results are given in Table 3. The decrease in the sheet resistance with the decrease of the value of x observed with the as-prepared Cu_xS films is expected. Namely, it is now a well-established fact that Cu_2S is a *p*-type semiconductor, while CuS exhibits more of a metallic character. The *p*-type conduction is generally attributed to free holes from acceptor levels of copper vacancies. The density of these vacancies in Cu_xS increases as x decreases from 2 to 1. A more detailed study of these defects has been made by Rau (17) for Cu_xS, where the value of x was between 2 and 1.8. A similar trend was observed with our layers for $1 \leq x < 2$.

A decrease in sheet resistance values was observed with all samples after annealing at 130°C for 30 min. Further annealing at this temperature for up to 72 hr did not bring about any changes in sheet resistance. Annealing of the film samples for 1 hr at 200°C resulted in a significant increase of sheet resistances with all film samples, probably due to chemical oxidation of the sulfides. Further annealing at this temperature resulted in a sharp increase in sheet resistance and eventually led to the destruction of the films.

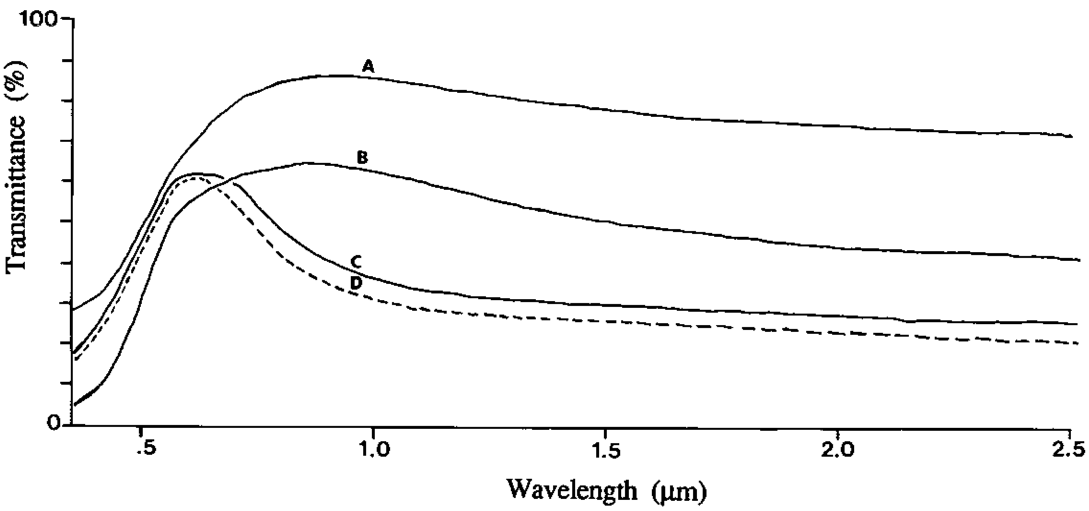

FIG. 7. Comparison of the optical transmission spectra of as-deposited Cu_xS films: (A) Cu_2S; (B) $Cu_{1.8}S$; (C) $Cu_{1.4}S$; (D) CuS.

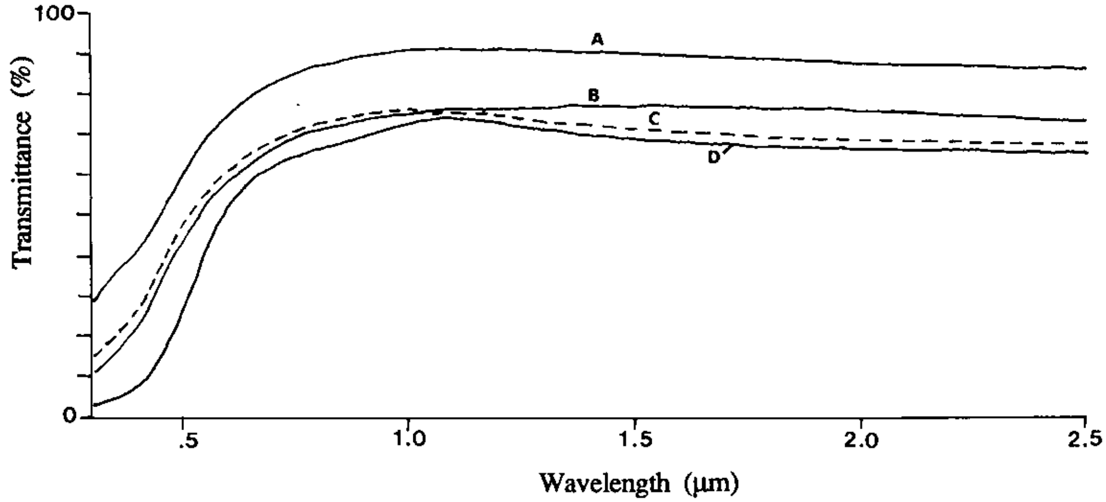

FIG. 8. Optical transmission spectra of Cu_xS films annealed at 200°C: (A) Cu_2S; (B) $Cu_{1.8}S$; (C) $Cu_{1.4}S$; (D) CuS.

