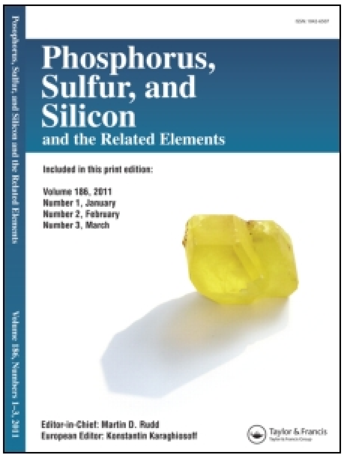

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CHEMICAL DEPOSITION OF THIN FILMS OF COPPER SULFIDE ON GLASS SURFACES MODIFIED WITH ORGANOSILANES

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CHEMICAL DEPOSITION OF THIN FILMS OF COPPER SULFIDE ON GLASS SURFACES MODIFIED WITH ORGANOSILANES

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CuS thin films were deposited on glass surfaces modified by treatment with 3-mercaptopropyltrimethoxysilane from a chemical bath made up of copper ions, sodium citrate and thioacetamide. The present method combines the advantage of using a non-ammoniacal aqueous bath for the deposition of these films with that of a surface treatment which inhibits the detachment of the film from the glass substrate when films grow thicker. Single depositions for durations of about 2–8 h at 25°C yield films of thicknesses in the range of 0.13–0.25 μm. Multiple depositions for a total period of 20 h result in a film thickness of 1 μm. X-ray photoelectron spectra of the films indicate the molar composition of CuS and X-ray diffraction pattern confirms the covellite structure for the thin films. Results regarding the thermal stability, optical transmittance spectra and electrical properties of the films are presented.

Key words: Organosilanes, copper sulfide films, X-ray photoelectron spectra, X-ray diffraction pattern, thermal stability.

INTRODUCTION

The preparation of thin films of copper sulfide by chemical deposition has been reported earlier.[1] Subsequent studies on the electrical and optical properties show that the films offer great prospects for applications as solar control coating in architectural and automobile glazing.[2,3] When deposited over other metal sulfide films, eg., bismuth sulfide and lead sulfide, the resultant multilayer combinations show solar absorbance in the range of 0.8 to 0.9 with reasonably low thermal emittance (0.4).[4] Based on these results a new approach to the design of all glass tubular collectors has been proposed.[5]

There are at least two major technical barriers to the utilization of chemically deposited CuS thin films in large scale applications. First, all of the deposition baths developed so far for the preparation of copper sulfide thin films require a high concentration of ammonia (as much as 1.1 M) in order to obtain good quality films[1–4,6,7] and this is a potential environmental and health hazard. Second, the films have been found to peel from glass substrates after long durations of deposition[1] which has limited the films to a maximum thickness of approximately 0.5 μm. Thus, it is desirable to develop an alternative chemical deposition bath devoid of ammonia and meanwhile giving adherent films of good quality and more widely adjustable thickness.

In this paper we present the chemical deposition of copper sulfide thin films from a non-ammoniacal bath that contains citrate as a complexing agent and thioacetamide as the source of sulfide ions. The pretreatment of glass substrates with 3-mercaptopropyltrimethoxysilane makes it possible for the films deposited on them to grow to thicknesses up to 1 μm without peeling from the substrate.

At room temperature, studies of the Cu-S system have shown the existence of five stable crystallographic phases, from chalocite (orthorhombic Cu_2S) on the copper rich side to covellite (CuS) on the copper deficient side. Thus, copper sulfide films may exhibit considerable compositional and structural complexity.[8] In the present study, the composition and structure of the thin films have been investigated using XPS and XRD analyses on the as-prepared and annealed samples. In addition, the thermal stabilities, the optical transmittance and sheet resistance of the films have been studied since such properties have a direct bearing on the potential applications of the films.

EXPERIMENTAL

Substrate Preparation. Microscope glass slides (1 × 3 inch from Corning Glass Co.) were cleaned with a solution of commercial detergent powder by scrubbing with a soft cotton cloth, followed by thorough rinsing with deionized water and finally methanol. The cleaned slides were allowed to dry in air before use.

