An electroanalytical study of chemiplated thin films of copper sulphide

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Thin films of copper sulphide have been deposited from aqueous solution onto glass, platinum and cadmium sulphide by two new methods: first, chemiplated Cu_2O films have been subjected to anion exchange with S^{2-} ions and second, copper (I) thiourea complexes have been hydrolysed in sodium tetraborate solution. The copper sulphide films Cu_xS have been analysed electrochemically and x has been found to have values within the range 1.83 to 1.93. The dominance of the digenite phase ($Cu_{1.8}S$) in these films has been confirmed by optical measurements.

1. Introduction

Two characteristic and closely-related features of copper sulphide have promoted an intense interest in its chemistry and physics: (i) the range of phases Cu_xS each with an identifiable composition range within the stoichiometric limits Cu_2S and CuS, and (ii) its role as an absorber-generator in the CdS/Cu_xS thin film photovoltaic cell. A major appeal of this cell, and probably the major reason for its position as a keen contender for wider adoption as a solar cell, is its simplicity of fabrication, although this simplicity disguises deep chemical and physical complexities. In outline, the cell fabrication involves first the deposition of a layer of cadmium sulphide of thickness about $20\,\mu m$ onto a suitable conducting substrate usually by vacuum evaporation; the interface is then formed by the deposition of a film of Cu_xS (x remaining unspecified at present) of thickness 0.1 to $0.3\,\mu m$, and finally electric contact to the front face is made by the formation of a metallic grid. Much attention has been focused on the formation of the Cu_xS layer, a process of pivotal significance if an efficient cell is to be produced. Historically, numerous methods and conditions have been explored, but the favourite fabrication mode appears to be topotaxial growth by immersion of the cadmium sulphide film in an aqueous copper (I) solution, a method sometimes referred to as the Clevite Process [1]. Although the exchange may be written formally as

$$2Cu^+ + CdS \rightarrow Cu_2S + Cd^{2+} \qquad (1)$$
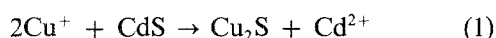
it is likely that other processes occur as well, since the stoichiometry of the copper sulphide overlayer always deviates from the expected value.

In the important compositional range $Cu_{1.8}S$ to Cu_2S, three room-temperature phases are known [chalcocite (Cu_2S–$Cu_{1.995}S$), djurleite ($Cu_{1.96}S$), and digenite ($Cu_{1.8}S$)], and since each phase has its own optical and carrier-photogeneration characteristics, it is necessary to define the stoichiometry of that phase most likely to optimize the efficiency of the CdS/Cu_xS
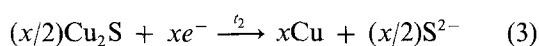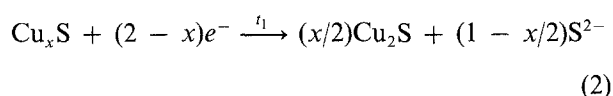
couple. Inspection of the optical and electrical properties of these phases readily demonstrates that chalcocite, a p-type defect semiconductor, is the most effective absorber and that only this phase has a photoelectron diffusion length beyond 5 nm [2]. Thus any acceptable mode of cell fabrication must aim with maximum reliability at producing the chalcocite phase although it is a frequent necessity to subject the cell to heat treatment in a reducing atmosphere in order to improve its performance. Since the effectiveness of the Clevite Process is probably dependent upon its efficiency in producing a large-area interface, relatively free from impurities, any hitherto untested methods likely to be worthy of trial will be ones involving deposition from aqueous solution. The chemical compositional features of two new methods of Cu_xS deposition are the subject of this paper: (i) the deposition from aqueous solution of Cu_2O films followed by sulphide exchange and (ii) the direct deposition of Cu_xS films from aqueous solution. Further, since it is clear that the final stoichiometry of the sulphide films prepared by the formal S^{2-}/O^{2-} exchange process must be influenced, at least in part, by the composition of the Cu_2O deposit, as a necessary preliminary study, the electroanalysis of chemiplated Cu_2O films has also been carried out.

