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Anodic formation of binary and ternary compound semiconductor films for photovoltaic cells*

M. I. SCHIMMEL, O. L. BOTTECHIA[‡], H. WENDT

Institute of Chemical Technology, Technical University of Darmstadt, Petersenstrasse 20, D-64287 Darmstadt, Germany

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By anodic oxidation of copper sheets in sulfide anion-containing electrolytes copper chalcogenide semiconductor films suitable for photovoltaic applications can be attained. Anodically chalcopyrite (Cu_2S) has been formed as pure, mechanically stable, homogeneous and adhesive polycrystalline films, consisting of well-developed large crystallites. Cu_2S coated copper sheets were produced with an area of 3 cm × 3 cm. P–n-junctions formed by evaporation of CdS onto the anodically formed Cu_2S films show an energy efficiency of 3.3%. The extension of this process to ternary systems, like copper/indium/sulfur, is likely to be possible. A mixture of Cu_2S and $CuInS_2$ could be formed by codepositing In_2S_3 together with Cu_2S. Cu_2Se-films with a thickness of up to 1 μm were formed by chemical bath deposition.

Keywords: *chalcopyrite*, *copper sheets*, *semiconductor films*, *photovoltaic cells*, *anode films*, *electrocrystallization*

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1. Introduction

Numerous investigations have been published in the last 20 years dealing with galvanic processes to prepare photovoltaically active semiconductor layers. Galvanic processes for semiconductor film formation are said to be cheaper than vapour deposition processes of any kind (PVD, CVD etc.). Nevertheless almost none of these electrochemical investigations has led to commercial implementation, because the photovoltaic quality of the layers is poor. Almost all authors concentrated on the formation of compact semiconductor films consisting of finely grained crystallites, sometimes even mixtures of different phases and almost always exhibiting a microscopic cauliflower-like appearance. It was not possible to construct p-n-junctions and photovoltaic devices from such layers.

The ternary chalcopyrites $CuInS_2$ and $CuInSe_2$ are believed to be the most promising compound semiconductors for photovoltaic applications. Both compounds may, depending on doping and stoichiometry, be p or n-semiconducting. The Cu to In ratio controls the type of majority carriers and the change from p to n-conductivity depends on a few per cent deviation of the In-content from the stoichiometry ($I–III–VI_2$) [1]. The bandgap of $CuInSe_2$ is 1.05 eV and the high absorption coefficient ($5 \times 10^{-5}\,cm^{-1}$) ensures complete absorption in coatings of only a few micrometres thickness. $CuInS_2$, with a bandgap of 1.52 eV and comparable absorption coefficient fits better to the spectral intensity distribution of sunlight and avoids selenium [1].

This investigation aims to obtain detailed kinetic information on the anodic formation of Cu_2S films, and to form photovoltaic films of the more complicated and more relevant ternary compound semiconductors $CuInS_2$ and $CuInSe_2$. In general electroformation appears to be a promising alternative to evaporation techniques since it is basically a low cost process which can be readily scaled up.

2. Galvanic formation of compound semiconductors

2.1. *Different galvanic formation processes*

The galvanic techniques for electroformation of compound semiconductors can be divided into three groups:

(i) Cathodic deposition of the constituents in almost stoichiometric ratio from electrolyte solutions of respective precursor compounds [2]. These films have to be annealed because the constituents do not form, for instance, the phase $CuInSe_2$, but only an ill defined mixture of different phases:

$$x\,Cu^{2+} + y\,In^{3+} + z\,SeO_2 + 4\,zH^+ + (2x + 3y + 4z)e^- \longrightarrow Cu_xIn_ySe_z + 2z\,H_2O \quad (1)$$

(ii) In contrast, almost stoichiometric semiconducting Cu_2S can be formed by anodic oxidation of

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[‡] Present address: Universidade Federal de Uberlândia, CP 593, 38400-902 Uberlândia, MG, Brazil.

