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Novel applications of chemically deposited Cu_xS thin films

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Abstract

Novel applications, such as electrically conductive and transparent surfaces on organic polymer sheets, elastic thin-film copper sensor electrodes that are immune to halide ion interference and contact electrodes on top of ferroelectric PZT films, are suggested for chemically deposited Cu_xS thin films. The economicity and simplicity of the electroless deposition technique employed for Cu_xS films is considered suitable for large-area and large-scale production of Cu_xS films on various substrates.

1. Introduction

Copper and sulfur are known to form a number of non-stoichiometric and mixed phases between the two chain members, Cu_2S and CuS [1]. Copper sulfides have a wide range of well established and modern prospective applications. Precipitate-based copper sensitive ion-selective electrodes use a membrane prepared by pressing a disk of coprecipitated copper and silver sulfides [2,3]. Copper sulfide films have been used in photothermal conversion applications [4,5], photovoltaic applications [6,7], solar control coatings [8] and other electronic devices [9,10].

Thin-film deposition of copper sulfides has been reported using vacuum evaporation [11], activated reactive evaporation [12], and chemical bath deposition [8,13–15]. In a recent study of the copper thiosulfate system with respect to thin film formation [16], we have reported four different phases of copper sulfides (Cu_2S, $Cu_{1.8}S$, $Cu_{1.4}S$ and CuS), deposited by electroless chemical deposition from aqueous solutions of copper(II) nitrate and sodium thiosulfate.

In this paper, we report on three novel applications of chemically deposited Cu_xS thin films. Although the results reported here were obtained specifically for $Cu_{1.8}S$ thin films, experiments carried out in our laboratory showed that any of the four phases mentioned above can be used for the same purposes.

2. Experimental procedure

$Cu_{1.8}S$ thin films with a thickness of 0.05 to 0.2 μm were deposited on top of clear polyester sheets (commonly used as overhead transparencies), or on ferroelectric PZT films, following the procedure described below. The polyester substrates were first ultrasonically cleaned, then soaked in 0.03% aqueous solution of tin(II) chloride for a few minutes, to ensure good wetting of the polyester surface, washed thoroughly with distilled water and dried in air before they were dipped into the chemical bath in which $Cu_{1.8}S$ films were deposited. The niobium and tin modified PZT films or $Pb_{0.9}Nb_{0.22}[(Zr_{0.5}Sn_{0.5})_{0.86}]_{0.98}O_3$, were deposited on a Pt passivated Si by the sol–gel technique, described elsewhere [17]. The patterning of the top $Cu_{1.8}S$ film was carried out by photolithography. The chemical bath

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for electroless deposition was aqueous solution of copper(II) nitrate and sodium thiosulfate, in molar ratio 1:1. The substrates were vertically dipped into the bath for several minutes at 40–50°C. More details about the experimental conditions for optimal growth of films can be found in Ref. [16]. After deposition of $Cu_{1.8}S$ films on top of the substrates, these were washed with distilled water, dried in air, and preserved for further study of their properties.

Rutherford backscattering spectrography (RBS) was used to determine the composition of the deposited copper sulfide films. Optical transmission spectra were taken 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 ellipsometry. Polyester strips (2.5 cm × 1 cm) coated with ≈ 0.1 μm thick $Cu_{1.8}S$ films were used as elastic sensor elsctrodes for Cu^{2+} ions, after a gold contact was pasted near the edge of the coated strips. About two thirds of the strips were dipped in solutions for mV and pH measurements.

3. Results and discussion

The chemistry and the kinetics of the deposition technique employed for $Cu_{1.8}S$ films have been reported earlier [16]. An RBS spectrum showing the ratio of copper to sulfur is presented in Fig. 1.

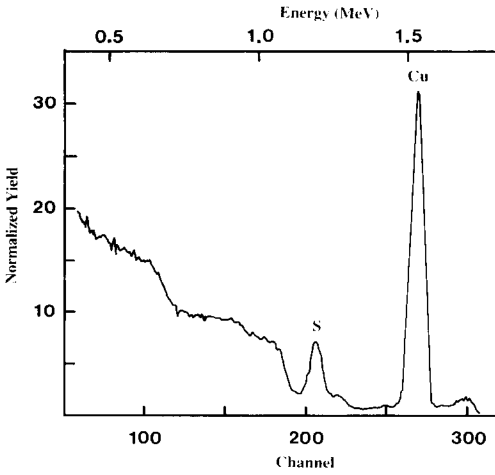

Fig. 1. RBS spectrum of $Cu_{1.8}S$ thin film.

