

Chemical bath fabrication of CuS/Ag₂S-mixed solid films

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Treatment of CuS films with AgNO₃ solutions gave CuS/Ag₂S films with concentration ratios Cu/Ag of 0.08–0.15. These materials were characterized by scanning electron microscopy and X-ray powder diffraction, and their Cu²⁺-detecting capabilities were studied by a potentiometric method. A uniform secondary-electron image was observed for a CuS/Ag₂S film prepared from a CuS film having a high crystallinity. An electrode constructed with the resulting mixed-sulfide film was capable of detecting Cu²⁺ ions down to a concentration as low as 10⁻⁷ mol dm⁻³. A CuS/Ag₂S film obtained from amorphous CuS had a heterogeneous surface and as an electrode was inactive towards Cu²⁺. The rate of reaction between CuS and Ag⁺ is dependent on the crystallinity of CuS, with CuS films of a high crystallinity being resistant to the attack of Ag⁺ so that the reaction is slow enough to provide a uniform and well-adhering CuS/Ag₂S film.

Metal sulfides exhibit important electrical and electrochemical properties, and some sulfides doped with other metal ions show better physical properties (such as electrical and photoelectrical conductivities) than the parent sulfides. An example for the use of doped sulfides in electrochemistry is that membranes of compressed CuS/Ag₂S pellets can selectively detect Cu²⁺ ions at lower concentrations than that of CuS membranes.^{1,2} CuS films have been obtained by chemical deposition methods with the objective of fabricating new functional thin films.^{3–10} The principle of chemical deposition is based on control of the rate of reactions between metal ions and sulfur sources.¹¹ If a metal sulfide film can be doped with other metal ions by a chemical method, the resulting film is expected to be useful for electronic and electrochemical devices. It has been reported that the electrical resistivity of an HgS film is decreased when the film is treated with a Ag⁺-containing solution;¹² this suggests a new method for doping metal sulfides, although the compositions of the doped materials have not been reported.

In our previous paper, we reported that amorphous and crystalline solids of CuS were obtained by reactions between [Cu(en)₂]²⁺ (en = ethylenediamine) and thiourea,¹⁰ with their electrical conductivity dependent on the degree of crystallinity.¹⁰ The crystallinity of CuS may also be a controlling factor of the chemical resistance of the material against attack of other metal ions. If amorphous and crystalline CuS solids react with other metal ions, therefore, their reaction rates will be different and the reaction products will show different physical properties. In this work, we have studied the reaction of CuS films with Ag⁺ and obtained the mixed CuS/Ag₂S films. The morphologies and the electrochemical properties of the resulting films are dependent upon the nature of the parent CuS films.

Experimental

Amorphous and crystalline CuS solids were synthesized by the method reported previously:¹⁰ reaction between [Cu(en)₂]²⁺ and thiourea in alkaline solution at 10 °C gave amorphous CuS (denoted CuS10 according to the reaction temperature), while reaction at 30 °C yielded crystalline CuS (CuS30). When a poly(ethyleneterephthalate) film was immersed in the reaction solutions, films of the corresponding sulfides were formed on the polymer substrate. Annealing of CuS10 and CuS30 at 100 °C gave crystalline copper sulfides (CuS10A and CuS30A, respectively). CuS30, CuS10A and CuS30A showed X-ray

powder diffraction patterns characteristic of crystalline CuS (covellite, JCPDS 6-464), with CuS10A having the highest crystallinity, as reported previously.¹⁰ These four materials were studied in their reactivity with Ag⁺.

When the CuS films were immersed in a 0.01 M AgNO₃ solution at 10 °C for 3 h and then at 40 °C for 2 h, dark films with metallic luster were obtained. The resulting identically treated films were then washed with water and ethanol, and dried in vacuum. Corresponding powder materials also were obtained under identical reaction conditions, and were used for studies of the bulk electrical resistance and X-ray powder diffraction.

Secondary-electron (SE) images and the compositions of the films were obtained using a JEOL JSM-5410LV scanning electron microscope (SEM) equipped with an Oxford EDS analyzer operating at 25 keV. Sample films were coated with Au for observation of morphologies, and uncoated films were used for EDS (energy-dispersive spectroscopy) analyses. X-Ray diffraction patterns were obtained using a Rigaku Geigerflex diffractometer with Cu-K α radiation and a curved graphite analyzer.