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copper metal in an alkaline solution containing sulfide anions:

$$2\,\mathrm{Cu} + \mathrm{S}^{2-} \longrightarrow \mathrm{Cu_2S} + 2\mathrm{e}^- \qquad (2)$$

(iii) The so-called electroless chemical bath deposition (CBD) of dicopper selenide obtained by reaction of selenosulfate anion with copper metal is a galvanic process because it can be shown to operate on coupled anodic copper oxidation and selenosulfate reduction.

$$2\,\mathrm{Cu} + \mathrm{SeSO_3^{2-}} \longrightarrow \mathrm{Cu_2Se} + \mathrm{SO_3^{2-}} \qquad (3)$$

It must be stressed, that galvanic formation of semiconducting layers is only possible, if the layer possesses a sufficiently high electronic conductivity of at least $10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. Poor conductors block and passivate the electrode surface and can only be grown to a very limited thickness. Therefore, galvanic formation processes are restricted to degenerated semiconductors such as doped silicon, $\mathrm{Cu_2S}$, CdSe, CdTe, $\mathrm{CuInS_2}$ or $\mathrm{CuInSe_2}$ which have a good, or at least moderate, conductivity.

2.2. *Anodic formation of chalcosite, Cu_2S*

For the formation of $\mathrm{Cu_2S}$ on copper metal substrates by anodic oxidation of copper in aqueous sulfide solutions a high mobility of at least one kind of the film forming ions in the semiconducting phase is indispensible for film growth. Indeed, the diffusivity of Cu^+-ions in the chalcosite phase is sufficiently high ($D = 10^{-10}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ [3]) and furthermore the electronic conductivity of this degenerated semiconductor is almost as high as that of a metal ($\kappa = 10^2\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at 25 °C) [4].

In the anodic formation of cuprous sulfide, $\mathrm{Cu_2S}$, three separate steps can be distinguished:

(i) At the interface copper/cuprous sulfide the copper oxidation takes place.

$$\mathrm{Cu} \rightleftharpoons (\mathrm{Cu}^+)_{\mathrm{Cu_2S}} + \mathrm{e}^-_{\mathrm{Cu}} \qquad (4)$$

(ii) Due to their established activity gradient and their high diffusivity, Cu^+-ions cross the $\mathrm{Cu_2S}$-film by diffusion.

$$(\mathrm{Cu}^+)_{\mathrm{Cu/Cu_2S}} \rightleftharpoons (\mathrm{Cu}^+)_{\mathrm{Cu_2S/electrolyte}} \qquad (5)$$

(iii) At the cuprous/electrolyte interface the Cu^+-ions and the sulfide ions from the bulk of the aqueous electrolyte form $\mathrm{Cu_2S}$, which is precipitated, and the film grows into the solution.

$$2(\mathrm{Cu}^+)_{\mathrm{Cu_2S}} + (\mathrm{S}^{2-})_{\mathrm{aq}} \rightleftharpoons \mathrm{Cu_2S} \qquad (6)$$

2.3. *Chemical bath deposition (CBD) of Cu_2Se*

Copper selenides form an important group of II–VI-compound semiconductors. They are not only intermediates for copper–indium diselenide synthesis but can also be used on their own in photovoltaic cells and Schottky diodes. [5]

An attractive way to prepare one of these compounds, $\mathrm{Cu_2Se}$, is CBD. If a copper substrate is dipped into a solution containing a selenium donor from which selenide ion, Se^{2-}, can be released reductively, copper selenide is deposited on the copper surface and this layer grows steadily. Taking selenosulfate as donor, the net reaction is

$$2\,\mathrm{Cu} + \mathrm{SeSO_3^{2-}} \longrightarrow \mathrm{Cu_2Se} + \mathrm{SO_3^{2-}} \qquad (3)$$

The process is likely to consist of anodic copper oxidation coupled to cathodic generation of selenide anions. This method can also be applied for semiconductors with a relatively low electric conductivity, since no external current is applied and the electrons only have to pass from the substrate to the electrolyte. However, only semiconductors allowing high mobility of cuprous ions can be formed as cuprous ions must cross the semiconducting layer in order to deposit $\mathrm{Cu_2Se}$. The low solubility product ($10^{-60.8}\,\mathrm{M}^3$ for $\mathrm{Cu_2Se}$ [6]) favours this redox process.