Chemical Treatment of Substrates. A volume of 1.5 ml of 3-mercaptopropyltrimethoxysilane, $(CH_3O)_3Si(CH_2)_3SH$, (from Hulse America, Inc.) was added to 150 ml of toluene (Analytical grade from EM Scientific) followed by five drops (about 0.2 ml) of glacial acetic acid as a catalyst.[9] The mixture was stirred at room temperature for 30 min before use. Four slides were immersed in the solution, mounted vertically against the wall of the beaker. The slides were removed after 15 min, rinsed with toluene, and then baked in an oven at 110°C for an hour. The glass slides treated in this way will be referred to as SH-slides or SH-surfaces since this describes the functional group of the silane. The silanization reaction and characterization of the modified surface were discussed in previous paper.[10]

Deposition of CuS Thin Films. Four ml of 0.5 M $CuCl_2$ aqueous solution, 24 ml of 0.5 M sodium citrate aqueous solution, and 70 ml of distilled water were mixed in a 100 ml beaker. This was followed by the addition of two ml of 1 M thioacetamide (TA) while stirring the mixture with a glass rod. Four modified SH-slides were placed almost vertically in the solution bath. The clear solution, initially blue in color, turned green and turbid in about two minutes. The duration of film deposition varied from 2 h to 12 h. At the end of the deposition the coated substrates were taken out, rinsed with distilled water, and dried in air.

When placed vertically in the deposition bath, substrates were coated on both surfaces. The coating on the side facing the wall of the beaker was a uniform thin film showing interference colors in daylight reflection while the film on the opposite side occasionally incorporated powdery deposit from the bath. Thus, for all physical and chemical characterizations, the film toward the wall side was used. A precipitate of copper sulfide was also formed during the deposition. This precipitate was separated by filtration, washed well with water, dried in air and stored as a powder sample.

Air annealing of the thin films and powder samples were done in a Fisher Coal analyzer model 490 oven/furnace unit. The samples were annealed at different temperatures up to 300°C for durations of one hour each, unless otherwise specified.

Characterization. X-ray photoelectron spectroscopy (XPS) depth profile spectra of the thin film samples were recorded on a Perkin-Elmer PHI 5500 ESCA unit using Mg-K_α radiation and argon ion sputtering. The ESCA spectra were recorded after every 5 minutes of argon-ion sputtering which removed about 0.03 μm of surface material. XRD patterns were recorded for both thin film and powder samples on a Rigaku X-ray diffractometer.

For electrical contacts, a pair of silver print electrodes of 5 mm length at a separation of 5 mm were applied to the surface of the film. The measurements were made using a Keithly 236 source-measure unit with an applied bias of 0.01 V.

The optical transmittance spectra of singly coated films were recorded using a Lambda 3B UV/VIS Perkin-Elmer spectrophotometer with film side incident to the beam and with air as the reference. The samples were prepared as follows. "Sandwiches" were constructed from pairs of glass slides and sealed with parafilm along the edges. These pairs were immersed in the chemical deposition bath in the usual way and were separated after the films were deposited. The slides with the single reflective film surfaces were then used for UV/VIS measurements.

RESULTS AND DISCUSSION

Chemical Deposition Bath

To prepare CuS thin films by chemical deposition requires controlled concentrations of Cu^{2+} and S^{2-} ions in solution which are appropriate for the slow and homogeneous deposition of CuS on the surface of a substrate. The concentration of Cu^{2+} was controlled by complexation with citrate. As a triprotic acid (H_3L) with pK1 3.128; pK2 4.761; and pK3 6.396,[11] citric acid may form many complex species with Cu^{2+} in a chemical deposition solution of pH 6.5. Previous investigation of the copper(II)-citrate system in aqueous solution revealed not only complex species containing one Cu(II) but also dimers such as $Cu_2H_{-1}L$, $Cu_2H_{-1}L_2^{3-}$, $Cu_2H_{-2}L_2^{4-}$ in the pH range of 4.5 to 10.[12] Although equilibria among various species in the solution is complicated, a low concentration of Cu^{2+} ions can be achieved by the dissociation of any citratocopper(II) complex species.

