Experimental study of the copper thiosulfate system with respect to thin-film deposition

I. Grozdanov[a]*, C. K. Barlingay[a], S. K. Dey[a], M. Ristov[b], M. Najdoski[b]

[a]*Department of Chemical, Bio, and Materials Engineering, Arizona State University, Tempe, Arizona 85287–6006, USA*
[b]*Faculty of Natural Sciences and Mathematics, Univerzitet "Kiril i Metodij", Skopje, Republic of Macedonia*

Abstract

An experimental study of the copper–thiosulfate system in mild acidic (pH $\sim$ 5) aqueous solutions, with respect to thin-film formation, was undertaken. Thin films of $Cu_x S$ ($1 \leqslant x \leqslant 2$) were deposited by a simple electroless technique on glass or transparent polyester films, at 50 °C. Thin films were deposited from chemical baths in which the ratios of copper to thiosulfate were varied from 1:1 to 1:10. Thin films of different compositions (Cu_2S, $Cu_{1.8}S$, $Cu_{1.4}S$ and CuS) were prepared and then characterized for morphological, optical and electrical properties. The deposited films chemically close to Cu_2S were found to be amorphous, while the CuS films were a mixture of both amorphous and polycrystalline phases. The optical spectra of the Cu_2S films exhibited high transmission both in the visible region of the spectrum (beyond 600 nm) and throughout the near-infrared region (800 to 2500 nm), while CuS films were found to be highly absorptive throughout the near-infrared region, with peaked transmission in the visible region at about 560 nm. The sheet resistances of the films, determined by the standard four-probe measurements, were between 100 and 650 Ω/square.

1. Introduction

The copper–sulfur system forms a number of phases, which are attractive for various optoelectronic applications. At least four stable phases are known to exist at room temperature, for which their mineralogical names are often used. On the 'copper rich' side of the copper–sulfur phase diagram are the orthohombic chalcocite (Cu_2S), djurlite ($Cu_{1.95}S$) and anilite ($Cu_{1.75}S$), while in the 'sulfur rich' side is covellite (CuS). Mixed phases are also known in the intermediate compositions [1]. The structure of the copper sulfide compounds is quite complicated [2]. Even the structures of Cu_2S and CuS, which appear to be stoichiometric, are not consistent with their formulations as Cu(I) and Cu(II) sulfides. Chalcocite (Cu_2S) can come in its low-temperature form with a rather complex structure or in its high-temperature form of disordered rearrangements of Cu atoms in a close-packed array of S atoms [2]. Likewise, the compound CuS, which occurs as the mineral covellite, has one-third of its metal ions surrounded by three neighboring S atoms at the corners of a triangle and the remainder have four S neighbors arranged tetrahedrally. Moreover, according to Wells [2], two-thirds of the sulfur atoms exist as S_2 groups like those in pyrites, so that if regarded as a normal covalent structure, it would be represented as $Cu_4^I Cu_2^{II} (S_2)S_2$.

Copper sulfides exhibit metallic or semi-metallic properties, intrinsic semiconductivities and, in some cases, ductility. Due to these characteristics, copper sulfides are exploitable in the fabrication of electronic devices [3–4].

Thin-film deposition of copper sulfildes with variable composition, usually denoted as $Cu_x S$, have been reported with different techniques, such as vacuum evaporation [5], activated reactive evaporation [6], and chemical bath deposition [7–11]. The latter have been performed in alkaline medium [7, 8, 10] or in acidic solutions [9, 11]. The sulfur source agents reported included thiourea, sodium sulfide and sodium thiosulfate, while copper ions were complexed by thriethanolamine, ammonia, EDTA, citric acid or 1,4,8,11-tetrazacyclo-tetradecane. Among the various chemical depositions reported previously, two have reported the use of the copper–thiosulfate system in acidic solutions. Gadave and Lokhande [9] used a tenfold excesss of thiosulfate to copper, while Yamamoto *et al.* [11] used equimolar amounts of copper and thiosulfate. However, the copper–thiosulfate system is much more complex and deserves a more detailed study with respect to thin-film deposition.