Similarly to the scheme of the $\mathrm{Cu_2S}$ formation, copper selenide grows on copper. The variance is that cuprous ions and electrons move in the same direction and the electrons cleave selenosulfate reductively at the $\mathrm{Cu_2Se}$/electrolyte interface according to the equation

$$\mathrm{SeSO_3^{2-}} + 2\mathrm{e}^- \longrightarrow \mathrm{Se}^{2-} + \mathrm{SO_3^{2-}} \qquad (7)$$

2.4. *Desired properties of semiconductor films*

To be suitable for photovoltaic uses the semiconductors have to fulfill several requirements. By appropriate choice of the process parameters: current density, temperature, chalcogenide anion or chalcogen donor concentrations and by preconditioning the metal substrate, it should be possible to achieve: (i) homogeneous, stable and adhesive polycrystalline films, (ii) highest possible lateral extension of columnar semiconductor crystals, (iii) highest possible purity of the semiconductor and (iv) optimal conditions to add another layer on top of the first semiconductor to establish the p–n-junction.

3. Experimental details

3.1. *Equipment*

For anodic film formation cylindrical 100 ml PTFE-vessels are used. The lids, covering these vessels have bores to fix the electrodes, a thermometer, an argon sparge-tube and the Luggin capillary. The vessels are inserted into an oil thermostat and stirred magnetically. The electrochemical equipment consists of potentiostats (Wenking HP 72, LB 75), galvanostats and scan-generators (Wenking VSG 72). All electrode potentials were measured against KCl-saturated Ag/AgCl.

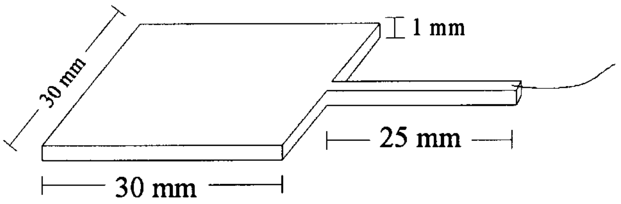

Fig. 1. Form and dimensions of copper substrates.

3.2. *Preparation of the copper electrodes*

For this initial investigation, which would be expected later to be supplemented by further preparations with the aim of obtaining layers of highest quality, the copper substrates are made of technical grade copper sheets (99%). (Fig. 1). To reduce the surface density of crystal nuclei these copper electrodes need to be electropolished before use as a substrate. For 10 min the substrates were electropolished with an anodic current density of 50 mA cm^{-2} in a 85% H_3PO_4/ethanol electrolyte [7].

To form semiconductor films of highest quality, copper is electrodeposited from $CuSO_4$-solution of the highest possible purity. The bath conditions are 0.1 M $CuSO_4$ and 0.5 M H_2SO_4. Copper is deposited with a current density of 2.5 mA cm^{-2}.

3.3. *Anodic film formation – Cu_2S*

The copper substrate is immersed into the sulfide containing basic electrolyte of pH 14 under cathodic load to reduce cathodically the initially formed copper oxide and copper sulfide film respectively, which both stem from surface oxides formed during electropolishing and handling on air. As shown in Fig. 2 during cathodic load the potential of the copper electrode changes from initially −1030 mV to more negative values. At −1100 mV vs Ag/AgCl hydrogen evolution begins and the electrode is cleaned of any adherent oxide or sulfide and the electrode potential becomes steady at approximately −1150 mV. The anodic formation of Cu_2S can then be initiated by inverting the current. Current inversion from cathodic to anodic load can be performed in two different ways. The current can be switched or it can be swept. In this latter case the potential reversal is executed galvanostatically by sweeping the current density at a rate from 1 to 10 μA s^{-1} cm^{-2} from cathodic to anodic. The electrolyte contains 1 M KOH, 5×10^{-2} M Na_2S and is kept at 90 °C.

3.4. *Film formation by CBD – Cu_2Se*

For formation of Cu_2Se coatings on copper by CBD the electropolished copper substrates are dipped into the thermostated, stirred and degassed electrolyte. The electrolyte contains from 5×10^{-3} to 2×10^{-2} M Na_2SeSO_3 and 0.1 M Na_2SO_3. The process temperature varies from 25 to 90 °C.