A low concentration of S^{2-} ions is achieved by the hydrolysis of thioacetamide in aqueous solution as given below:

$$CH_3C(S)NH_2 + H_2O = H_2S + CH_3C(O)NH_2$$

The H_2S produced will dissociate in water yielding sulfide,

$$H_2S + H_2O = SH^- + H_3O^+ \quad K_1 = 10^{-7}$$

$$SH^- + H_2O = S^{2-} + H_3O^+ \quad K_2 = 10^{-15}.$$

Since the second dissociation constant of hydrogen sulfide is very low, only highly insoluble sulfides can be precipitated in such conditions. Both copper(II) and copper (I) sulfide are those with low solubility product constants, Ksp 1.28×10^{-36} and 2.24×10^{-48}, respectively.[13] Thus, their solid phases can be precipitated even from solutions containing very low concentrations of sulfide ions.

The growth rate of thin films is not only dependent on concentrations of Cu^{2+} and S^{2-} ion in solution, but also the number of nucleation centers available at the surface of the substrate. A number of molar ratios of the components in the deposition bath were tested and the molar ratio of $CuCl_2$/citrate/TA 1:6:1 was found to be the optimum in terms of growth rate and film thickness. When the TA concentration in the bath was doubled under these conditions, rapid precipitation occurred and resulted in the formation of thinner and less uniform films. When the $CuCl_2$ to citrate molar ratio was changed to 1:8 while the $CuCl_2$/TA molar ratio was maintained at 1:1, the film quality seemed unaffected but the growth rate was slightly slower. When the molar ratio of $CuCl_2$/citrate of 1:4 was used, a rapid precipitation of copper sulfide occurred upon addition of thioacetamide.

Thin films of copper sulfide prepared using the citrate-method are specularly reflective and uniform in appearance—features that they have in common with films deposited from ammoniacal baths.[1,3] The thicknesses of the films that have been deposited for durations of two to eight hours in the chemical bath are in the range of 0.14–0.26 μm as determined using an Alphastep-200 thickness measurement unit. Immersion in the deposition baths for more than eight hours brought little increase in thickness and this is attributed to depletion in the concentrations of the reacting species. Thicker films can be obtained by multiple depositions from fresh deposition baths. A thin film that has grown in three such successive depositions, for a total period of 20 h, can be 1 μm in thickness. For comparison, films on untreated glass substrates were found peel after one hour in solution, yielding a thickness of ≤ 0.1 μm.

The merit of the newly described chemical deposition bath lies not only in the elimination of the use of ammonia in solution but also in the fact that it can take advantage of the use of organosilane modified substrates which allow the preparation of non-peeling films having greater thicknesses. This occurs because organosilane layers are stable in near-neutral pH but hydrolyze from the glass surface in strongly alkaline solutions, such as the ammonia containing deposition baths with a pH of 12.

Chemical Bond Formation between Copper Ions and Thiol Group

A previous study demonstrated that untreated substrates and the substrates treated with 3-mercaptopropyltrimethoxysilane solution behaved differently in terms of the characteristics of chemically deposited Bi_2S_3 thin films.[14] Peeling occurred in the case of the films deposited on untreated substrates after a certain period of deposition while those deposited on the SH-surface remained intact. Evidence was presented that a chemical bond, Bi—S, was formed between Bi (III) and the SH-surface.

Copper(II) reagents are known to react with various thiol group and have been used extensively for the detection and determination of various thiol containing compounds.[15] The chemical analysis is based on the color change of a redox reaction as follows

$$4RSH + 2Cu^{2+} = RS\text{—}SR + 2RSCu + 4H^{+}$$

During the reaction the thiol is oxidized to disulfide while Cu(II) is reduced to Cu(I) and forms a copper(I) mercaptide. The color of the products varies depending on the conditions of titration and structure of the thiol compounds to be detected.

To investigate the reaction between Cu^{2+} ions and the SH-reagent, the following experiment was performed. A solution was prepared by mixing 1 ml of 0.5 M $CuCl_2$ solution, 6 ml of 0.5 M sodium citrate solution and 18 ml of distilled water to simulate the chemical deposition bath except that no thioacetamide was present. To this solution was added 0.5 ml of 3-mercaptopropylsilane drop by drop with stirring. A greenish yellow precipitate formed instantly upon the addition of the silane reagent. The precipitate was collected by filtration immediately and rinsed with methanol. In aqueous solution hydrolysis of $(CH_3O)_3Si$— to $(HO)_3Si$— occurs, and the latter condenses to form insoluble products by the loss of water. These complications make separation of products difficult.