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*On leave from the Institute of Chemistry, Skopje, Republic of Macedonia.

Copper is known to form at least three consecutive complex compounds with the thiosulfate: $[Cu(S_2O_3)]^-$, $[Cu(S_2O_3)_2]^{3-}$ and $[Cu(S_2O_3)_3]^{5-}$, with corresponding instability constants (pK) of 10.27, 12.22 and 13.84 respectively [12]. Before complexation takes place, thiosulfate readily reduces Cu(II) to Cu(I).

The objective of this work is therefore to carry out an experimental investigation of various ratios of copper to thiosulfate in aqueous solutions with respect to thin-film deposition, to identify the composition of the deposited materials and determine the basic optical and electrical characteristics of the different compositions.

2. Experimental details

Copper sulfides of variable composition were deposited on glass and transparent polyester sheets (commonly used as overhead transparencies), by a simple electroless deposition technique based on hydrolytic decomposition of copper–thiosulfate complexes in mild acidic media (pH ~ 5). Stock solutions of 0.5 M $CuSO_4$ and 0.5 M $Na_2S_2O_3$ were prepared by dissolving appropriate amounts of the chemicals in distilled water. The substrates were first ultrasonically cleaned, then soaked in 0.03% aqueous solution of $SnCl_2$ for a few minutes, washed with distilled water and dried in air before they were dipped into the chemical bath composed of appropriate amounts of $CuSO_4$ and $Na_2S_2O_3$. For example, the bath for the study of the 1:1 copper to thiosulfate system was prepared by mixing 10 ml of 0.5 M $CuSO_4$ and 10 ml of 0.5 M $Na_2S_2O_3$ in a 100 ml glass beaker and diluting to a total volume of 100 ml by distilled water. A few drops of dilute acetic acid were also added. The pH of the bath was about 5. For the study of other copper to thiosulfate systems (1:2, 1:3, etc.), an adequate amount of $Na_2S_2O_3$ was added to a fixed amount (10 ml) of 0.5 M $CuSO_4$. The substrates were then vertically inserted into the chemical bath. No stirring was applied. The temperature of the bath was slowly raised to 50 °C and kept at this temperature. The films were taken out 30 min after precipitation began, except when terminal thickness vs. deposition time was studied. Films were washed with distilled water, dried in air and preserved for characterization of morphological, optical, and electrical properties.

X-ray studies were performed on the film samples, using Cu Kα radiation at 50 kV and 30 mA, nickel-filtered, on a Phillips X-ray diffractometer. Optical transmission studies were done on a CARY 5 UV-VIS-NIR spectrophotometer. The standard four-probe method was used for resistivity measurements. The thickness of the films was determined by elipsometry.

3. Results and discussion

3.1. The chemistry of the technique

In this technique, three important properties of the thiosulfate ions were utilized to deposit copper sulfide thin films, as shown below.

(a) The reducing ability of thiosulfate, described by the following half-cell reaction:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \qquad (1)$$

$$2Cu^{2+} + 2e^- \rightarrow Cu_2^{2+} \qquad (2)$$

(b) The complexing ability of thiosulfate, whereby consecutive copper–thiosulfate complexes are formed in excess of the complexing agent:

$$Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2[Cu(S_2O_3)]^- \qquad (3)$$

$$[Cu(S_2O_3)]^- + S_2O_3^{2-} \rightarrow [Cu(S_2O_3)_2]^{3-} \qquad (4)$$

and so on for the remaining consecutive complexes.