At the inception of or during the course of this work, two related papers have been published and it is appropriate to refer to them at this stage. First, Ristov *et al.* [3] have described a method for chemiplating thin films of Cu_2O that has proved more reliable than the one we were employing at that time (a similar dipping process involving the reduction of copper (II) by sulphite); therefore we have adopted their procedure. Second, Bhattacharya and Pramanik [4] have described a method for chemiplating films of "$Cu_{1.8}S$"; this work may be criticised for its failure to establish the *presumed* identity of their product and further, their method has been found highly unreliable in our hands. Thus we describe an independent method of preparation. The composition and mass of all

chemiplated films were examined by means of an electroanalytical method developed first by Castel and Vedel [5] from the previous work of Mathieu and Rickert [6] and although discussed in the context of Cu_xS films, this method may be used also for the analysis of Cu_2O films. This method depends upon measurement of the e.m.f. of the following cell

$$\text{Reference electrode } |S^{2-}_{(aq)}|Cu_xS|Pt$$
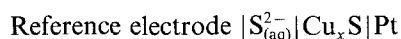
as a function of the galvanostatic reduction of Cu_xS. The thermodynamic requirement, that over the compositional range of the material the e.m.f. will be constant only if there coexist two copper sulphide phases, thus allows direct analytical determination of x. The reduction may be represented as a two-stage process:

$$Cu_xS + (2 - x)e^- \xrightarrow{t_1} (x/2)Cu_2S + (1 - x/2)S^{2-} \tag{2}$$

$$(x/2)Cu_2S + xe^- \xrightarrow{t_2} xCu + (x/2)S^{2-} \tag{3}$$

where t_1 and t_2 (sec) are respectively the times required to effect each stage of the reduction. Thus $x = 2t_2/(t_1 + t_2)$ or, if δ is defined as the deviation $(2 - x)$ from the stoichiometric Cu_2S, then $\delta = 2t_1/(t_1 + t_2)$. Finally, the total mass of the film may be readily calculated (and here expressed as the mass of copper deposited m_{Cu}):

$$m_{Cu} = (it_2M)/F \tag{4}$$

where i is the current flowing (A), M the relative atomic mass of copper (mol^{-1}), and F is Faraday's constant (C mol^{-1}).

2. Experimental details

Electrical reductions were carried out in a Pyrex cell fitted with a nitrogen bubbler and ground-glass standard sockets to which could be fitted a calomel reference electrode, a platinum anode, and the $Cu_xS/$Pt or Cu_2O/Pt cathode. Galvanostatic conditions $(\sim 1.4\,A\,m^{-2})$ were ensured by use of a stabilized d.c. power supply of 300 V in series with a 2.8 mΩ resistor. The inert electrolyte was aqueous sodium ethanoate $(0.10\,mol\,dm^{-3})$ and the cell e.m.f. was measured by means of a high impedance voltmeter and chart recorder in parallel.

In preparation for the deposition of the thin films, glass or platinum substrates were first degreased by immersion in boiling trichloroethene and then the cleaning process completed by their standing in a chromic acid bath followed by prolonged washing in distilled water. Details of the chemiplating procedures are as follows.

2.1. Cadmium sulphide

To an aqueous solution of $CdSO_4$ $(10\,cm^3;$ $1.0\,mol\,dm^{-3})$ was added $200\,cm^3$ of aqueous NH_3 $(2.0\,mol\,dm^{-3})$, an aqueous solution of thiourea $(10\,cm^3; 1.0\,mol\,dm^{-3})$, and distilled water $(100\,cm^3)$. The substrates were rotated slowly in the solution while the temperature of the latter was increased to $70°C$ over a period of about 30 min. The solution was maintained at this temperature for a further 30 min when the samples were withdrawn. An excess of loose crystalline deposit was removed from the substrate by means of a moistened soft brush leaving usually a smooth and reflective thin film of CdS. Sometimes thicker films were formed that had a somewhat duller appearance, and occasionally rather granular films were produced.

2.2. Copper sulphide

To a slurry $(10\,cm^3)$ of CuI $(0.2\,mol\,dm^{-3})$ in aqueous KCl $(1.0\,mol\,dm^{-3})$ was added copper granules $(\sim 1.0\,g)$, an aqueous solution of thiourea $(20\,cm^3;$ $1.0\,mol\,dm^{-3})$, and an aqueous solution of $Na_2B_4O_7$ $(80\,cm^3; 0.05\,mol\,dm^{-3})$. The substrate was mounted vertically in the solution which was stirred magnetically. The temperature of the solution was slowly increased; at $\sim 55°C$ deposition commenced. The temperature was further increased to $\sim 70°C$ at which it was maintained until the elapse of a total deposition time of 60 min.

