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DEPOSITION OF TRANSPARENT AND ELECTROCONDUCTIVE CHALCOGENIDE FILMS AT NEAR-ROOM TEMPERATURES

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Abstract An economic and pollution-free technique for electroless chemical deposition of transparent and electrically conductive sub-micron films on the surfaces of glass, ceramics, transparent polyester films, metal, and ferroelectric thin films has been developed. The technique is based on hydrolytic decomposition of metal-thiosulfate or metal-selenosulfate complexes in aqueous solutions, and has been successfully used for deposition of transparent and electroconductive copper sulfide and copper selenide thin films of a variable composition. The basic optical and electrical characteristics of the as-deposited and annealed films are also reported.

The Cu_2S films were highly transparent ($\geq$ 80 %) throughout the visible and near-infrared region of the electromagnetic spectrum (0.5 to 2.5 μm wavelength), while the rest of the films exhibited stoichiometrically adjustable absorbance in the near-infrared region (0.7 to 2.5 μm wavelength). The sheet resistivities of the films were found to be between 15 and 1200 Ω/sq. The most conductive among the chalcogenides were the Cu_2Se films with sheet resistivities, R, of ~ 15 Ω/sq. , while the Cu_2S films were the least conductive (R ~ 1200 Ω/sq.).

INTRODUCTION

Many opto-electronic devices require an electroconductive, and in some cases also a transparent surface coating. Low temperature (room temperature to 70 °C) deposition of transparent and conductive coatings on ferroelectrics is desirable for electro-optic and photovoltaic applications. Copper sulfides and selenides exhibit metallic or semi-metallic properties, intrinsic semiconductivities, and in some cases, ductility. Due to these characteristics, these chalcogenide materials have a wide range of established and potential applications, including photothermal and energy conversion,[1,2] photovoltaic, [3,4] electroconductive electrodes, [5,6] and other electronic devices.[7,8]

Copper sulfides with variable composition, usually denoted as Cu_xS, have been fabricated in thin film forms by different techniques such as vacuum evaporation,[9] activated reactive evaporation,[10] and chemical bath deposition.[5,7,8, 11-12] The latter technique has also been used to make CuSe films.[13,14] In all of these reports, however, the characteristic optical and electrical properties of the various phases in these compounds were not specified. For example, copper and sulfur are known to form at least

four stable phases at room temperature. On the copper rich side are chalcocite (Cu_2S), djurlite ($Cu_{1.95}S$) and anilite ($Cu_{1.75}S$), while on the sulfur rich side is covellite (CuS). Mixed phases are also known in the intermediate compositions. Despite these differences, the deposited material is referred to as Cu_xS. The situation is similar with copper selenides, although only CuSe has been reported so far.

The objective of this work was to develop a simple deposition technique for a variety of electroconductive copper sulfides and selenides at near-room temperature, and to report on their chemical and physical properties. This paper presents and discusses the chemical precursor synthesis, thin-film processing, and electrical/optical characterization of the above mentioned chalcogenide thin films. Additionally, the hysteresis behavior of a PZT thin film with Cu_2S as the top electrode, is reported.

EXPERIMENTAL DETAILS

Four kinds of copper sulfide compounds and two kinds of copper selenide compounds were deposited on a variety of substrates, such as glass, polyester films, metal, ceramics and PZT thin film. The solution growth deposition technique employed is based on the hydrolytic decomposition of copper sulfide and copper selenide complexes in aqueous solutions, at a pH ~ 5 for the sulfides and ~ 10 for the selenides. Stock solutions of 0.5 M copper sulfate and 0.5 M sodium thiosulfate (TS) or sodium selenosulfate (SeS) were prepared by dissolving appropriate amounts of the chemicals in distilled water. The substrates were first ultrasonically cleaned and dried in air before they were vertically supported into the chemical bath composed of a fixed amount of copper sulfate and variable amounts of sodium thiosulfate or sodium selenosulfate. The temperatures of the baths were 40 to 70 °C, depending on the material to be deposited. Films with thicknesses between 0.1 and 0.3 μm were deposited, usually on both surfaces of the substrate, within 30 min to an hour. Then the films were washed with distilled water, dried in air and stored for further investigations. Unless otherwise specified, films deposited on standard microscope glass slides (76 x 26 x 1.0 mm) were used to examine the physical properties of the film material. X-ray diffractometry (XRD) and Rutherford Back-scattering analysis (RBS) were used to determine the composition of each film, before any optical and electrical measurements were performed. The film thicknesses were determined by elipsometry. Electrical conductivity was determined by a standard four probe method. Optical spectra were taken by a CARY 5 UV-VIS-NIR Spectrophotometer, in the spectral range of 0.3 to 2.5 μm wavelength.