3.5. *Characterization of the films*

The morphology of the films was investigated by scanning electron microscopy (Jeol, JSM T 330A) with an integrated energy dispersed X-ray system (Link analytical QX 2000). X-ray powder diffraction analyses of films removed by scratching the semiconductor material from the substrate were performed by a Stoe Mikro 1 011 diffractometer. For the photovoltaic characterization of p–n-junctions a solar constant 250 sunlight simulator (AM1.5) was used together with a computer supported system.

3.6. *Chemicals*

Except the technical grade copper substrates all chemicals were ACS reagent grade. The electrolytes were saturated with argon to remove oxygen.

4. Results

4.1. *Anodic growth of polycrystalline Cu_2S layers*

4.1.1. Optimal conditions for film formation. Largest crystals are obtained by galvanostatic oxidation of electropolished and cathodically conditioned copper sheets in an alkaline electrolyte containing sulfide-ions at a bath temperature of 90 °C, a concentration of S^{2-}-ions of 5×10^{-2} M, a pH of 14 and a current density of only 300 μA cm^{-2}. At this current density a dense chalcocite layer of 5 μm thickness grows within 3 h. The applied current density has to be maintained so low, because the surface density of crystal nuclei increases strongly with current density and the crystal size is therefore drastically reduced at higher current densities. Lower temperatures and higher current densities both result in smaller crystals.

It is possible to form Cu_2S-films of 10 μm film-thickness; these are still mechanically stable and are composed of well-developed large crystallites with a mean size of more than 20 μm with typical twinning texture. The comparison of the X-ray diffractogram of the powdered Cu_2S coating, with data for chalcosite from reference data [8] is shown in Fig. 3 and demonstrates that the deposit is at least 99% pure chalcosite.

4.1.2. Film morphology and crystal nucleation. Anodic film formation without cathodic preconditioning of the copper surface produces a finely grained structure indicative of a high nucleation density as seen in Fig. 4.

The appearance of the film obtained by oxidizing the copper surface with a steady anodic current of 300 μA cm^{-2} after cathodic conditioning and reversing the current by switching is shown in Fig. 5. At 300 μA cm^{-2} the crystallites attain a size of more than 20 μm. A cross section of these films shows their columnar structure. The grain size of the Cu_2S films can still be further improved by using current sweep instead of switching to invert the polarity from

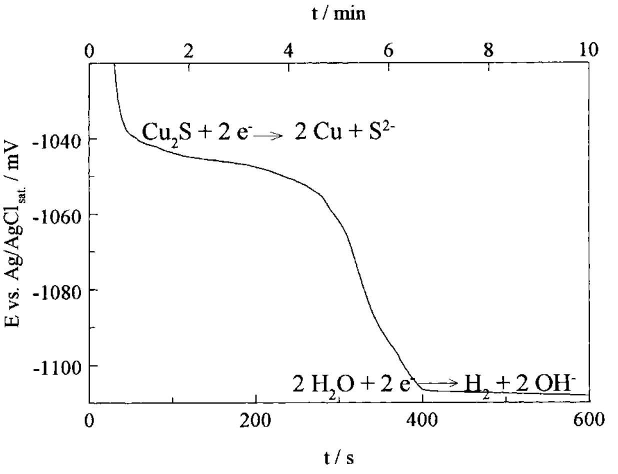

Fig. 2. Potential-time behaviour of a copper electrode in a sulfide electrolyte under cathodic load (300 μA cm^{-2}) prior to oxidation.

cathodic to anodic. Sweeping was performed at a rate of 10 μA s^{-1}cm^{-2}. A statistical evaluation shows that nuclei density is reduced by more than one order of magnitude to approximately 10^6 cm^{-2}.

4.1.3. Photovoltaic cells from anodically formed Cu_2S layers. Photovoltaic cells obtained by vapour deposition of CdS on the anodically formed chalcosite layers possess an open circuit voltage of $V_{oc} = 400$ mV and a short-circuit current of $I_{sc} = 10$ mA cm^{-2} under white-light insolation at 70 mW cm^{-2}. The current–voltage curve of this cell is depicted in Fig. 6 and results in an energy efficiency of 3.3%. The filling factor amounts to 59%.

