

# Co-Deposition of PbS–CuS Thin Films by Chemical Bath Technique

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Chemical bath deposition of thin film PbS–CuS from solution containing  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  and thiourea is presented. X-ray fluorescence analyses show the relative abundance of Pb, Cu, and S in the films as a function of the duration of deposition. These results along with those obtained from X-ray diffraction analyses support the formation of thin film of the type  $(\text{PbS})_{1-x}(\text{CuS})_x$ . An important feature of these films is their good adhesion to glass substrate even at long durations of deposition (24 h); a characteristic basic to chemically deposited PbS thin films. The near infrared optical transmittance (70%) as well as the p-type sheet resistance (1 M $\Omega$ ) of the as prepared films drop considerably to typically 15% and 300  $\Omega$  when annealed at 200°C in air or nitrogen ambient, both being basic behaviors of chemically deposited CuS thin films. © 1996

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## INTRODUCTION

In previous reports, we discussed the chemical bath deposition of CuS (1, 2) and PbS (3) thin films for solar control applications. In order to overcome the peeling of CuS thin films from glass substrates at film thickness  $>0.3 \mu\text{m}$ , we suggested the use of glass substrates already carrying a chemically deposited PbS thin film of typically 0.05–0.1  $\mu\text{m}$  in thickness. Such PbS–CuS thin films could offer a wide range of solar control characteristics not possible in CuS-only or PbS-only coatings (4). Further studies indicated that annealing of these films brings about diffusion of the metal ions across the PbS–CuS interface leading to the formation of films with ternary composition,  $\text{Pb}_x\text{Cu}_y\text{S}$  (5).

In the present paper, we report the chemical bath deposition of PbS–CuS thin films from a single bath, with the objective of depositing adherent films for solar control, solar absorber, or other applications. Similar work on co-deposited metal sulfide thin films of Pb and Hg (7), Cd and Pb (8), and Bi and Pb (9) by chemical bath technique have been reported before by other research groups. In

most cases these mixed phase films were shown to possess structural and optical properties distinct from those of the respective films of binary composition. In the present paper we report the formation of good quality thin films, whose composition is of the type  $(\text{PbS})_{1-x}(\text{CuS})_x$ . The X-ray diffraction confirms the presence of PbS and traces of CuS in the films, whereas the electrical characteristics indicate p-type conductivity due to the CuS component of the film. Such conductivity arises from the copper deficiency of the CuS component, a characteristic of the CuS–Cu<sub>2</sub>S system (10, 11).

## EXPERIMENTAL

The chemical bath used for the deposition of PbS–CuS thin films reported in this paper was constituted in the following manner. First, a mixture of 1 M solutions of lead acetate (5.0 ml), sodium hydroxide (20.0 ml), thiourea (8.0 ml), and triethanolamine (4.0 ml) was prepared and the volume taken to 160 ml with deionized water. Second, a mixture of 1 M copper(II) chloride (1.5 ml) and 3.2 ml of 1 M triethanolamine was prepared and the volume was made up to 40 ml with the addition of deionized water. The mixture mentioned first was added to the second mixture under stirring for 1 min. PbS-only films were deposited (for reference purpose) by the addition of 2.5 ml of 1 M lead acetate, 10 ml of 1 M sodium hydroxide, 6 ml of 1 M thiourea, and 2 ml of 1 M triethanolamine, added in this sequence and the volume taken to 100 ml with deionized water.

The molar ratio of lead to copper ions in the deposition bath was 3.3 to 1. Considering that the solubility product of PbS is  $10^{-28}$  and that of CuS is  $6 \times 10^{-36}$  (6), the above molar ratio of the ions in the bath is not expected to be translated into atomic ratios in the thin film. A lower solubility product implies relatively fast condensation of a solid phase from the deposition bath as precipitate settling to the bottom of the bath and as thin film depositing over the substrates. Thus, the composition of the film deposited from the multi-component bath is in general expected to vary along the thickness of the film unless the complexing

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agents for each metal ion (e.g.,  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ ) is manipulated so as to maintain a constant ratio of the precipitation rate for the components (PbS and CuS). In the present case specularly reflecting films were deposited from the above bath maintained at room temperature ( $25^\circ\text{C}$ ) on clean glass slides ( $76\text{ mm} \times 26\text{ mm} \times 1\text{ mm}$ ) for duration of deposition of 2 to 40 h. Reduction in the concentration of copper ions in the bath lead to deposition of films with electrical and optical characteristics very close to that of PbS films. Increase in the concentration of copper ions lead to the deposition of CuS-like films with the inherent problem (of CuS films) of peeling from glass substrates at duration of deposition longer than 6 h (i.e., before reaching the final thickness). The thickness of the films were determined using Alpha-Step 100 step thickness measuring equipment (Tencore Instruments, USA).