Thermoelectric probe testing of all samples confirmed the inheritable *p*-type conductivity of copper sulfides.

3.4. Application Considerations

The copper sulfide films obtained by the chemical deposition technique employed in this work have two useful properties: they are transparent and electrically conductive. As already mentioned, the Cu_2S films, and to a great extent the $Cu_{1.8}S$ films, exhibit high transparency throughout the spectral region beyond 0.5 μm. Being of high electroconductivity at the same time, these films can be used as *transparent, highly conductive top electrodes.* In our work, these films were successfully deposited on transparent polyester films to give an electroconductive surface on a flexible substrate (14), which can then be used with various devices requiring flexible substrates. Most of the other deposition techniques, such as vacuum deposition, sputtering, and spray pyrolysis, cannot be readily used with plastic substrates, due to the high temperatures commonly employed by such techniques. We also deposited these films as top electrodes on ferroelectric PZT films and the preliminary results are encouraging: an excellent hysteresis loop at 100 Hz and a 90 kV/cm sinusoidal field were produced, with a coercive field value of 18 kV/cm, indicating good contact. In addition, we are also examining these films as sensor (ion selective) thin film electrodes for copper ions. Preliminary results show that all of these copper sulfide films are sensitive to copper ions in concentrations of 10^{-6} to 10^{-1} mol/liter and do not indicate any interference from chloride ions, unlike the commercial solid electrodes based on the $CuS–Ag_2S$ matrix.

The CuS films exhibit peaked transmission in the visible region matching the phototropic vision of the human eye (at ~0.55 μm), while remaining nontransmissive for near-infrared radiation (0.8–2.5 μm). This makes these films suitable for use as solar control coatings on architectural windows and automobiles in the regions with warm climates, as already suggested by Nair and Nair (4). The transmittance in the near-infrared region can be brought to zero by choosing appropriate thickness. Figure 10 shows the transmission of CuS films as a function of film thickness. A thickness of about 0.2 μm CuS film on a glass sheet can bring infrared radiation in the interior close to zero, while maintaining sufficient transmission (10–30%) in the visible region. In short, CuS films can act as *shielding from near-infrared radiation* and this can find a number of practical applications.

TABLE 2
Band Gap Energy (E_g) for CuS Films, Determined Graphically

Compound (formula)	E_g—extrapolated from absorption spectrum	$\alpha/h\nu$ (eV)	$\alpha^{1/2}/h\nu$ (eV)	$(\alpha h\nu)^2/h\nu$ (eV)
Cu_2S	1.8	1.70	1.70	2.40
$Cu_{1.8}S$	2.0	2.00	2.00	2.55
$Cu_{1.4}S$	2.0	2.00	2.00	2.50
CuS	2.0	2.18	2.00	2.58

