JOURNAL OF MATERIALS SCIENCE **21** (1986) 4169–4172

Formation of Cu_2S thin films by an electrochemical procedure

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The formation of copper sulphide thin films on copper substrates has been studied. The method of preparation is based on a chemical bath deposition process during which a cathodic potential is applied to the substrate. The composition, optical and electrical characteristics have been measured and their variation with the applied potential is analysed. The film obtained when the appropriate potential value was applied to the substrate was confirmed by transmission electron diffraction (TED) studies to be chalcocite.

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1. Introduction

The metal chalcogenides usually possess semiconductor properties and have potential use in photovoltaic devices. Their electrodeposition has received growing interest in the past few years due to its being an inexpensive and rather simple method of producing chalcogenide thin films. They can be grown on the parent metal by anodic oxidation [1, 2] but cathodic reduction from a solution containing the required components, metal and chalcogen, generally leads to better results [3, 4]. In particular Cu_xS thin films have been obtained following this technique [5, 6]. However, the major problem with this method seems to be the difficulty in producing stoichiometric material. In fact, the formation of copper sulphide thin films by electrodeposition with a compositional ratio lying between $x = 1.995$ and $x = 2$, which have the low-chalcocite structure, has not been reported in literature. Instead covellite (CuS), digenite (Cu_9S_5) or djurleite ($Cu_{31}S_{16}$) phases are normally obtained.

Because chalcocite copper sulphide thin films have the better photovoltaic properties an electrochemical procedure has been developed to obtain more stoichiometric copper sulphide films.

In a previous paper [7] a method of producing Cu_xS thin films by a chemical bath deposition process was described. These films were formed on glass substrates from a bath containing a triethanolamine complex of copper ions, ammonia and thiourea.

The reaction of thiourea and the triethanolamine complex of Cu(II) ions in basic media proceeds at a slow rate and is easily controllable, but the results obtained show that the compositional ratio, x, of the copper sulphide formed in this way is normally around $x = 1.8$, a ratio which corresponds to the digenite phase. By depositing the copper sulphide thin films on conducting substrates a cathodic potential can be applied to that substrate to bring about the reduction of Cu^{2+} ions to Cu^+ ions, and in this way to obtain phases richer in copper. This has been tested for the deposition of Cu_xS on copper substrates and the results obtained are summarized in this article.

2. Experimental procedure

The deposition of Cu_xS films has been carried out directly by dipping a plate of copper in a solution which was typically 0.1 M copper acetate, 0.37 M triethanolamine, 0.8 M NH_4OH and 0.04 M thiourea. To obtain Cu_xS film with a composition corresponding to the chalcocite phase, a cathodic potential lying between -0.425 and -0.5 V, against a saturated calomel electrode (SCE), was applied to the substrate during the process of chemical deposition. An ordinary electrochemical cell with a capacity of 50 ml was used; the substrates were copper plates of nearly 1 cm^2. The counter electrode was a platinum plate with sufficient area to completely "shadow" the 1 cm^2 cathodes. The SCE, connected to the cell by a salt bridge filled with cell solution, served as reference electrode. The temperature of the cell was kept at 40° C. Under these conditions the deposition time was about 25 min.

Substrate preparation was found to be critical in relation to uniformity and adherence of the deposits. Copper substrates were washed with 20% HNO_3 and doubly distilled water and then rinsed in acetone and throughly dried. A potentiostat PAR 363 was normally used as the deposition power supply and was also used for the conduction of voltammetric mesurements in conjunction with a Universal Programmer PAR 175 (Princeton Applied Research, New Jersey) and a HP 7000 A X-Y recorder.

The electrochemical determination of the composition of the copper sulphide films was carried out using the method proposed by Mathieu and Rickert [8] based on e.m.f. measurement of the galvanic cell $Cu/Cu^{2+}(aq)/Cu_xS/Au$.