X-ray diffraction (XRD) patterns of the PbS-CuS film deposited for 25 h from the PbS-CuS bath described above and of the precipitate filtered from the bath after the 25 h deposition were recorded in a Siemens D 500 diffractometer. Analysis of the X-ray fluorescence (XRF) peaks (Pb, Cu, and S) of the films was done as a function of duration of deposition (3, 7, 15, and 25 h) to study the variation in the composition of the film. A Siemens SRS 303 XRF machine was used for this study. Optical transmittance and reflectance spectra of the films were recorded in a Shimadzu 365 UV-VIS-NIR spectrophotometer for 7 h films annealed in air for 1 h each at temperatures of 100, 200, 240, 260, and  $300^\circ\text{C}$ . Variation of the sheet resistance of the films as a function of temperature and duration of annealing was studied using pairs of silver paint electrodes (5 mm long, 5 mm separation) printed on the film surface after each heat treatment. A Keithley 619 multimeter and a Keithley 230 programmable voltage source were used to measure the current-voltage relation to determine the sheet resistance. The applied bias was varied in the 10–0.1 V range so that current level was in the nA– $\mu\text{A}$  range in the more resistive films (PbS-CuS films as deposited and PbS-only films) and did not exceed mA range in the less resistive films (annealed PbS-CuS thin films).

## RESULTS AND DISCUSSION

Figure 1 shows the variation of thickness of the PbS-CuS thin films as a function of duration of deposition (bath temperature,  $25^\circ\text{C}$ ). It follows the growth pattern generally observed in chemical bath deposition of metal chalcogenide thin films (12): an initial slow growth involving the creation of centers of nucleation (*nucleation* or *incubation phase*), not shown in the figure, a growth phase (3–9 h) at which the film thickness increases steadily with time, and a terminal phase in which the growth slows down and the film thickness approaches a terminal value—approx-

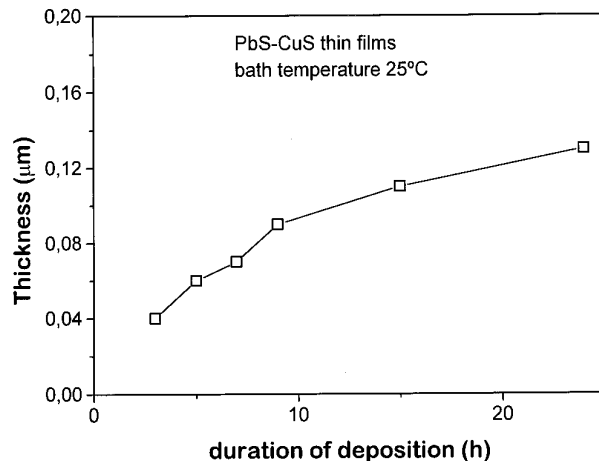


FIG. 1. Thickness versus duration of deposition of PbS-CuS thin films; bath temperature,  $25^\circ\text{C}$ .

imately  $0.15\ \mu\text{m}$ . Films may be deposited for 40 h from the bath described above, without peeling from the glass substrates. However, the quality of the films (based on the criteria of uniformity and specular reflection) may be rated as good only for durations of deposition up to 25 h (film thickness  $0.13\ \mu\text{m}$ ).