RESULTS AND DISCUSSION

Four kinds of copper sulfides and two kinds of copper selenide thin films were deposited by varying the ratio of copper to thiosulfate or selenosulfate ions in the chemical baths.

Table I illustrates the details.

TABLE I Chemically deposited copper sulfides and selenides on glass substrates.

Bath composition (Cu to TS or SeS)	Compound deposited (formula)	Thickness (μm)	Dep. time (min.)
1 : 2	Cu_2S	0.14	30
1 : 1	$Cu_{1.8}S$	0.10	30
1: 2.5	$Cu_{1.4}S$	0.12	40
1 : 3	CuS	0.09	60
1 : 1	Cu_2Se	0.12	25
1 : 5	CuSe	0.10	45

Optical considerations

The optical transmission spectra of the films were taken in the VIS-NIR region (0.3 to 2.5 μm) of the spectrum. Figure 1 indicates that the transmission spectra of the copper sulfide films are dependent on the stoichiometry of the deposited material.

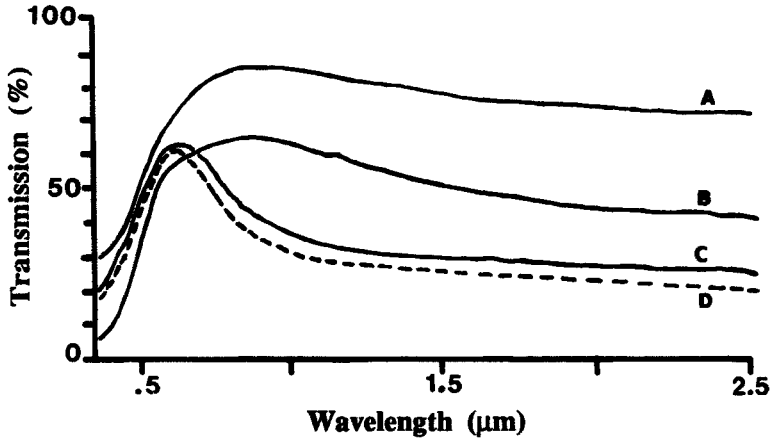

FIGURE 1 Optical transmission spectra of copper sulfide films: (A) $Cu_{1.8}S$; (B) Cu_2S; (C) $Cu_{1.4}S$; (D) CuS.

The optical transmission gradually reduces as the stoichiometry changes from Cu_2S to CuS, via the intermediate compounds $Cu_{1.8}S$ and $Cu_{1.4}S$. The optical characteristics of these films do not change upon annealing at temperatures below 200 °C. Above this temperature, all four kinds of the copper sulfide films exhibited higher transmissions

(between 75 and 90 %) within the same wavelength range, due to oxidation of the deposited material. Figure 2 shows the optical spectra of the copper sulfide films, after annealing for 3 h at 220 °C.

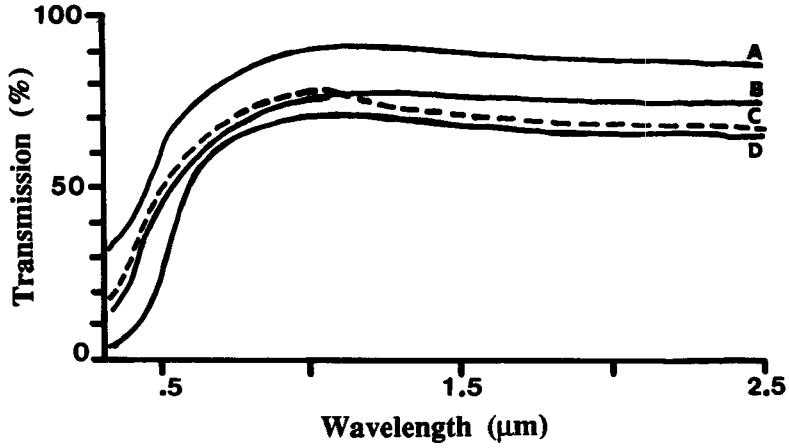

FIGURE 2 Optical transmission spectra of copper sulfide films, annealed for 3 h at 220 °C: (A) $Cu_{1.8}S$; (B) Cu_2S; (C) $Cu_{1.4}S$; (D) CuS.

Figure 3 illustrates the optical transmission spectra of selenides, namely, Cu_2Se and CuSe films.