XPS analysis was performed on the precipitate and the results are shown in Figure 1. The XPS peaks of Cu $2p_{3/2}$ and $2p_{1/2}$ were found at 935.8 and 955.6 eV, respectively, about 3 eV higher than the standard values[16] due to electrostatic charging. Two peaks of S 2p were found, which is consistent with the equation above, namely that there are two different species of sulfur in the product. The S 2p peak at 167.4 eV should be assigned to that of disulfide where sulfur has the oxidation state of (-1). This value is in agreement with the reported XPS peak at 164.10 eV for a similar compound $(CH_3CH_2CH_2CH_2S—)_2$[17] if the shift to higher energy caused by electrostatic charging is taken into account. No reported XPS data for copper mercaptide were found but it is reasonable to expect the sulfur in copper mercaptide should have a lower binding energy (166.1 eV) than disulfide since it possesses a lower oxidation state. The peak at 157.4 eV was due to silicon.[10] ESCA results show a molar ratio of Cu/S as 1:2.1 in the powder sample, which is also in accordance with the theoretical ratio suggested by the equation above.

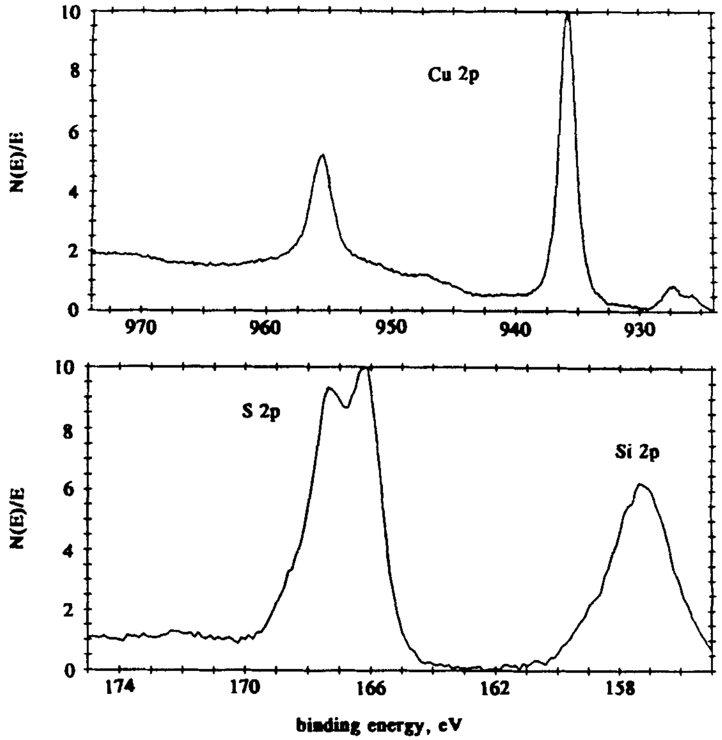

FIGURE 1 XPS peaks recorded as counts per second in relative units vs binding energies for copper and sulfur species present in the powder sample that was isolated by the reaction of 3-mercaptopropylsilane with citrato complex of copper.

The immediate formation of a precipitate and color change upon mixing the materials and the XPS results demonstrate the occurrence of a reaction between copper(II) and the SH-group of the silane reagent. Moreover, chemical binding between the CuS film and the SH-surface through the thiol group seems likely and is presumably responsible for preventing the peeling of the film from the substrate, the same phenomenon that has been observed with Bi_2S_3 films.[14]