Electrical resistivities were determined by the standard two-probe method.¹⁰ The electrode potential induced for a sulfide film vs. an Ag/AgCl reference electrode was measured at 25 °C by the use of a Keithley 614 electrometer (input impedance >5 × 10¹³ Ω). A CuS film of dimensions 8.5 × 28 mm was vertically mounted on a Teflon holder, together with a double junction reference electrode at a separation of 1 cm. The top edge of the CuS film was connected to a Cu wire with Aquadag, and the bottom area of 8.5 × 18 mm was immersed in the sample solution. Sample solutions were prepared by dissolving Cu(ClO₄)₂·6H₂O in 0.1 M KNO₃ and standardized by colorimetry with neocuproine (2,9-dimethyl-1,10-phenanthroline).

Results and discussion

All four CuS films reacted with Ag⁺ ions and gave dark films with a metallic luster. The parent CuS films were initially characterized by SEM, since their reactivities towards Ag⁺ differed. Fig. 1 and 2 show the SE images of the films studied. The images of CuS10 and CuS30 show the formation of a fairly uniform surface. The particle size of amorphous CuS10 is smaller than that of CuS30. On the surface of each material, weakly bound large particles are observed as white images. The

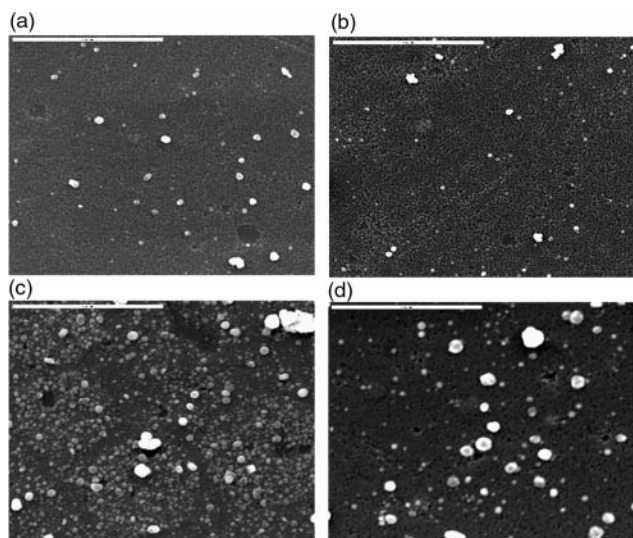


Fig. 1 Secondary-electron images of films: (a) CuS10, obtained at a reaction temperature of 10 °C; (b) CuS10A, obtained by annealing CuS10; (c) Ag₂S/CuS10, obtained by treating CuS10 with Ag⁺; (d) Ag₂S/CuS10A, obtained by treating CuS10A with Ag⁺. The scale bar of each image is *ca.* 5 μm.

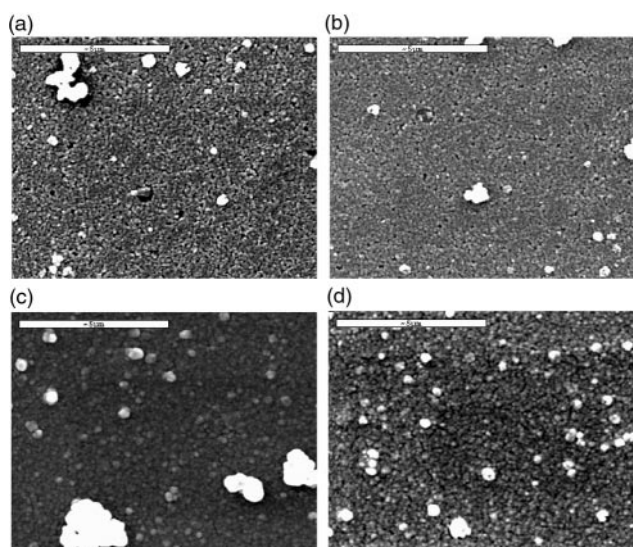


Fig. 2 Secondary electron images of films: (a) CuS30, obtained at a reaction temperature of 30 °C; (b) CuS30A, obtained by annealing CuS30; (c) Ag₂S/CuS30, obtained by treating CuS30 with Ag⁺; (d) Ag₂S/CuS30A, obtained by treating CuS30A with Ag⁺. The scale bar of each image is *ca.* 5 μm.