2.3. Copper (I) oxide

The substrate was dipped consecutively into an aqueous solution of NaOH $(2.0\,mol\,dm^{-3})$ held at $70°C$ for ~ 1 sec and then into an aqueous solution containing a freshly-prepared mixture (volume ratio 1 : 5) of $CuSO_4$ $(0.5\,mol\,dm^{-3})$ and $Na_2S_2O_3$ $(0.5\,mol\,dm^{-3})$. This process was repeated (number of passes) until a required film thickness was reached.

The exchange reaction in aqueous solution of sulphide ions was carried out under nitrogen by dipping the deposited Cu_2O films in a buffered solution $(Na_2B_4O_7; 0.05\,mol\,dm^{-3})$ of Na_2S $(0.03\,mol\,dm^{-3})$ at $20°C$.

3. Results and discussion

3.1. Copper (I) oxide films and sulphide exchange from aqueous solution

In their investigation of Cu_2O films chemiplated from aqueous solution, Ristov et al. [3] used X-ray diffraction as a criterion for the purity of their products. Clearly, this criterion may not be very sensitive to a small quantity of a crystalline component or to a larger quantity of any amorphous component; indeed, it might be considered even unlikely that sulphide impurity would be absent considering that the method of preparation depends upon the reaction of a copper (I)-thiosulphate complex. The presence or absence of copper (I) or copper (II) sulphide or copper (II) oxide is readily demonstrable by electrochemical analysis since each material would be reduced at a different potential. Also the relation between the film thickness and the number of passes (see experimental details) may be easily established. Considering the latter point first, Fig. 1 demonstrates this relation; here the apparent average thickness of the deposit is calculated on the basis of the presumption that the film density of Cu_2O is the same as that of the bulk material. In view of the qualitative nature of the dipping technique, there is a surprising consistency in the linear dependence of film thickness on the number of passes as represented by the line of slope $(13.3 \pm 2.2)\,nm$.
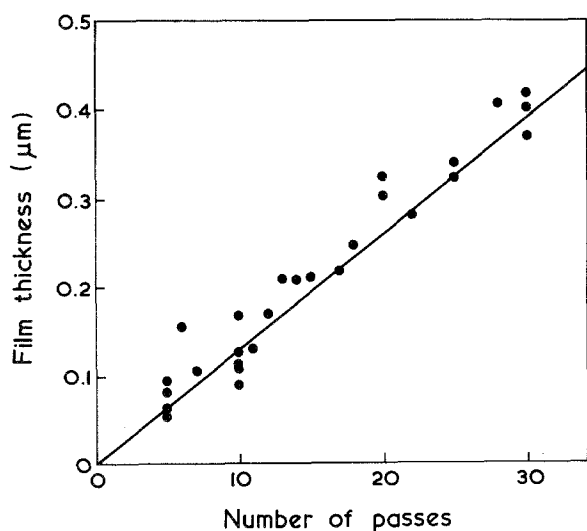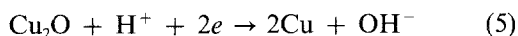
Figure 1 Thickness of Cu_2O films as a function of the number of passes.

Fig. 2 is a typical example of the galvanostatic reduction of a thin film of Cu_2O whose average thickness is $0.13\,\mu m$. The reduction follows the general pattern that would be expected, the major reduction time (in the region A → B) involving the process:

$$Cu_2O + H^+ + 2e \rightarrow 2Cu + OH^- \qquad (5)$$

A minimum potential occurs at A. This is followed by a positive drift to C, after which a slow negative drift is maintained. Mean values of the potential (against the calomel, $3.0\,mol\,dm^{-3}$ reference electrode) at A and C, $E'(Cu_2O) = (-0.830 \pm 0.021)$ V and $E(Cu_2O) = (-0.779 \pm 0.024)$ V, respectively, have been calculated from the analysis of thirty films. Variations are unrelated to film thickness or to any other observed property. Areas of the reduction curve in Fig. 2 that are of particular interest are shown in enlarged form. In the electroanalysis of all films reduction steps occurred at potentials $E(CuS) = (-0.649 \pm 0.043)$ V and $E(Cu_2S) = -1.005 \pm 0.054)$ V corresponding to the two stages of the reduction of the impurity Cu_xS in Cu_2O. The value of δ varied from 0.08 to 0.20 and the mass impurity from 4 to 8%. There appeared to be no relation between the total film thickness and either the impurity level or the value of δ. Prepared under identical conditions, we

conclude that the films of Ristov *et al.* also contained some sulphide impurity that could not be detected by X-ray diffraction. We have confirmed that the sulphide impurity is non-crystalline, and as discussed later, X-ray diffraction from Cu_xS films has also failed to yield any evidence for their crystallinity. It is noteworthy that the Cu_2O films were free from CuO, although after allowing films to stand in air, it was readily detected by a reduction inflection at -0.140 V.