3.1. Transparent and electrically conductive surface on organic polyester films

Numerous inorganic materials would be of interest as surface coatings on a flexible (elastic) polymer substrates, but most of the techniques used for deposition of inorganic coatings (vacuum deposition, electrodeposition, chemical vapor deposition, etc.) cannot be used with organic polymer substrates. Achieving good adherence of the inorganic layer onto the organic polymer surface is an additional difficulty.

Our low temperature (40°C) electroless deposition technique was successfully used to make transparent and electrically conductive surfaces onto organic polymer sheets. The pretreatment of the polymer surface in tin(II) chloride solution as described in Section 2 provided excellent adherence of the inorganic layer onto the organic substrates. The optical spectra of the polymer substrate with and without the $Cu_{1.8}S$ coating are shown in Fig. 2. Spectrum B shows 50 to 70% transmission of the coated polymer throughout the Vis–NIR region of the electromagnetic spectrum. The four-probe electrical measurements gave a value of about 190 Ω/square for the sheet resistance of 0.12 μm thick $Cu_{1.8}S$ film on top of organic polymer sheets. These transparent and electrically conductive surfaces on organic polymers can find various applications where an elastic and non-breakable substrate is required or preferred. The technique employed here is simple, inexpensive and suitable for large-area depositions [13]. One obvious disadvantage is that these coated organic polymers cannot be used at temperatures above 130°C.

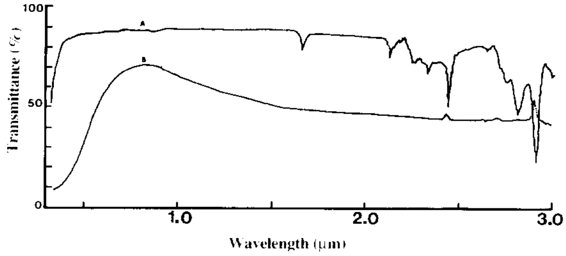

Fig. 2. Optical transmission spectra of (A) clear polymer substrate and (B) thin film of $Cu_{1.8}S$ deposited on top of the clear polymer substrate.

3.2. Elastic thin-film sensor electrodes

Small polymer strips (2.5 cm × 1 cm) previously coated with 0.12 μm $Cu_{1.8}S$, with gold-pasted contact were tested as Cu^{2+} sensor electrodes in aqueous solutions. Potentiometric measurements with 0.1 mV readings were carried out with an electrochemical cell made of $Cu_{1.8}S$ elastic electrode as a sensor electrode and Ag/AgCl as a reference electrode in 0.1 M KNO_3. Before the actual potentiometric measurements, the $Cu_{1.8}S$ elastic electrode was conditioned overnight in 10^{-3} M Cu^{2+} aqueous solution. The calibration curve of the potential (E) versus the concentration of copper ions (pCu) shown in Fig. 3 was produced by the addition of copper(II) nitrate solution to 0.1 M KNO_3 at 25°C. The thin film elastic electrode was tested in the concentration range 10^{-8} to 10^{-2} M Cu^{2+}. The response time of the electrode was tested by measuring the time required to achieve 95% steady potential reading and it was found to be 5 to 10 s. The solution was rapidly stirred during introduction of each new aliquot of Cu^{2+} and turned off before reading the potential. The average Nernstian slope was found to be 33 ± 2 mV/decade with a straight line between 10^{-2} and 10^{-7} M Cu^{2+}. This value is higher than the theoretical value of 29.5 mV, but at least it was consistent and reproductive. The pH response profile of the elastic thin-film electrode was examined by use of 10^{-3} M $Cu(NO_3)_2$ aqueous solution adjusted with 0.1 M HNO_3 and 0.1 M NaOH. The useful pH range was found to be 3–6.5. At above 6.5 the potential was found to decrease, due to the formation of copper hydroxide in the solution, while at pH lower than 3 the potential increased, indicating that some $Cu_{1.8}S$ from the sensor electrode was dissolving into the testing solution, thus increasing the Cu^{2+} concentration.

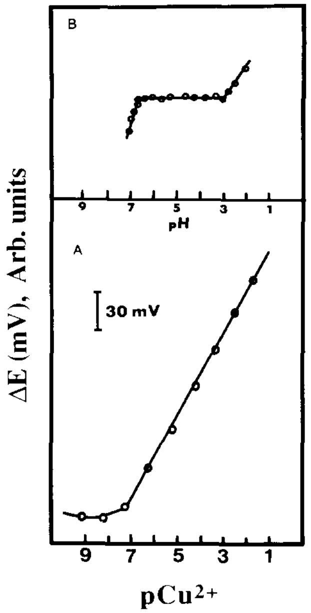

Fig. 3. Elastic thin-film electrode responses for Cu^{2+} ions: (A) Change of potential versus concentration of Cu^{2+} ions; (B) effective pH range for Cu^{2+} ion determinations.