Cu : S ratios determined by EDS analyses on the entire surface of CuS10 and CuS30 were *ca.* 0.7 : 1, and all the regions of the white areas had a practically identical composition. It is probable that CuS particles formed at a later reaction stage were weakly attached. The SE images of the annealed materials resemble that of CuS30. The compositions of the annealed materials are: Cu/S \approx 1.3 for CuS10A and 0.7 for CuS30A. The surface of CuS10A has the highest uniformity among the four CuS films and is responsible for the low surface electrical resistivity (10 kΩ □ at 300 K). These observations show that the synthesis of amorphous CuS followed by annealing is a better method for the fabrication of CuS films than the direct chemical deposition of crystalline CuS.

For all films treated with Ag⁺-containing solutions, EDS analyses showed that the Ag : S ratio was *ca.* 2 : 1, and that Cu was present at a Cu/Ag ratio of 0.08 for a film obtained from CuS10 while this ratio was 0.15 for the other three CuS films; no other elements were detected by EDS analyses. The X-ray

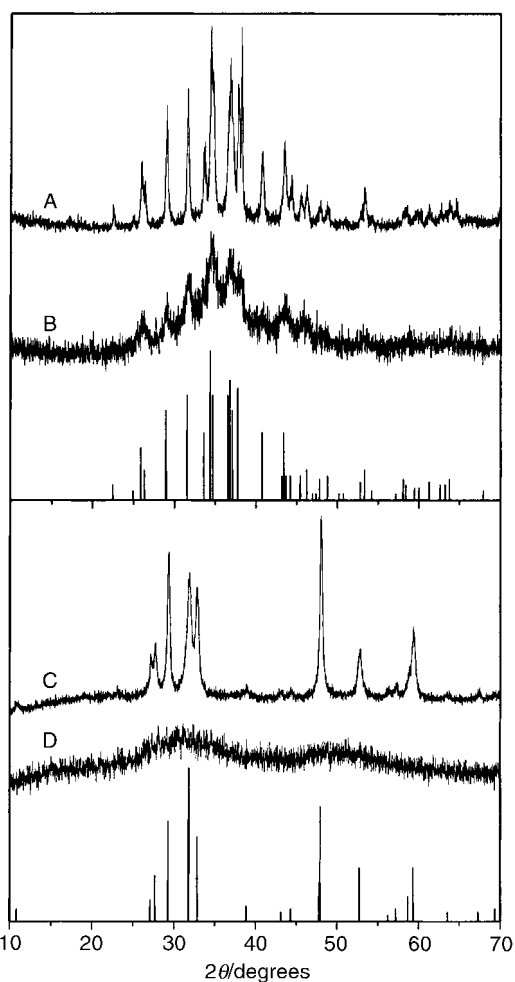


Fig. 3 X-Ray powder diffraction patterns of (A) Ag₂S/CuS10A, (B) Ag₂S/CuS10 and their parent CuS materials, (C) CuS10A and (D) CuS10; the scale of the ordinate is different for all patterns. The vertical lines show the diffraction patterns of (top) Ag₂S (acanthite, JCPDS no. 14-72) and (bottom) CuS (covellite, no. JCPDS 6-464). The diffraction patterns observed for Ag₂S/CuS30 and Ag₂S/CuS30A were more similar to pattern A rather than B.

powder diffraction patterns of the corresponding powder materials showed the formation of monoclinic Ag₂S (acanthite, JCPDS 14-72), while diffraction peaks assignable to crystalline CuS (covellite) were weak and masked by the peaks of Ag₂S, as shown in Fig. 3. These observations indicate that a large part of Cu atoms in CuS were replaced by Ag during treatment with Ag⁺-containing solutions, and that Ag₂S doped with CuS (acanthite mixed with covellite) was formed; these materials are thus denoted Ag₂S/CuS10, Ag₂S/CuS10A, Ag₂S/CuS30 and Ag₂S/CuS30A. Ag₂S/CuS10 obtained from amorphous CuS10 has a low crystallinity compared with the other Ag₂S/CuS solids (Fig. 3). The SE images show that the surface of the Ag₂S/CuS10 film is heterogeneous whereas the other films are fairly uniform (Fig. 1 and 2). For each film, weakly bound particles are observed as white images. These particles had a lower Cu concentration than that of the overall film: the Cu/Ag ratio was 0.05 for Ag₂S/CuS10, 0.1 for Ag₂S/CuS30, 0.08 for Ag₂S/CuS10A and 0.05 for Ag₂S/CuS30A. The uniformities of the Ag₂S/CuS films are related to the crystallinities of the parent CuS films. CuS10A, which has the highest crystallinity, is the most resistant towards attack by Ag⁺, and hence the replacement of Cu by Ag occurs slowly enough to result in good adherence of CuS/Ag₂S-mixed solids on the substrate. By contrast, amorphous CuS10 is highly reactive, and hence its reaction with Ag⁺ precedes too fast to lead to the formation of a uniform surface and formation of crystalline particles. The surface electrical resistivities of all the Ag₂S/CuS films were