Since the formal Cu(II) content in Cu_2O films is so low, it is appealing to consider the possibility of utilizing the exchange process

$$Cu_2O_{(s)} + HS^-_{(aq)} \rightarrow Cu_2S_{(s)} + OH^-_{(aq)} \qquad (6)$$
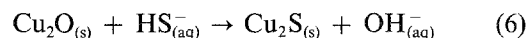
whose equilibrium favours the forward reaction, as a route to Cu_xS films with x very close to two. Initial experiments demonstrated the facility of this process, although two features of the reaction limit its application. First, when the thickest films ($> 0.3\,\mu m$) were exchanged completely, loss of adhesion to the substrate was common. Second, although the exchange reaction was carried out using purged solutions under nitrogen, some oxidation to Cu(II) occurred, and in some samples CuO was detected electrochemically. The analysis of a typical partially-exchanged film is illustrated in Fig. 3. The general form of the Cu_2O reduction curve is retained: the minimum potential $E'(Cu_2O) = -0.902$ V is followed by an increase to $E(Cu_2O) = -0.853$ V. There follows a further decrease until the reduction of Cu_2S at $E(Cu_2S) = -1.100$ V. Nineteen partially-exchanged films were studied leading to the following mean values of reduction potential: $E'(Cu_2O) = (-0.890 \pm 0.032)$ V; $E(Cu_2O) = (-0.833 \pm 0.035)$ V; $E(Cu_2S) = (-1.032 \pm 0.049)$ V. It will be noted also that the CuS reduction $E(CuS) = (-0.715 \pm 0.039)$ V has become more prominent. Values of δ were found in the range 0.08 to 0.17, and although a general increase of δ with exchange time was observed, exceptions invalidate any generalization. Although our data do not merit *detailed* kinetic analysis, since the exchange rate has only been measured at one temperature and at one (effectively constant) S^{2-} concentration, Fig. 4 demonstrates an acceptable parabolic relation between the thickness (l) of the sulphide layer and the exchange time (t), and a consequence of a
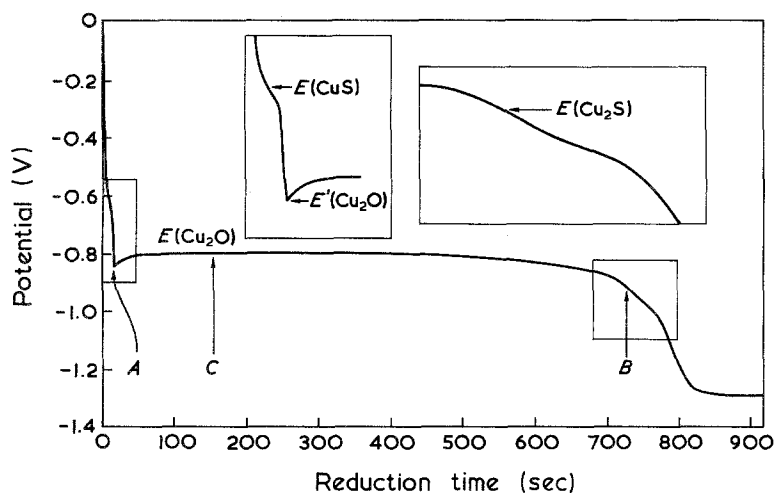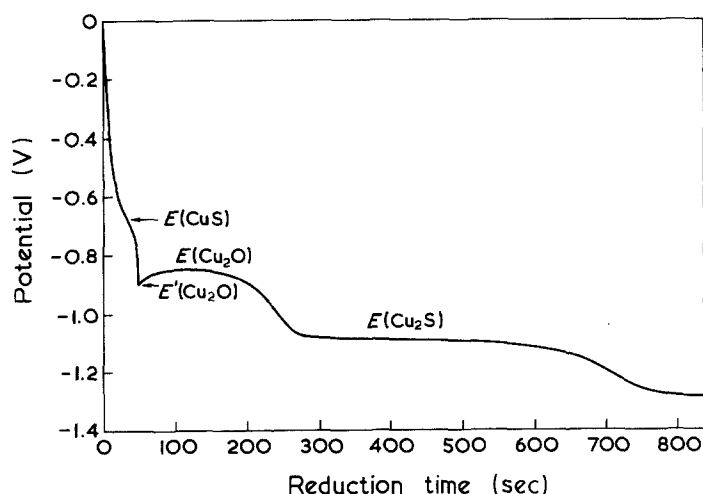