(c) The ability of thiosulfate to gradually release sulfide ions upon hydrolytic decomposition, in acidic media, according to:

$$S_2O_3^{2-} + H^+ \rightarrow S + HSO_3^- \qquad (5)$$

$$S + 2e - (\text{from reaction (1)}) \rightarrow S^{2-} \qquad (6)$$
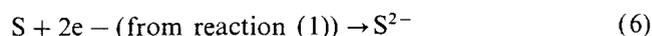
The copper ions then combine with the sulfide ions, to form insoluble copper sulfide:

$$Cu^{2+} + S^2 \rightarrow Cu_2S \qquad (7)$$

The above is but a simplified reaction mechanism. There are probably other side-reactions, because the hydrolysis of the thiosulfate itself is no less complex than the copper–sulfur system. As thiosulfate undergoes hydrolysis a number of species are produced, including H_2S, SO_2, S, and $S_4O_6^{2-}$. The thiosulfate ion is a very versatile chemical, and its reactions in aqueous solution can be used for gas formation, precipitate formation, complex formation, acid–base interaction, redox interaction, catalysis and more [13]. It is not always possible to figure out the exact mechanism in a thiosulfate-containing system. Such is the case of the system 'copper-excess of thiosulfate', from which CuS is precipitated, rather than Cu_2S. Just how did Cu(I) get oxidized back into Cu(II) is not easy to explain. However, it is reasonable to anticipate that some $H_2S_2O_3$ is formed in acidic solutions of $Na_2S_2O_3$. According to Tykodi [13], once thiosulfuric acid is formed, it decomposes into H_2S and SO_3 at room temperature. Perhaps it is SO_3 then, that oxidizes Cu(I) into Cu(II). This problem, however, is beyond the scope of this paper.

3.2. Deposition of the copper sulfide films

The first system under investigation contained equimolar amounts of copper(II) and thisulfate. Upon
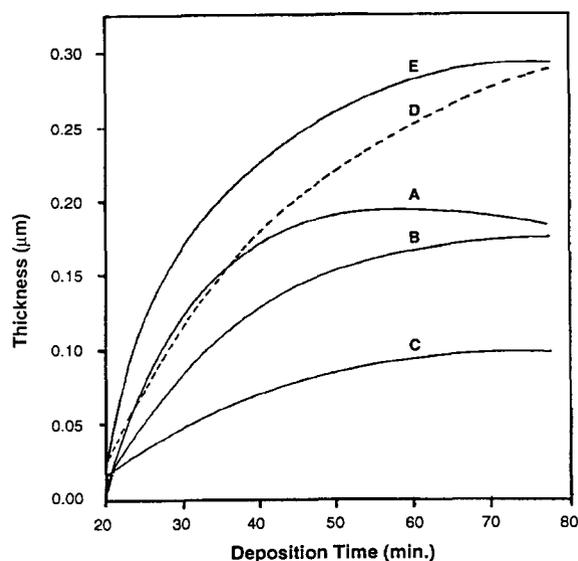
Fig. 1. Plot of film thickness vs. deposition time for variable copper to thiosulfate ratios: (A) 1:1; (B) 1:2; (C) 1:3; (D) 1:4; (E) 1:5.

introduction of the thiosulfate into the copper(II) sulfate solution, a change of color from blue to green was observed, indicating the reduction of Cu(II) to Cu(I) has taken place. Upon heating, the clear green solution turned into yellow at around 40 °C. In the absence of acetic acid, an opaque solution is observed at this point, due to the finely divided sulfur being produced by reaction (1). A few drops of dilute acetic acid at this point clear the solution instantly. When acetic acid was introduced in the beginning, no opaque solution was observed.

A brown precipitate begins to fill the bath as the temperature reaches 45–48 °C, and yellow-to-brown thin films start to cover the substrates. The reaction is completed after about 80 min, at 50 °C. If the films are left in the bath until the reaction is completed, peeling of the films often occurs. However, if the films are taken out before the reaction is completed (15–30 min after precipitation begins), uniform and well-adhered films are produced. Thinner films were golden-yellow in appearance and thicker films were brown. Terminal thickness of about 0.18 μm from a single bath was achieved after about 1 h at 50 °C. The dependence of the film-thickness vs. deposition time is shown in Fig. 1, curve A.