4.2. *Chemical bath deposition (CBD) of thin Cu_2Se layers*

4.2.1. Conditions. For Cu_2Se film formation by CBD the electrolyte has to contain an excess of sodium sulfite, because selenosulfate decomposes and selenium precipitates. The presence of excess sulfite produces a second advantage, as it eliminates dissolved oxygen: $2\,SO_3^{2-} + O_2 \rightarrow 2\,SO_4^{2-}$, and oxidation of copper by oxygen is safely avoided.

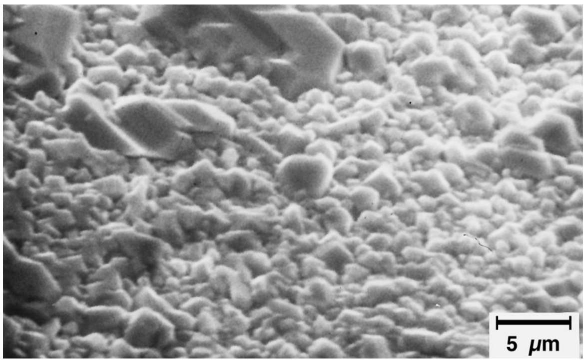

Fig. 4. Morphology of a Cu_2S coating after anodic oxidation for 2.5 h. Cu_2S was formed on the initially present sulfide film.

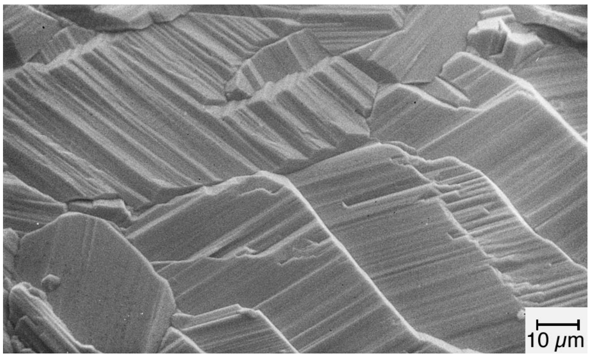

Fig. 5. Morphology of a Cu_2S coating formed by anodic oxidation of a copper sheet for 2.5 h after cathodic reduction of the initially present copper sulfide and oxide layers.

4.2.2. Kinetics of Cu_2Se CBD. The growth of Cu_2Se films was investigated gravimetrically in sodium selenosulfate solutions of varying selenosulfate concentration with excess 0.1 M Na_2SO_3. Figure 7 shows the expected $t^{0.5}$ growth rate at a deposition temperature of 25 °C.

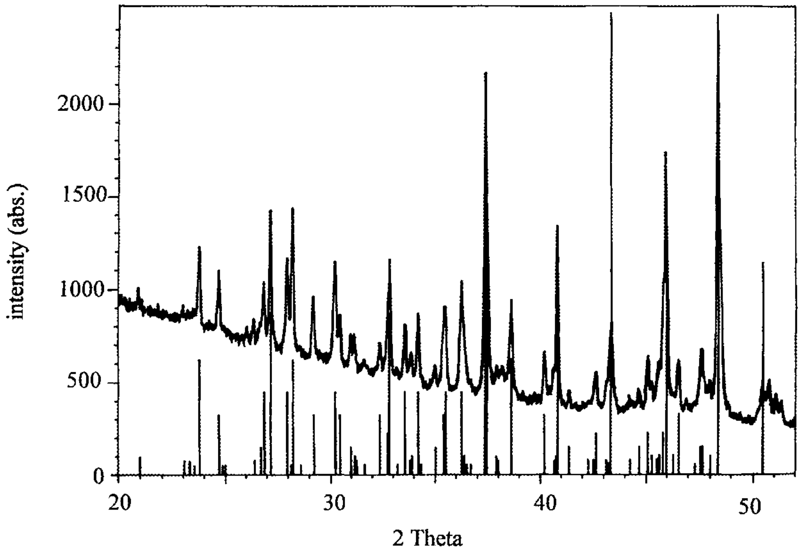

Fig. 3. X-ray powder diffractogram of a Cu_2S sample, mechanically removed from the substrate. JCPDS-Data [8] are included.