Reduction time (sec)

Figure 2 Electroanalysis of a Cu_2O film.

kinetic equation of the form $dl/dt = k'/l$, where k' ($= 224\,\mu m^2\,sec^{-1}$) is the pseudo-rate coefficient. Known to be valid in the formation of many corrosion layers [7] this kinetic form suggests that the exchange rate is controlled by the passage through the surface sulphide film. Provided that the exchange reaction was limited to films of thickness less than $\sim 0.2\,\mu m$, all of the oxide could be exchanged (see Fig. 5). The values of δ appropriate to these Cu_xS films were in the same range as those quoted for the partially-exchanged films and indicate that digenite must be a major component. Since each of the Cu_xS phases may be distinguished by its optical properties, we have measured the optical absorbance of exchanged films on glass. A prominent characteristic of the optical absorbance of digenite [8], an intensity minimum at about 750 nm, is confirmed in Fig. 6. It is evident both from optical and electrical measurements that the method of reacting S^{2-} with Cu_2O does not lead to a product whose composition approaches that of chalcocite and it cannot be described simply (even in formal terms) as S^{2-}/O^{2-} exchange. The significant copper (II) component, considerably in excess of that present in the original oxide, probably results from some disproportionation of copper (I)

$$2Cu(I) \rightarrow Cu(0) + Cu(II) \qquad (7)$$
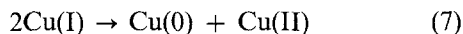
a known characteristic of Cu_2O on dissolution. We suggest, therefore, that the quasi-free Cu^+ ions in the defect solid may undergo reactions reminiscent of those associated with the solution phase.

3.2. Direct deposition of Cu_xS films

A large number of films of Cu_xS has been chemiplated onto glass and platinum substrates. The thickness of the deposit varied within the approximate range 0.06 to $0.15\,\mu m$. Heavier films were produced by means of a second, and identical, treatment leading to an approximate thickness range of 0.15 to $0.30\,\mu m$. Adhesion of the deposit was good for films up to a thickness of about $0.3\,\mu m$, but attempts to increase thickness beyond this value frequently led to adhesion loss. The electroreduction curve follows expectation, its form identical with that of Fig. 5. Thirty measurements led to the following mean reduction potentials: $E(CuS) = (-0.746 \pm 0.012)$ V and $E(Cu_2S) = (-1.076 \pm 0.019)$ V. The values of δ, which again bear no relation to film thickness, have a mean of 0.129 ± 0.025. It is again apparent that the main product of the chemiplating of Cu_xS films is digenite, although not the pure phase as claimed by Bhattacharya and Pramanik. This observation has been confirmed by optical measurements that are included in Fig. 6. The characteristic absorption minimum is again observed. X-ray diffraction studies have demonstrated the lack of crystallinity in the Cu_xS deposits,
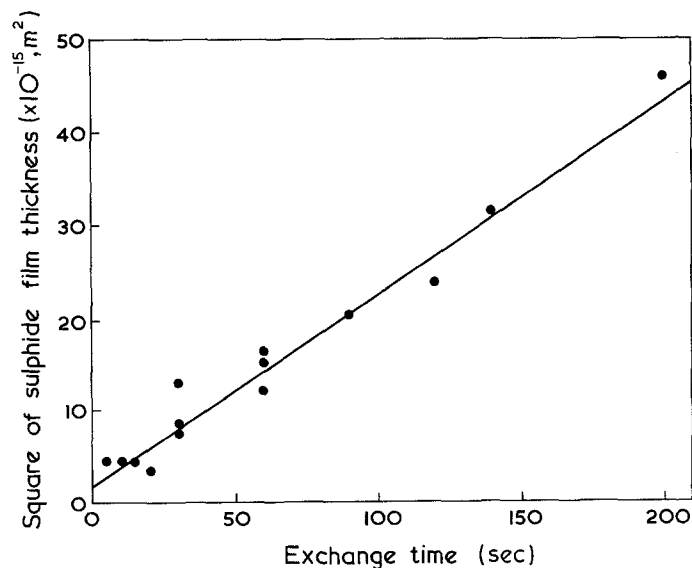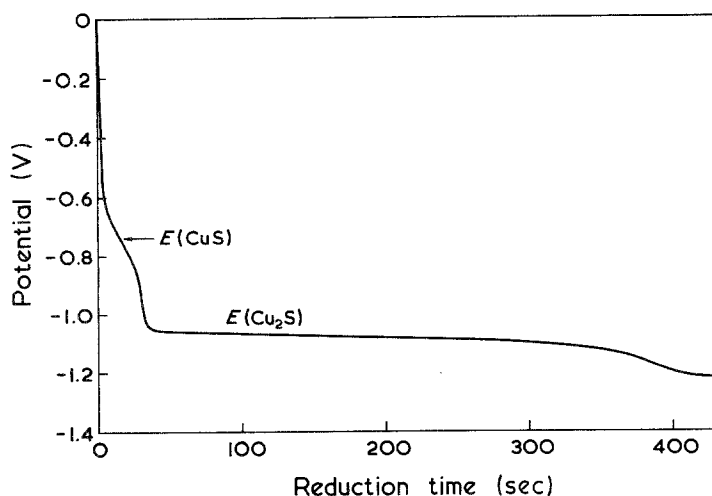