The 1:2 copper to thiosulfate system turned out to be thermally more stable and precipitation was observed after 1 h at 50 °C. The color of the solution was yellow from the beginning and until brown precipitate started to form. The films produced with this system were of a brighter yellow color compared to those from the 1:1 system. Terminal thickness of about 0.16 μm was achieved from a single bath after 2 h at 50 °C. Thicker

films of up to 0.3 μm were produced by re-introducing the initially deposited films into a fresh bath. The dependence of the thickness vs. deposition time for these films is shown in Fig. 1, curve B.

The 1:3 copper to thiosulfate solution was pale yellowish at the beginning. After about 100 min at 50 °C, brown precipitate started to form, but turned olive-green within a few minutes. The deposited films were greenish-yellow in appearance. A terminal thickness of about 0.1 μm from a single bath was achieved after 2.5 h at 50 °C. The plot showing the dependence of the thickness vs. deposition time is included in Fig. 1 (curve C).

The 1:4 copper to thiosulfate solution was colorless upon mixing of the bath components. The solution turned yellow after 1 h at 50 °C and yielded a brown precipitate after 80 min at 50 °C, which turned olive-green within a few minutes. Transparent, bright-green films were produced with this system, of a terminal thickness around 0.3 μm, in about two additional hours after precipitation begins.

At 1:5 and higher, up to 1:10 copper to thiosulfate ratios, no significant differences from the 1:4 system were observed, except that the deposited films were of a more intense green color and the precipitation time was prolonged to about 5 h at 50 °C. Thus, a higher temperature (70–80 °C) of the bath was required to achieve film deposition within 1–1.5 h.

3.3. X-ray studies of the films

The X-ray studies of the deposited films showed that most of the deposited materials were amorphous. At higher copper to thiosulfate ratios, the polycrystalline phase in CuS films could be detected and the X-ray diffraction pattern of a film produced from a 1:10 bath is shown in Fig. 2. After comparison against the JCPDS-ICCD diffraction pattern #6-464, from PDF-2 Sets 1-43 Database, the deposited material was identified as the covellite phase (CuS).
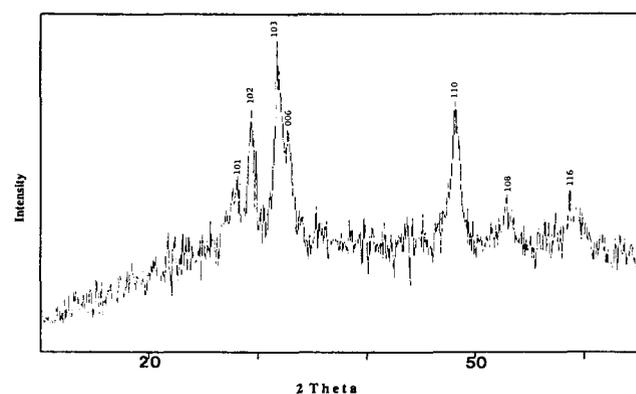

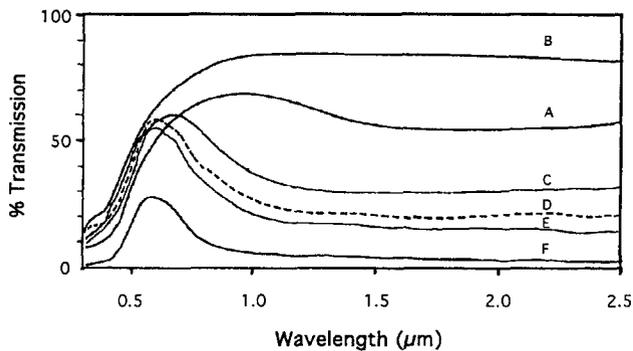Fig. 2. X-ray diffraction pattern of a CuS thin film.

Fig. 3. Optical transmission spectra for Cu$_x$S films obtained from various copper to thiosulfate ratios: (A) 1:1; (B) 1:2; (C) 1:2.5; (D) 1:3; (E) 1:4; (F) 1:5.