The Cu/Cu^{2+} system was shown to be suitable as a reference by measuring its potential against SCE. Oxygen was removed from the cell solution by means

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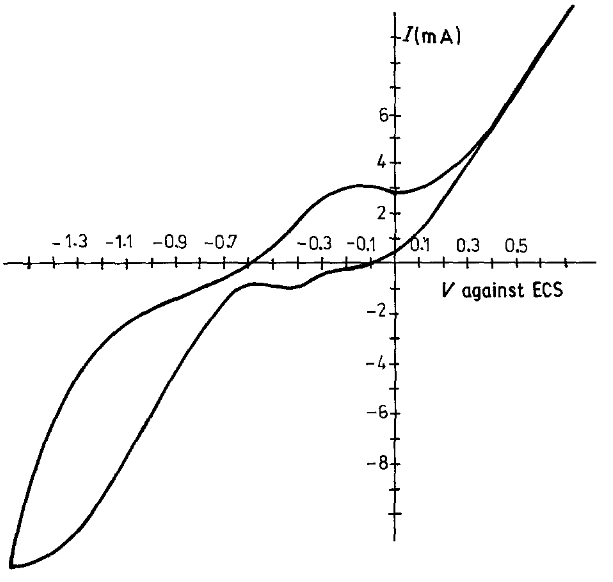

Figure 1 Linear potential scan for a solution containing 0.1 M copper acetate, 0.04 M thiourea, 0.8 M ammonia and 0.37 M triethanolamine, at a copper electrode scan rate 0.1 V sec^{-1}. Reference electrode: SCE.

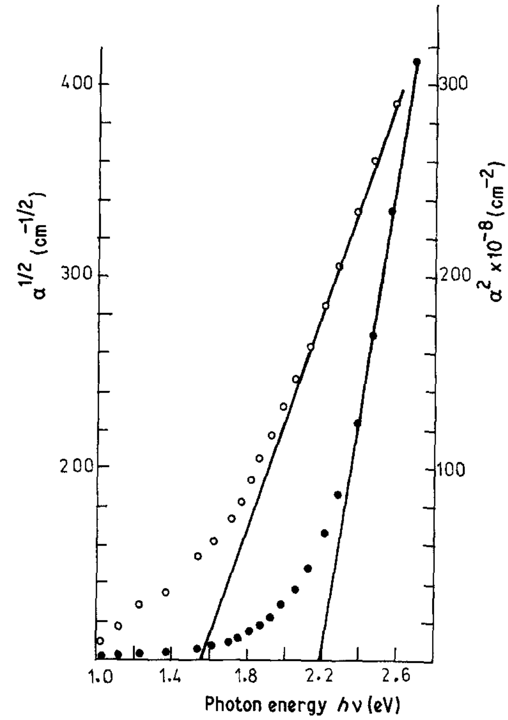

Figure 2 Determination of (●) direct and (○) indirect gaps for the sample grown at −450 mV.

of purified nitrogen. The reference electrode was separated from the working electrode by means of a diaphragm to avoid contamination of the Cu_xS by Cu^+ ions resulting from $2Cu^+ \rightleftarrows Cu + Cu^{2+}$.

The chalcocite films were analysed by transmission electron diffraction (TED) in a Siemens 102 microscope to 100 kV.

Determination of the absorption coefficient α and reflectivity r were based on the transmittance and reflectance measurements of the films carried out using a Cary 17D spectrophotometer. The method followed has been described in [9, 10]. We took into account the multiple incoherent reflection both in the film and in the substrate to determine the refractive index and the direct and indirect band-gaps.

The lack of smoothness of the metallic substrates hindered the accurate determination of film thickness by mean of a stylus Talystep, therefore all film thicknesses were determined by weighing.

Van der Pauw's method [11] was used to determine the resistivities, mobilities and carrier concentration of the samples produced. In each case, four gold points evaporated on the copper sulphide layers, providing good ohmic contact, served as electrodes. Measurements were carried out with the samples in magnetic fields of 5 k Gauss and currents ranged between 10 μA and 1 mA.