Figure 4 Kinetic analysis of S^{2-}/O^{2-} exchange in Cu_2O.

Figure 5 Electroanalysis of a Cu_xS film.

although some small modulation in intensity could be observed after long exposure times; this observation is consistent with the lack of diffraction evidence for Cu_xS in chemiplated Cu_2O films [3]. Provided that measurements were made immediately after deposition, no evidence for copper oxide formation could be found. However, if the Cu_xS films were allowed to stand in air for about 30 min, some CuO was formed, as indicated by the appearance of a reduction step at -0.143 V.

3.3. Deposition of Cu_xS films on cadmium sulphide

In the early development of CdS/Cu_xS photovoltaic cells, formation of the interface by reaction of CdS in a Cu_2O slurry was reported [9]. Although subsequently abandoned in favour of copper (I) halide exchange, reinvestigation using the plating technique seems appropriate. Immersion of the cadmium sulphide substrate in the Cu_2O plating solutions led to deposition and rapid exchange: films of apparent average thickness from 0.15 to 0.20 μm after five passes (a twofold

increase in the value expected on the basis of previous measurements on platinum). The composition of the Cu_xS overlayer again showed the dominant contribution of digenite, the value of δ (0.15 to 0.18) being consistently in the higher range compared with those observed in Cu_xS films on platinum that had been fully-exchanged from solution. Although the values of δ (0.07 to 0.10) observed in films of Cu_xS plated directly onto CdS, indicate a lower digenite contribution, nevertheless it still dominates the optical absorption spectrum. It may be significant, and relevant to the thickness data noted above, that the thickness of the deposits (0.15 to 0.30 μm) is identical with that observed in related measurements on platinum suggesting that the direct deposition of Cu_xS on CdS is predominantly a plating rather than an exchange process.

It is perhaps disappointing that the stoichiometry of the Cu_xS films produced in these procedures is not closer to that of the chalcocite phase. However, it does not necessarily preclude their usefulness as possible routes to a photovoltaic couple: if the CdS/Cu_xS interface is of high quality it is not inconceivable that the stoichiometry of the Cu_xS phase might be improved by exposing the film, for example, to a hydrogen glow discharge [10].

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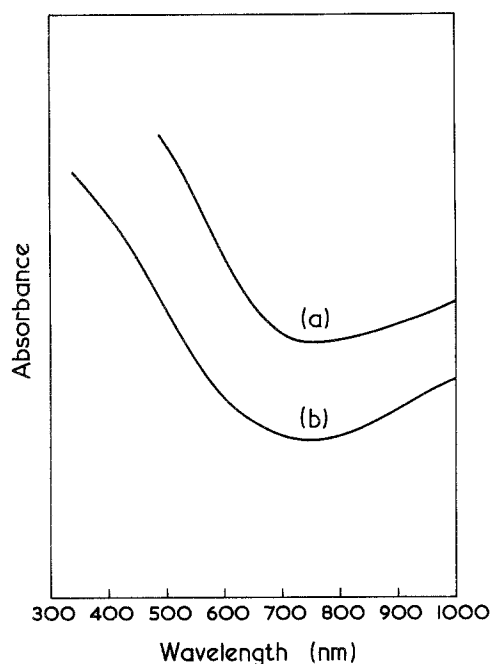
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Figure 6 Optical absorption of Cu_xS films. (a) From Cu_2O by S^{2-} exchange, (b) by direct deposition.