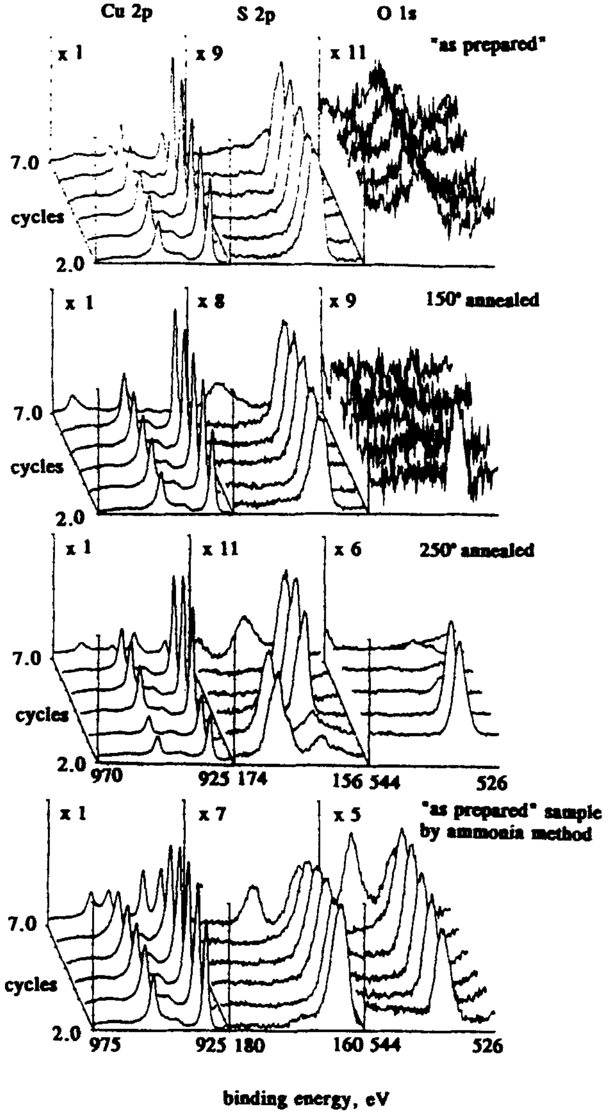

FIGURE 2 XPS depth profiles recorded at different sputtering cycles as counts per seconds vs binding energies of S, Cu and O in thin film samples of copper sulfide. From top to bottom are "as prepared" samples; samples annealed at 150°C; and samples annealed at 250°C, exhibiting strong peaks of oxygen and shift in the binding energies of sulfur species indicating thermal decomposition of the sample, "as prepared" sample by ammonia method, exhibiting a considerable amount of oxygen in the film.

Composition and Structure of Thin Films

Figure 2 shows the XPS depth profiles of these films. For "as prepared" thin film (0.15 μm, 4 h deposition), Cu $2p_{3/1}$ and S 2p peaks are observed in their standard regions[16] with the binding energy of 931.0 eV and 162.0 eV, respectively. It can be seen that intensities of the peaks through the depth of the film remain almost constant until the film is totally removed by sputtering and the glass surface of the substrate emerges (supporting cycle 7) and this suggests that the composition is uniform throughout the entire thickness of the film. Almost no oxygen was detected in the film. Calculations of relative atomic concentrations based on the ESCA results show Cu/S atomic ratio as 1:1.08 on the surface which corresponds to the molecular formula CuS.

Annealing the films in air at 150°C for 1 h does not seem to alter the composition

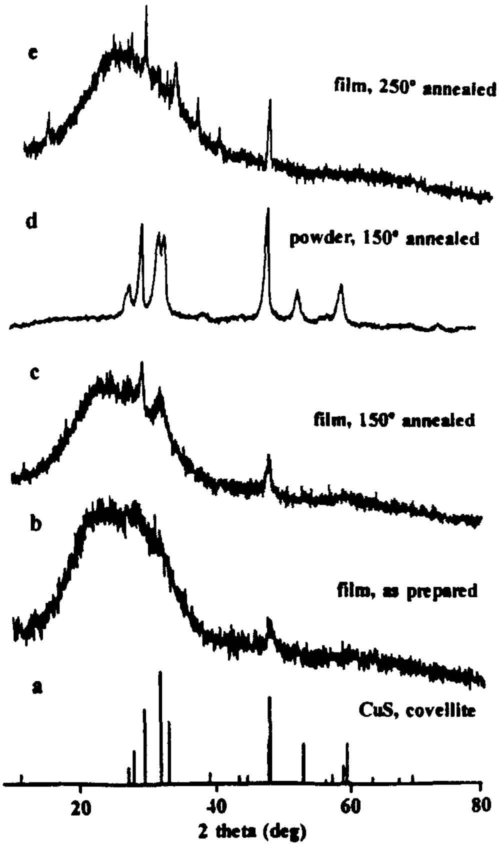

FIGURE 3 XRD patterns of thin film and powder samples of copper sulfide obtained by the citrate method from bottom to top: (a) simulated pattern for CuS, covellite (JCPDS 6-0464); (b) "as prepared" thin film, 1 μm thickness, 20 h deposition indicating a little crystallinity in the sample; (c) thin film (1 μm) sample annealed at 150°C for 12 h which indicates improvement in crystallinity; (d) powder sample annealed at 150°C for 1 h; the XRD pattern matches fully with CuS, covellite and by comparison establishes the structure of the thin films in (b) and (c) as that of covellite; (e) thin film (1 μm) sample annealed at 250°C for 12 h indicating the decomposition of the film.