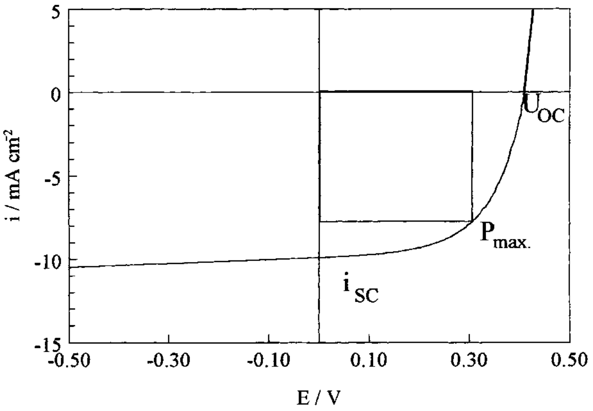

Fig. 6. Current–voltage curve of an illuminated Cu_2S/CdS p–n-junction.

The reaction order with respect to selenosulfate is 1. At 25 °C the rate law is

$$d\delta/dt = k c_{SO_3Se^{2-}}(1/\delta) \qquad (8)$$

with k equal to

$$k_{(25\,°C)} = (2 \pm 0.2)10^{-10}\,\mathrm{cm^2\,s^{-1}\,M^{-1}}$$

4.2.3. Morphology. Micrographs show the growth of almost completely closed layers with some porosity which adhere to the substrate, if their thickness, δ, does not exceed 0.5 μm. Layers thicker than 0.8 μm begin to detach from the substrate under mechanical stress and are fissured (Fig. 8). X-ray powder diffraction reveals the formation of $Cu_{2-x}Se$ (berzelianite), Cu_2Se (belliodite) and $CuSe_2$ (krutaite).

5. Ternary compound semiconductors

The procedure to form Cu_2S was tentatively extended to the formation of ternary systems like copper indium disulfide ($CuInS_2$) or copper gallium disulfide ($CuGaS_2$) by trying to codeposit indium or gallium sulfide together with the anodically formed cuprous sulfide.

It was impossible to codeposit copper, gallium and sulfur, but it was possible to form films containing indium up to a stoichiometric ratio of Cu/In = 4/1 in the presence of dissolved In^{3+} cations, if strongly alkaline solutions were used to enhance the solubility of In^{3+} up to a value of 1.5×10^{-2} M by complexing this cation with hydroxyl ions. In(III)-ions were added to the solution by repeated addition of a $In_2(SO_4)_3$-solution to the sulfide containing electrolyte (pH 14).

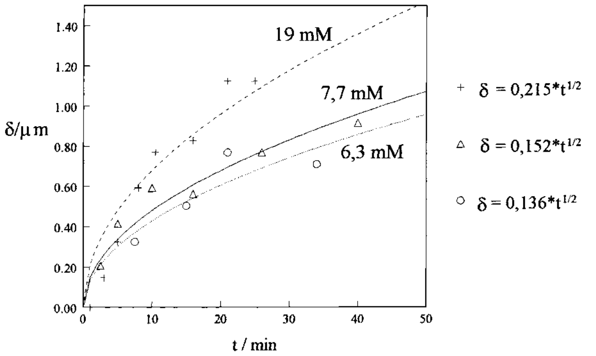

Fig. 7. Thickness of Cu_2Se-films against CBD-time. The films are formed on a copper substrate in 0.1 M Na_2SO_3 solution at different concentrations of Na_2SeSO_3.

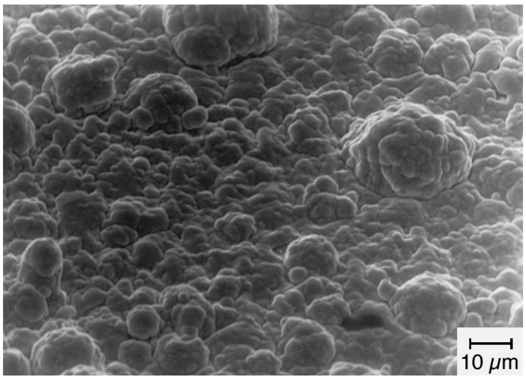

Fig. 8. Micrograph of a Cu_2Se-film formed by chemical bath deposition. $c_{SeSO_3^{2-}} = 10^{-2}$ M, $c_{SO_3^{2-}} = 0.1$ M.