3. Results

To determine the range of potentials at which the reduction of Cu^{2+} ions to Cu^+ ions on the copper electrode occur, for a copper electrode sheet immersed in a solution containing 0.1 M copper acetate, 0.04 M thiourea, 0.8 M ammonia and 0.37 M triethanolamine, the cyclic voltammetric curves have been recorded. In this voltagram (Fig. 1) a small cathodic peak at about −450 mV is observed. This can be assigned to the reduction of Cu^{2+} ions to Cu^+ ions in the chemically deposited Cu_xS, according to the reaction:

$$Cu_{2-\delta}S + \delta\, Cu^{2+} + \delta e \rightarrow Cu_2S$$

Cathodic potentials greater than 0.6 V give rise to a further reduction to metallic copper.

Since the cathodic peak is not exactly determined but lies between −400 and −500 mV, series of samples were prepared for different potentials in this range to determine the better potential value for obtaining copper sulphide films in the chalcocite phase. Four potentials were tried, i.e. −425, −450, −475 and −500 mV, giving reproducible compositions and physical properties of the copper sulphide films grown at each potential except for the −475 mV value. The composition ratios obtained were $x = 1.76$ when the applied potential V_D was −425 mV, $x = 1.87$ for $V_D = -450$ mV, $x = 1.998$ for $V_D = -500$ mV, but differing compositional ratios ranging between $x = 1.91$ and $x = 1.96$ were obtained for $V_D = -475$ mV.

Hence we find that characteristic compositions of

TABLE I Compositional ratio (x), film thickness (t), resistivity (ϱ), mobility (μ) and carrier concentration (p) of samples formed at different cathodic potential (V_D)

V_D (mV)	x	t (nm)	ϱ (Ω cm)	μ (cm^2 V^{-1} sec^{-1})	p (cm^{-3})
−425	1.750	160	3.5×10^{-2}	2.2×10^{-2}	8.1×10^{21}
−450	1.870	160	7.3×10^{-2}	3.9×10^{-2}	2.2×10^{21}
−475	1.91–1.96	310	8.9×10^{-2}–7.2×10^{-2}	4.1×10^{-2}–7.2×10^{-2}	1.7×10^{21}–4.9×10^{20}
−500	1.998	310	1.56	8.3×10^{-2}	4.9×10^{19}

TABLE II Direct and indirect gaps and refraction index (n) of samples formed at different cathodic potentials (V_D)

V_D (mV)	Energy gap (eV)		n (600 nm)
	Direct	Indirect	
−450	2.18	1.23	2.60
−475	2.17	1.22	2.98
−500	1.89	1.20	3.36

digenite and chalcocite are obtained when the applied voltage is $V_D = -425$ mV and $V_D = -500$ mV, respectively. For intermediate values of the applied potential, compositions corresponding to a mixture of phases, digenite and djurlite, are obtained. A similar behaviour is observed in relation to the electrical properties of the samples. In Table I the resistivities, mobilities and carrier concentrations of the samples are presented.

The electrical properties of samples grown at −475 mV vary according to the different compositional ratios obtained for this potential, as would be expected.

Table II shows values of energy gap and refractive index of samples grown at the potentials already mentioned (see Figs 2–4). These results are in good agreement with those reported in the literature [12, 13].

As is well known [14] the stable room temperature phases of the Cu–S system, covellite (CuS), anilite ($Cu_{1.75}S$), digenite (Cu_9S_5). djurleite ($Cu_{31}S_{16}$) and low-chalcocite (Cu_2S) are structurally distinct. In particular, the low-chalcocite phase has a monoclinic structure with lattice constants $a = 1.5246$ nm, b = 1.1884 nm, $c = 1.3494$ nm and $\beta = 116.35°$. In this work the copper sulphide thin films formed by applying a −500 mV cathodic potential were analysed by selected area transmission electron diffraction to determine their structure.

In Fig. 5 a diffraction diagram of one of these copper sulphide samples is shown. The diagrammatic interpretation was made according to published electron diffraction data of copper sulphide [15] and all the diffraction lines were identified corresponding to low-chalcocite. The sample area inside the diffraction aperture was a 0.1 μm diameter circle, and consequently the crystallite size is smaller than 100 μm. Therefore it can be said that the copper sulphide thin films formed at a −500 mV cathodic potential are polycrystalline fine grained films of low-chalcocite.