Figure 2 shows the XRD patterns of a PbS-CuS thin

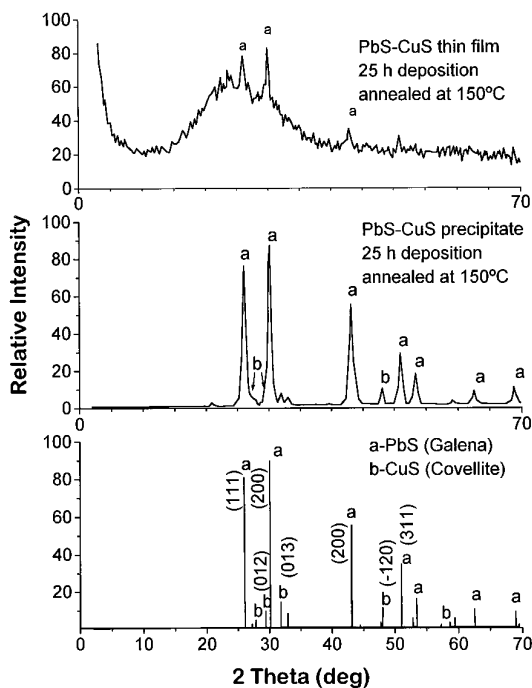


FIG. 2. X-ray diffraction patterns ( $\text{CuK}_\alpha$ ) of a PbS-CuS thin film (25 h deposition at  $25^\circ\text{C}$  and annealed at  $150^\circ\text{C}$  for 1 h) shown along with the pattern recorded for the precipitate (collected from the bath at the end of the 25 h deposition and annealed in the same way) and the standard patterns for PbS and CuS.

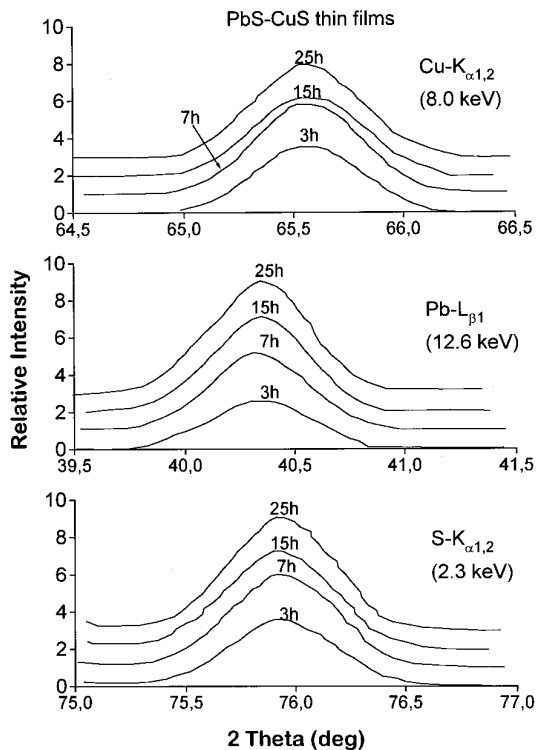


FIG. 3. X-ray fluorescence spectra of the as prepared PbS–CuS thin films deposited for various durations (3–25 h) at 25°C indicating the variation of Cu, Pb, and S content in the films as a function of the duration of deposition.

film (25 h deposition), given along with that of the powder sample collected from the bath at the end of the 25 h deposition. The patterns were recorded after annealing the samples at 150°C for 1 h. This was done to improve upon the peak intensities. Line positions of standard XRD patterns of PbS (galena, JCPDS 5-0592) and CuS (covellite, JCPDS 6-0464) are also given. The standard pattern illustrates that the relatively high atomic scattering factor of lead produces higher peak intensities in the case of PbS. The XRD pattern of the thin film sample shows only the strongest of the PbS peaks. However a comparison of the XRD pattern for the powder sample (precipitate) with that of the standard patterns suggest that the powder is a mixture of PbS and CuS. The same may be said about the thin film, if one considers that the thin film formation and precipitation of particulate in the bath follows the same mechanism. This suggests a film composition type  $(\text{PbS})_{1-x}(\text{CuS})_x$ .