The potential time behaviour of a copper electrode under anodic load, on addition of In^{3+}-ions, is shown in Fig. 9. The potential changes from −1020 to −982 mV upon addition of In^{3+} indicating the formation of a phase different from chalcosite. A powder diffraction analysis of these films shows the formation of a mixture of chalcosite and $CuInS_2$-phase. The morphology of these films is drastically different from that of Cu_2S layers as shown in Fig. 10. Thin packages of leaflets of $CuInS_2$ are growing perpendicularly to the substrate surface. Reduction of the current density from 300 to 10 μA cm^{-2} leads to some improvement in crystallinity: the lamella become a little thicker (0.2 μm instead of 0.1 μm), but their orientation does not change. The Cu/In-ratio remains too high at 4/1 and the film is a mixture of $CuInS_2$ and Cu_2S. The chalcosite can be removed by dissolution in sodium cyanide and almost pure $CuInS_2$ remains in a relative porous layer which, unfortunately, does not form a closed coating. Further investigations will show whether by parameter

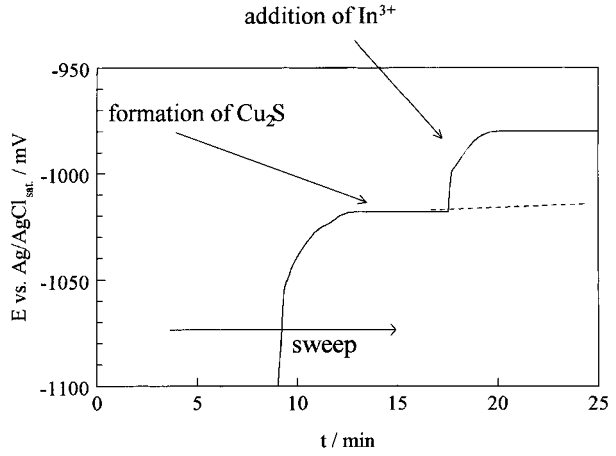

Fig. 9. Potential time behaviour of a copper electrode in a sulfide electrolyte, after current reversal. An In(III) containing electrolyte is added after 17 min.

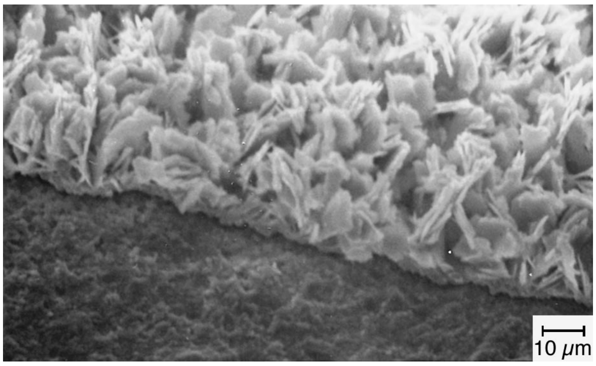

Fig. 10. SEM micrograph of an anodic codeposit of Cu_2S and In_2S_3.

variation the morphology and stoichiometry can be changed significantly towards generating coarse base oriented crystals of pure $CuInS_2$ or whether annealing of these coatings leads to recrystallization and the formation of closed $CuInS_2$-layers.

6. Conclusions

This research shows that it is possible to form compound semiconductor films with a morphology suitable for photovoltaic applications. Cu_2S-films can be formed by galvanic oxidation of a electropolished and cathodically conditioned copper sheet at low current densities of several $100\,\mu A\,cm^{-2}$. P–n-junctions formed with these galvanic films exhibit cell efficiencies of 3.3% , although only technical grade copper has been used as substrate in this case. It is possible to extend the procedure of the anodic Cu_2S-film formation to more complicated, ternary systems. Mixtures of Cu_2S with $CuInS_2$ up to a ratio $Cu/In = 4$ have, so far, been obtained in such layers by codepositing In_2S_3 together with Cu_2S. Cu_2Se-films formed by CBD cannot be used for photovoltaic devices. They are a mixture of different copper/selenium phases ranging in composition from Cu_2Se to $CuSe_2$.

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