of the film as seen from the XPS depth profile of the film. The amount of oxygen present is too small to determine quantitatively. It is known that copper sulfide is decomposed in air at temperatures higher than 220°C.[18] In accordance with this, significant changes were observed in the XPS of the samples annealed at 250°C as shown by the strong O 2s peak near the surface. A shift to higher binding energy of the S 2p peak indicates a higher oxidation state of sulfur. The ratio of Cu/S/O becomes 1:1.85:2.34 on the surface. An XPS depth profile of an "as prepared" sample using the ammonia method is also displayed in Figure 2. The presence of a considerable amount of oxygen can be noted in the film. Another difference between these films appears in their conductivities. This will be discussed later.

The XRD patterns of thin films and powder samples obtained by the present deposition method are given in Figure 3. A simulated pattern (Figure 3a) of CuS, covellite is also presented to compare. The "as prepared" film appears mainly amorphous (Figure 3b), but the peaks become pronounced after annealing for 12 h at 150°C (Figure 3c). This is attributable to the increase in grain size which occurs upon annealing of the thin film. The XRD peaks of the annealed powder samples (Figure 3d) are well defined and matches very well that of CuS, covellite (JCPDS 6-0464). It is seen that the intense peaks in the XRD pattern of the powder samples match the XRD peaks of the thin film deposited by the present method. When annealed in air at 250°C for an hour, the thin film gives an entirely different pattern (Figure 3e) indicating chemical conversion of the film. This observation is consistent with XPS results which show that the sulfide is oxidized during air annealing.

Optical and Electrical Properties

The transmittance spectra of "as prepared" and annealed samples are shown in Figure 4. The films are specularly reflective and are devoid of any powdery deposits. It is seen that air annealing results in a drop in the infrared transmittance of the films because of the enhancement of absorption of the electromagnetic radiation due to increased free carrier concentration.[19]

In Figure 5 the reciprocal of sheet resistance is plotted as a function of deposition time. This relationship can be interpreted as a growth curve of the films. At short times (less than 2 h) there appears to be a nucleation period followed by linear growth (from approximately 2 h to 8 h) and then only slow growth due to the depletion of the reagents. The variation of $R_\square$ with temperature of annealing is shown in Figure 6. $R_\square$ drops following one hour of annealing in air. However, as expected, the thin films becomes less conductive when heated above 200°C. This is a result of the oxidation of copper sulfide thin films as evidenced by the XPS and XRD. The Figure also includes two curve for the $R_\square$ vs temperature of annealing of a thin film prepared by the ammonia-method. They display a similar trend in thermal stability.[20] Another detail worthy of note in this figure is that with similar thicknesses (0.15 μm, 3 hour deposition by ammonia method and 0.13 μm, two hour deposition by citrate method), the "as prepared" film using the present method possesses a higher conductivity at room temperature and it also appears to be more resistant to oxidation.