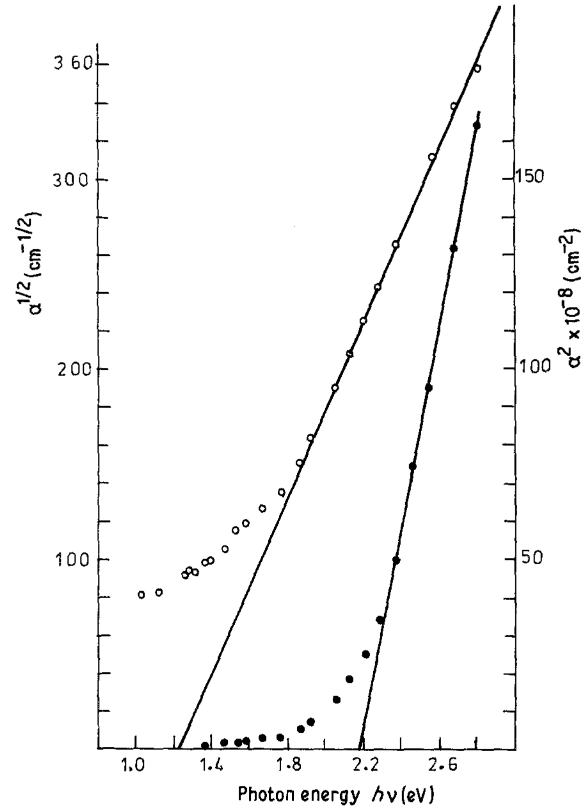

Figure 3 Determination of (●) direct and (○) indirect gaps for the sample grown at −475 mV.

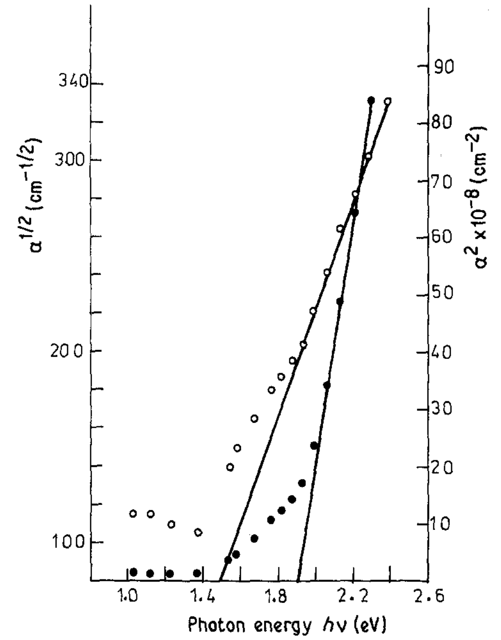

Figure 4 Determination of (●) direct and (○) indirect gaps for the sample grown at −500 mV.

4. Conclusions

From the results presented, it can be concluded that the composition of the copper sulphide films formed by the electrochemical method described can be controlled by varying the value of the applied cathodic potential. For a potential value of −500 mV, low-chalcocite polycrystalline fine grained films are always

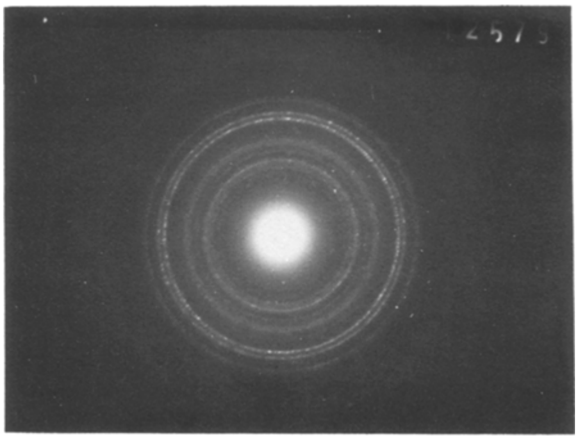

Figure 5 Electron diffraction pattern of a Cu_2S sample grown at −500 mV.

obtained. The optical and electrical properties of these films seem to be appropriate for solar cell applications.

Acknowledgement

This study was supported by the Spanish Comisión Asesora de Investigación Científica y Técnica, Madrid. Proyect 104481.

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Received 12 August 1985
and accepted 11 February 1986