3.4. Optical studies

Optical transmission spectra in the VIS-NIR region were recorded for the various copper sulfide species and are shown in Fig. 3. Some differences in the spectra are noteworthy. Curve A on Fig. 3 represents the transmission spectrum of a film obtained from 1:1 copper to thiosulfate solutions. This material was identified as Cu$_{1.8}$S (see Table 1). Its spectrum reveals high transmission after the absorption edge at about 600 nm, throughout the visible part of the electromagnetic spectrum. However, a slight drop in transmission of these films is observed at the beginning and throughout the near-infrared region, resembling similarity with the spectrum of CuS. This is in contrast with the optical properties of Cu$_2$S films (Fig. 3, curve B), which maintain high transmission throughout the visible and near-infrared region of the spectrum. The transmission spectra of the films obtained from baths in which the ratio of copper to thiosulfate was 1:2.5, 1:3, 1:4 and 1:5 change in such a way that the transmission in the visible region becomes more and more remarkably peaked around 560–650 nm, while at the same time a substantial decrease in transmission throughout the NIR region is observed (Fig. 3, curves C, D, E and F). As is obvious, the CuS films or those chemically close to CuS transmit ≤ 25% of the near-infrared radiation, depending on the composition and thickness of the films. This

makes the CuS films suitable as solar control coatings (non-transmitting for the NIR-waves) in the warm climate regions, as already suggested by Nair and Nair [14]. The transmission of the CuS films is peaked at 560 nm, matching the phototropic sensitivity of the human eye, and making this material interesting for the architectural or automobile glazings, to prevent heating due to near-infrared penetration into the interior.

3.5. Chemical analysis

Rutherford back scattering (RBS) was used to analyze the chemical compositions of the films. Fig. 4 illustrates RBS spectra of Cu$_2$S and CuS films obtained with this technique. Chemical composition of the films obtained from different baths is given in Table 1. The films obtained from the thiosulfate-rich solutions (i.e. baths D, E and F) were found to be CuS. Cu$_{1.8}$S films were deposited from bath A, Cu$_2$S films were obtained from bath B and Cu$_{1.4}$S films were deposited from bath C. In bath A, where the ratio of copper to thiosulfate
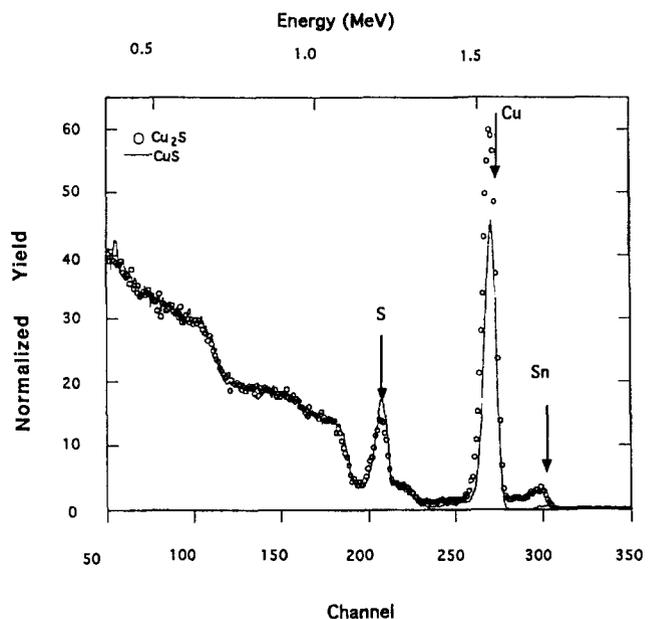

Fig. 4. RBS spectra of CuS and Cu$_2$S thin films on glass.