The presence of Pb, Cu, and S in the thin film and the relative variation of their abundance as a function of duration of deposition are illustrated in the XRF spectra given in Fig. 3. The XRF emissions studied were:  $\text{CuK}_{\alpha 1,2}$  (0.15425 nm; 8.0 keV)  $\text{PbL}_{\beta 1}$  (0.9829 nm; 12.6 keV), and  $\text{SK}_{\alpha 1,2}$  (0.53736 nm; 2.3 keV). LiF crystal ( $2d = 0.2848$  nm;

$2\theta$  for  $\text{PbL}_{\beta 1} = 40.38^\circ$  and  $\text{CuK}_{\alpha} = 65.58^\circ$ ) and pentaerythrite crystal ( $2d = 0.8742$  nm;  $2\theta$  for  $\text{SK}_{\alpha} = 75.85^\circ$ ) were used for the analyses. It is clear from Fig. 3 that the Cu peak height tends to saturate after 7 h of deposition, where as the Pb and S peaks continue to grow. This is not surprising because the relatively low solubility product of CuS would lead to ready condensation of CuS which would deplete the bath in  $\text{Cu}^{2+}$  ions during prolonged deposition.

The optical transmittance (T%) and specular reflectance (R%) spectra of the 7 h PbS–CuS sample is given in Fig. 4. The nature of the reflectance and transmittance spectra of the as prepared film resemble that of PbS-only film (3). The reduction in near infrared optical transmittance of the film upon annealing in the temperature range from 100 to 200°C is due to an increase in the electrical conductivity which is a basic feature of CuS films (2). Annealing the films in air at temperatures above 220°C, which is the decomposition temperature of CuS (6), leads to the chemical conversion of dark CuS into lightly colored oxysulfates of copper (13). This causes an increase in the optical transmittance of the film.

Figure 5 shows the variation in sheet resistance of the PbS–CuS thin films deposited for 3–24 h (0.04–0.13  $\mu\text{m}$  thickness) at 25°C and annealed for 1 h each at 200, 250, and 300°C in air and nitrogen atmosphere (at atmospheric pressure). The rapid drop in sheet resistance with annealing is seen in both cases of annealing. This is a characteristic

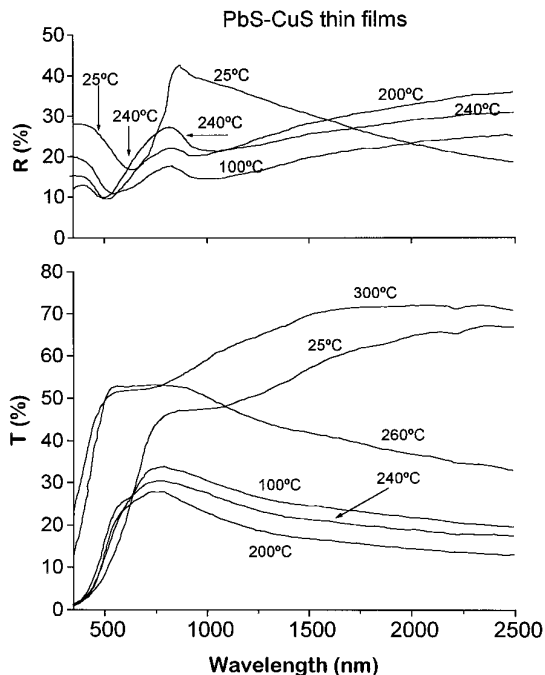


FIG. 4. Optical transmittance (T%) and near-normal specular reflectance (R%) spectra of PbS–CuS thin films deposited for 7 h at 25°C and annealed in air at the specified temperatures for 1 h each.

feature of CuS films and attributed to improvement in the crystallinity, changes in stoichiometry, and oxygen incorporation in the film taking place during the annealing (2). It is the increase in electrical conductivity corresponding to these changes in the film which is responsible for the reduction in the near infrared transmittance of the films (due to increased free carrier absorption of the radiation) shown in Fig. 4. The relatively higher sheet resistance of the films annealed at 250 and 300°C indicates the deterioration of the CuS component of the films. The deterioration is relatively low when the annealing is done in nitrogen atmosphere. The sheet resistance of the annealed film is minimum (100  $\Omega/\text{sq.}$ , nitrogen annealing or 300  $\Omega/\text{sq.}$ , air annealing at 200°C) for 5 h deposition (film thickness, 0.06  $\mu\text{m}$ ). The electrical conductivity of this film is, therefore, about  $10^3 \Omega^{-1} \text{cm}^{-1}$ . In the application of these films as solar control coatings, the temperature of the film under normal operation rises only to 50–60°C (14). Thus once the film is annealed at about 200°C, the film would acquire the desired optical properties of the film for solar control applications, and may maintain such characteristics without degradation during prolonged operation.