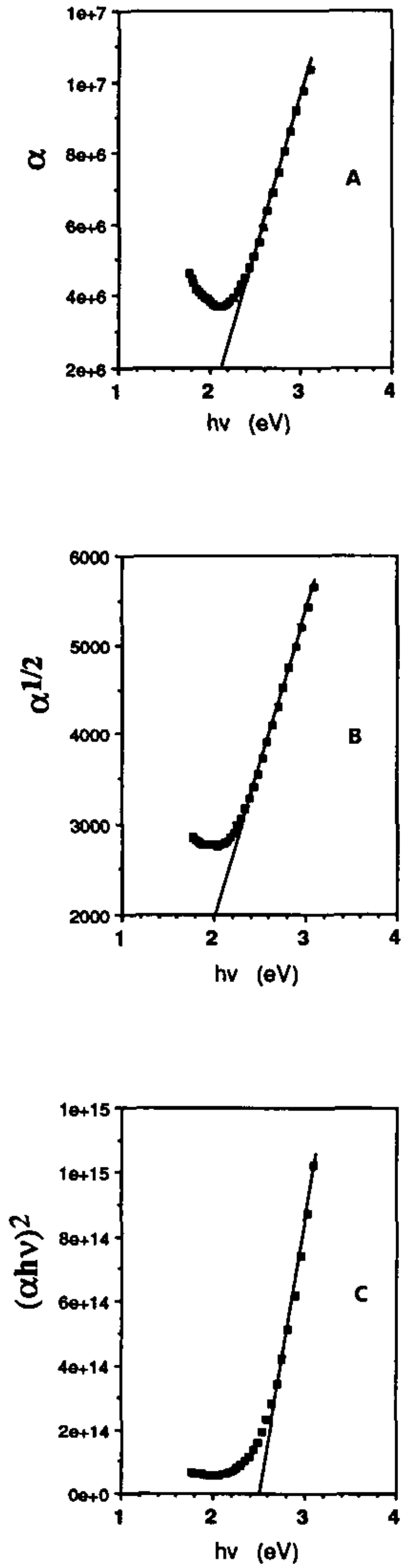

FIG. 9. The optical band gap energy for CuS films, determined in three ways: (A) α vs $h\nu$; (B) $\alpha^{1/2}$ vs $h\nu$; (C) $(\alpha h\nu)^2$ vs $h\nu$.

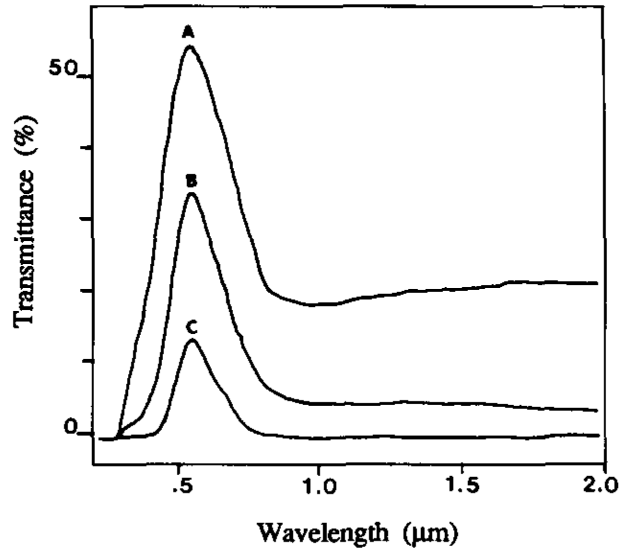

FIG. 10. Optical transmission of CuS films as a function of film thickness: (A) 0.08 μm; (B) 0.15 μm; (C) 0.26 μm.

These copper sulfide films can also be considered in *photothermal conversion applications*. In our work, copper sulfides were successfully deposited on metal substrates, such as copper, aluminum, zirconium, and titanium. Furthermore, this electroless deposition technique makes it possible to deposit thin copper sulfide films onto planar glass, plastic, or metal substrates or onto the interior and/or exterior of tubular substrates with equal ease. Certain photothermal conversion applications could make use of this advantage.

Additionally, some of the copper sulfides studied in this work can be considered for *photovoltaic applications*. Cu_2S remains an inexpensive and attractive photovoltaic material, due to its large minority carrier diffusion length combined with its low sheet resistivity (18). Some of the other copper sulfides studied in this work may also meet these requirements.

4. CONCLUSIONS

This work presented the basic optical and electrical characterization of four copper sulfide film materials of different chemical composition. Cu_2S, $Cu_{1.8}S$, $Cu_{1.4}S$, and CuS were chemically deposited as thin films and then optically and electrically characterized. It was shown that the materials differ in the optical transmission in the near-infrared region, with Cu_2S being highly transmissive and CuS highly absorptive for the microwave radiation in the spectral region 0.8–2.5 μm. The transmissions of $Cu_{1.8}S$ and $Cu_{1.4}S$ were between those of the two chain members. The optical energy band gaps of these materials were also studied, and it was shown that the values obtained can

TABLE 3
Sheet Resistances of As-Deposited and of Annealed Cu_xS Films

Compound (formula)	R_1 (as deposited) (Ω/square)	R_2 (annealed 130°C) (Ω/square)	R_3 (annealed 200°C) (Ω/square)	Thickness (μm)
Cu_2S	1200	600	3650	0.08
$Cu_{1.8}S$	300	160	30200	0.12
$Cu_{1.4}S$	210	110	34700	0.10
CuS	105	45	2438	0.09

differ significantly depending on the method of determination. All films were found to be highly conductive. Conductivity was found to increase from Cu_2S toward CuS. Some practical prospective applications of the film materials, such as electroconductive transparent electrodes, ion-selective thin film electrodes, photothermal and photovoltaic applications, solar control window coatings, or microwave shielding, were also discussed.

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