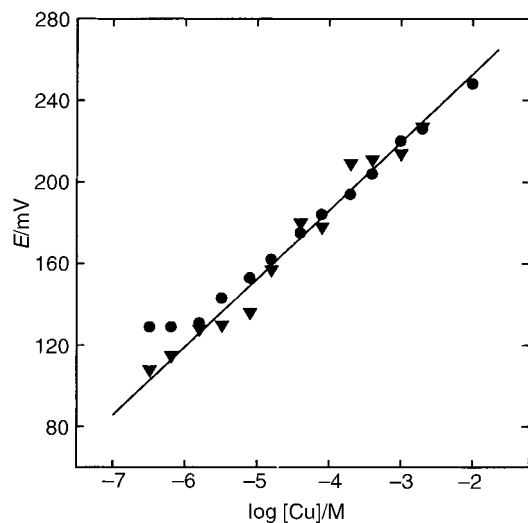


Fig. 4 Electrode potentials of CuS10A (●) and Ag₂S/CuS10A (▼) films vs. an Ag/AgCl reference electrode in 0.1 M KNO₃ at 25 °C. The straight line indicates the Nernst relation with a slope of 33 mV.

> 200 GΩ □. The bulk electrical resistivities of the corresponding powder materials were of the order of 2 MΩ cm at 300 K, except for Ag₂S/CuS10 the resistivity of which was > 100 MΩ cm. Electrical conduction in the other three Ag₂S/CuS materials is a result of Ag₂S being doped homogeneously by CuS, since pure Ag₂S is an electrical insulator. On the other hand, Ag₂S/CuS10 is probably a heterogeneous mixture of Ag₂S and CuS, which results in its high electrical resistivity.

A combination of a CuS film and a reference electrode leads to a Cu²⁺-sensing electrode. The induced potential of the electrode obeyed the Nernst equation, $E = E_0 - C \log [\text{Cu}^{2+}]$ ($C = 27\text{--}30$ mV) down to $[\text{Cu}^{2+}] = 10^{-5}$ M in 0.1 M KNO₃. Fig. 4 shows the potential observed for a film of CuS10A. The response times of all the films studied were < 5 min throughout the concentration range for which the Nernst relation was valid. Electrodes prepared from CuS30 and CuS10A films showed high stability of electrical readings and a rapid response in comparison with the CuS10 film. These better properties of the former two electrodes are related to their low impedances owing to the high electrical conductivities of the constituent materials.

An electrode constructed with the Ag₂S/CuS10A film followed the Nernst relation down to a Cu²⁺ concentration of 5×10^{-7} M, as shown in Fig. 4. This concentration is much lower than that for the parent CuS film (CuS10A) and is comparable to that of commercially available Cu²⁺-sensing electrodes consisting of compressed CuS/Ag₂S pellets.¹³ The Ag₂S/CuS10A electrode was electrically less stable than that of

CuS10A, and showed a relatively large fluctuation in the potential readings which is due to the high surface electrical resistivity (> 200 GΩ □). The other Ag₂S/CuS films did not show a Nernst-type response with respect to Cu²⁺ concentration. Since the Cu:Ag ratios of the four films are practically identical, the Cu²⁺-sensing capability is related to physical properties (such as contact between CuS/Ag₂S particles in the conducting layer) rather than chemical properties (such as chemical composition). The most sensitive electrode, Ag₂S/CuS10A, has the highest uniformity in the dark SE image area that is believed to be responsible for the good Cu²⁺-sensing capability, and has the lowest surface electrical resistivity.

In conclusion, the formation of amorphous CuS followed by annealing gives superior films of crystalline CuS (covellite). The high crystallinity of such films reduces the rate of the reaction with Ag⁺, resulting in the formation of a uniform CuS/Ag₂S film, which is beneficial for sensing Cu²⁺. Since any metal ions that are nobler than Cu²⁺ can replace Cu atoms in CuS films, such reactions are expected to be useful for the fabrication of a variety of doped metal sulfide films.

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