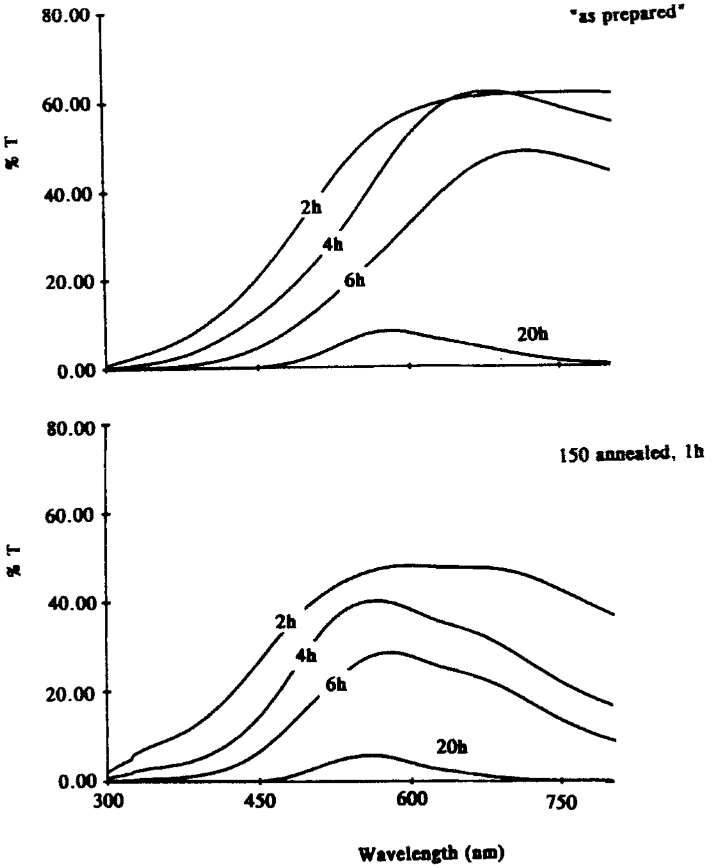

FIGURE 4 Optical transmittance, T%, spectra of "as prepared" and annealed samples of copper sulfide thin films.

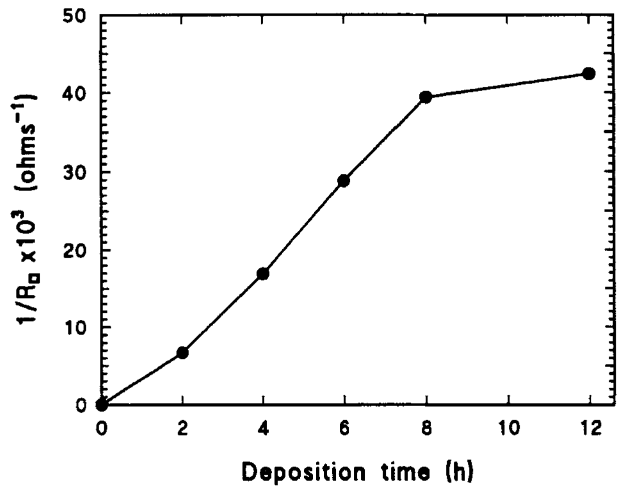

FIGURE 5 Reciprocal of sheet resistance (1/R) of thin films vs time of deposition.

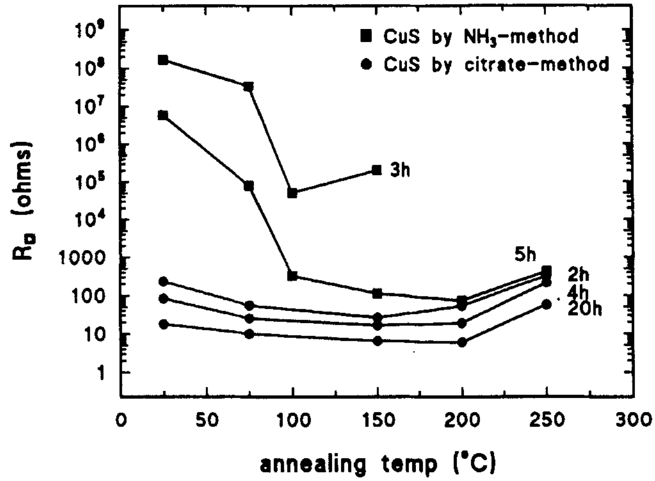

FIGURE 6 Variation of sheet resistance as a function of annealing temperature (annealing time 1 h) of copper sulfide thin films deposited for two, four and 20 hours using the citrate method, and for three and five hours using the ammonia method.

CONCLUSION

A new chemical deposition bath of CuS thin films has been developed in which the toxic and highly volatile ammonia is not involved. The films prepared in this chemical deposition bath are of good quality and can grow up to a thickness of 1 μm with no indication of peeling. A 3-mercaptopropyltrimethoxysilane solution has been employed to modify the glass substrates to overcome the peeling problems encountered in these films. XPS result on the product of the reaction between copper(II) and 3-mercaptopropyltrimethoxysilane suggests the formation of a chemical bond between copper and the thiol group, and this is considered to be responsible for the reduction of peeling of film from the substrate. The composition of the films has been found to be Cu/S, 1:1 from XPS data and the structure as CuS (covellite) from XRD data. This is the same as found for films deposited by the ammonia method. The present method is more adaptable to large scale operation and it also illustrates the need and possibilities of surface modification of the substrate to overcome certain limitations of the chemical deposition technique as applied to the production of semiconductor thin films.

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