TABLE 1. Bath composition and basic characteristics of Cu$_x$S films

Bath	Cu: Thiosulfate (molar ratio)	Composition	Color	Thickness (μm)	Sheet resistance (Ω/square)
A	1:1	Cu$_{1.8}$S	Brown	0.12	190
B	1:2	Cu$_2$S	Yellow	0.05	650
C	1:2.5	Cu$_{1.4}$S	Yel-Green	0.10	170
D	1:3	CuS	Grn-Yellow	0.09	115
E	1:4	CuS	Green	0.11	110
F	1:5	CuS	Green	0.09	100

was 1:1, we suggest that only a part of the thiosulfate is spent to reduce $Cu(II)$ into $Cu(I)$ according to reactions (1) and (2), while the remaining thiosulfate is used to complex the $Cu(I)$ ions according to reaction (3). Because of this, part of the $Cu(II)$ ions remain unreduced. We believe that this is the reason for precipitation of $Cu_{1.8}S$ rather than Cu_2S from bath A. In bath B, where the ratio of copper to thiosulfate was 1:2, we suggest that one half of the thiosulfate is used to reduce $Cu(II)$ into $Cu(I)$ and the other half to complex the $Cu(I)$ ions according to reaction (3). Thus, the final product from this bath was Cu_2S, as expected and confirmed by RBS. The $Cu_{1.4}S$ films deposited from bath C, in which the ratio of copper to thiosulfate was 2.5, indicate that at this and higher ratios of the specified chemicals the chemical composition of the films begins to shift from Cu_2S towards CuS. Indeed, CuS films were deposited from baths D, E and F.

It is difficult to explain the formation of CuS films, or films chemically close to CuS, from baths in which the ratios of copper to thiosulfate was 1:2.5, 1:3, 1:4, etc. Somehow, in excess of thiosulfate, the $Cu(I)$ ions get oxidized back into $Cu(II)$, leading to precipitation of $Cu_{1.4}S$ or CuS, as shown by RBS analysis. The only explanation we can think of is the one already discussed in Section 3.1.

The thickness of the films estimated from the RBS peak width analysis was in agreement with the ellipsometric measurements, presented in Table 1. The thickness of the films (Table 1) was determined by an AUTO EL II ellipsometer with a visible laser source (wavelength of 0.6328 mm).

3.6. Electrical properties

The sheet resistances of the films, measured by the standard four-probe method, are presented in Table 1. A decrease in sheet resistance was observed as the amount of thiosulfate in the chemical bath was increased, i.e. as chemical composition changed from Cu_2S to CuS. The range of sheet resistances for the films under consideration was between 100 for the CuS films and 650 Ω/square for Cu_2S films.

4. Conclusions

A systematic experimental study of the copper–thiosulfate system has been carried out in aqueous solutions

at 50 °C and pH $\sim$ 5, with the purpose of copper sulfilde thin-film deposition. A solution growth technique based on hydrolytic decomposition of copper–thiosulfate complexes was used to deposit copper sulfide submicron films on glass or polyester transparency sheets. It was concluded that different copper sulfides, Cu_xS ($1 \leqslant x \leqslant 2$), can be deposited from a chemical bath composed from a fixed amount of copper(II) sulfate, by varying the molar ratio of sodium thiosulfate from 1 to 10. The 'copper rich' phases in the copper–sulfur phase diagram (Cu_2S, $Cu_{1.8}$ and $Cu_{1.4}S$) were deposited from chemical baths in which the copper–thiosulfate ratio was 1:1 to 1:2.5 and the 'sulfur rich' covellite phase (CuS) was obtained from baths of 3:1 or higher molar excess of thisulfate. X-ray studies showed that most of the deposited materials were amorphous, with crystallinity detectable only in the CuS films. The optical spectra revealed differences in the NIR transmission of the various species, with Cu_2S being highly transmissive throughout the VIS and NIR region, CuS being highly absorptive in the NIR region and the $Cu_{1.8}S$ and $Cu_{1.4}S$ films in between these two. The sheet resistances were found to decrease from Cu_2S towards the films of compositions closer to CuS.

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