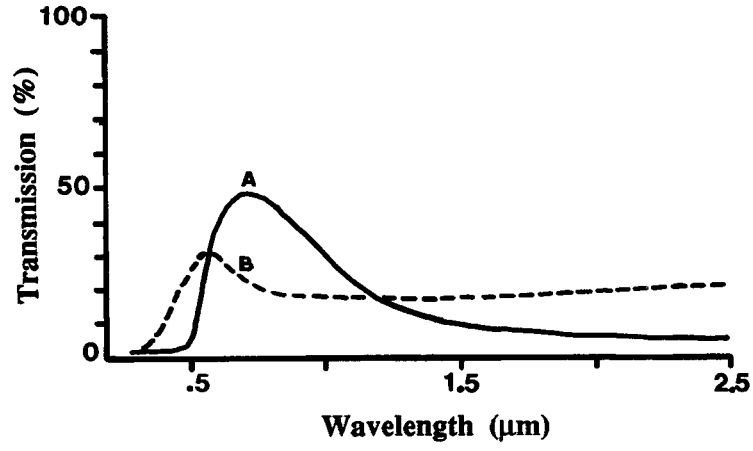

FIGURE 3 Optical transmission spectra of copper selenide films: (A) Cu_2Se; (B), CuSe.

Although there are qualitative similarities in the optical spectra of copper selenides with those of copper sulfides, the former (i.e., Cu_2Se and CuSe) exhibits a peak in

transmission in the visible part of the spectrum at about 0.6-0.7 μm wavelength, and a low transmission (≤ 20 %) in the near-infrared region of the electromagnetic spectrum.

Electrical characteristics

The results of the sheet resistivity measurements are summarized in Table II. The CuSe films were the most conductive, while Cu_2S films exhibited the lowest conductivity of all chalcogenide films under consideration in this paper. In essence, all of these films are highly conductive and can be used as conductive surface coatings.

TABLE II. Sheet resistivities of copper sulfide and copper selenide films.

Compound (Formula)	R (as-depos.) (Ω / sq.)	R' (annld. 130 °C) (Ω / sq.)	R" (annld. 220 °C) (Ω / sq.)
Cu_2S	1200	600	3650
$Cu_{1.8}S$	300	160	30,200
$Cu_{1.4}S$	210	110	34,700
CuS	105	45	2538
Cu_2Se	1000	300	2300
CuSe	70	10	1200

Chalcogenide Films on Polymer and Ferroelectric Films

All of the above materials, with the exception of CuSe were successfully deposited on transparent polyester sheets (such as those commonly used as overhead transparencies) to give a conductive surface. Such transparent and electrically conductive films on polymer sheets can find various applications in devices which require flexible substrates.

In yet another preliminary experiment, Cu_2S film was deposited on top of a ferroelectric PZT thin film. The PZT film was deposited on a Pt passivated Si by the sol-gel technique described previously.[15] The patterning of the top Cu_2S electrode was carried out by photolithography. Figure 4 illustrates a well saturated hysteresis loop, obtained on $Pb_{0.99}Nb_{0.02}[(Zr_{0.5}Sn_{0.5})_{0.86}\ Ti_{0.14}]_{0.98}O_3$ thin film, at 100 Hz and 90 kV/cm sinusoidal field. The maximum polarization (P_{max}), remanent polarization (Pr), and coercive field (Ec), were 31 μC/cm^2, 13 μC/cm^2 and 18 kV/cm, respectively.

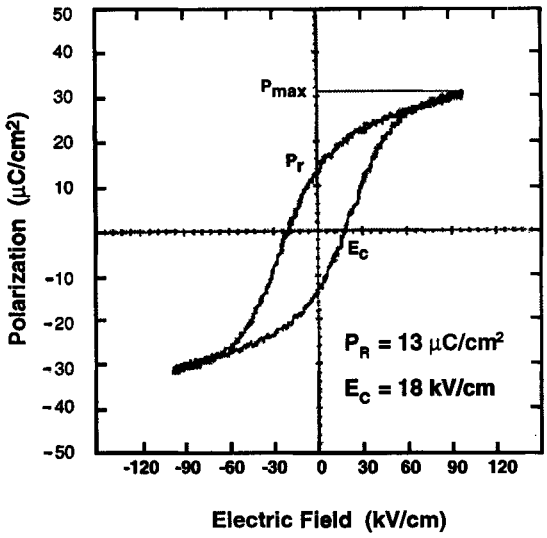

FIGURE 4 100 Hz hysteresis loop of a niobium and tin modified PZT thin film with Cu_2S as the top transparent electrode.

CONCLUSIONS

An electroless technique for the deposition of chalcogenide thin films at near-room temperatures was developed. Four kinds of copper sulfides and two kinds of copper selenides were successfully deposited on various substrates, including glass, ceramics, and ferroelectric films. The deposited films were electrically conductive, and most of them were highly transparent in the visible region of the spectrum. This makes them suitable for use as transparent electroconductive electrodes. In the initial experiments, most of these films were successfully deposited on transparent polyester films, producing an electrically conductive surfaces. Additionally, PZT thin films with Cu_2S as the top transparent electrode exhibited good hysteresis properties.

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