Figure 6 establishes that the low sheet resistance of the PbS-CuS thin films reported here is due to their CuS component. As prepared, PbS and PbS-CuS thin films deposited for 2 h each have sheet resistance of about  $10^8 \Omega$ . Annealing leads to competing processes in the film: grain size growth, oxygen incorporation, and disproportionation (in the case of CuS film).

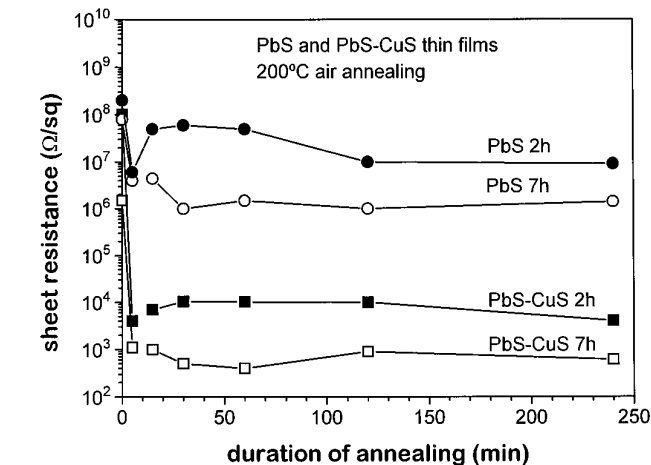


FIG. 6. Sheet resistance of PbS and PbS-CuS thin films deposited for 2 and 7 h at 25°C and annealed in air at 200°C for various durations.

These affect the film conductivity to different extent as a function of annealing time and annealing temperature. In the case of the 2 h PbS film, there is a reduction by less than one order of magnitude of the sheet resistance with annealing at 200°C. In contrast, the sheet resistance of the PbS-CuS thin film drops by more than four orders of magnitude, to  $<10^4 \Omega$ . Similar results are obtained upon annealing in the case of films deposited for 7 h. This shows that the electrical conductivity of the PbS-CuS thin films reported here is dominated by the CuS component of the film. A hot probe thermoelectric test indicated p-type conductivity for the film which arises from copper deficiency in the CuS component (10).

The basic advantage of the co-deposition of PbS-CuS thin films by the present technique is that adherent films can be deposited from a single bath thereby saving time and reagents. Another desirable aspect is that the chemical bath reported here does not involve the use of ammonia (aq.), a basic constituent of the CuS deposition bath reported before (2) and a health hazard when industrial production of the coatings is considered.

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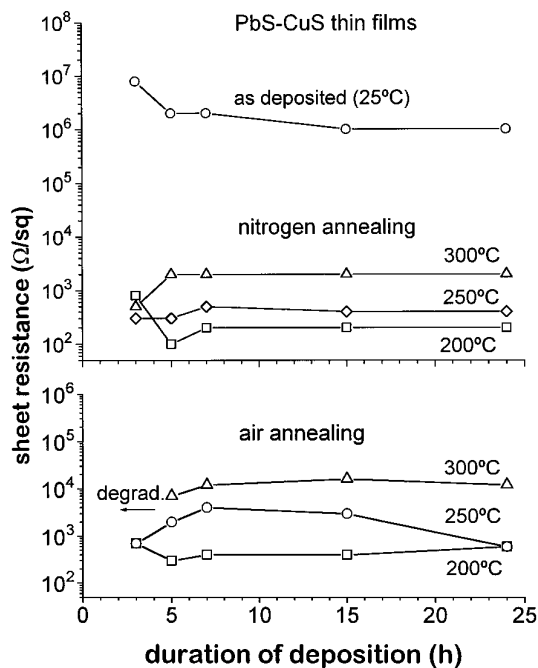


FIG. 5. Sheet resistance of PbS-CuS thin films deposited for 3 to 24 h at 25°C and annealed in air and nitrogen ambient at atmospheric pressure at the specified temperatures for 1 h each.

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