Although further experiments will be needed to study the effect of interfering ions, strong interference of Hg^{2+} and Ag^{+} was observed, changing the chemical composition of the electrode, while even mild concentrations of Na_2S were found to be corrosive to the electrode. Unlike the commercial CuS/Ag_2S electrodes, halide ions were not interfering with our elastic $Cu_{1.8}S$ sensor electrode. This is not surprising, taking into account a previous study [3] in which it was shown that halide ions react with the silver sulfide component of the CuS/Ag_2S membrane electrodes. In the same study, it was suggested that pure copper sulfide membranes may provide electrodes which are less susceptible to halide interference. The latter was confirmed with our $Cu_{1.8}S$ electrode. Due to this advantage, $Cu_{1.8}S$ electrode may prove to be very useful as a copper sensor electrode in high halide media and marine waters, where copper is an important pollutant.

Again, the economicity and simplicity of the electroless deposition technique for $Cu_{1.8}S$ films is suitable for large area coatings on organic polymers and many other substrates [13,16].

3.3. Transparent top $Cu_{1.8}S$ electrode on PZT

Pt has been commonly used as an electrode material for Pb-based ferroelectric thin films. It has been very difficult to obtain ohmic contacts to insulators such as ferroelectrics because of the metal–dielectric incompatability. Several problems associated with the ferroelectric–metal interface include: (1) insufficient adherence, (2) buildup of interfacial layer which causes degradation of electrical properties and (3) increase in coercive field as well as distortions in hysteresis loops. In the past, Ruppel [18] utilized a multilayer or graded technique to form ohmic contacts by

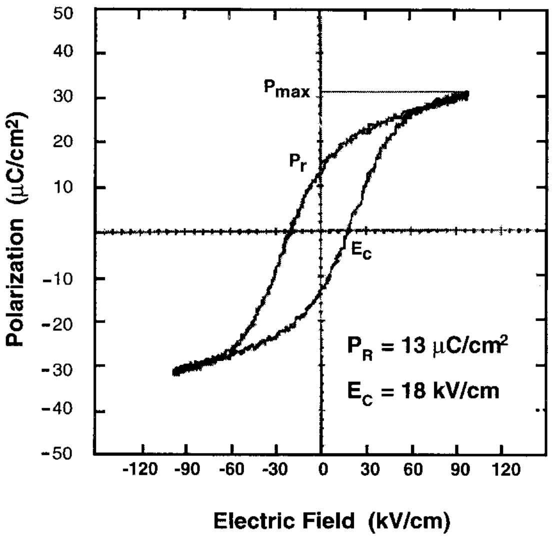

Fig. 4. 100 Hz hysteresis loop of PZT thin film with top $Cu_{1.8}S$ transparent electrode.

placing a semiconductor in between the metal and insulator. Additionally, conducting SnO_2 was reported [19] to form intimate contact with $Bi_4Ti_3O_{12}$ thereby improving the ferroelectric properties. Therefore, the hysteresis properties of PZT thin films with conducting $Cu_{1.8}S$ as the top electrode were investigated.

Niobium and tin modified ferroelectric PZT film was previously deposited by a sol–gel process on a Pt passivated Si. Top $Cu_{1.8}S$ electrode was patterned by a photolithographic technique. Fig. 4 illustrates a well saturated hysteresis loop, obtained at 100 Hz and 90 kV/cm sinusoidal field. The maximum polarization (P_{max}), remanent polarization (P_r) and coercive field (E_c) were 31 $\mu C/cm^2$, 13 $\mu C/cm^2$ and 18 kV/cm, respectively. A significant reduction in the coercive field was observed (compared to ≈ 30 kV/cm with top Pt electrode) which indicated good $Cu_{1.8}S$–ferroelectric contact.

4. Conclusion

Three novel applications for chemically deposited $Cu_{1.8}S$ films were successfully tested in our laboratory and demonstrated in this paper. (1) Making electrically conductive (190 Ω/square) and 50–70% transparent surface on elastic organic polymer sheets, which may find a variety of applications, especially when elastic and transparent substrate is required or preferred. (2) Using $Cu_{1.8}S$ coated elastic strips as Cu^{2+} sensor thin-film electrodes, free of halide ion interference. (3) Depositing $Cu_{1.8}S$ thin film as top transparent electrode on ferroelectric PZT films, while preserving the essential properties of the PZT films.

The electroless deposition technique for $Cu_{1.8}S$ films is also considered suitable for large-area coatings and large-scale production.

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