

Preparation of polycrystalline thin films of CuInSe₂ by electrodeposition

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Received 28 August 1988; revised 5 November 1988

CuInSe₂ thin films with the chalcopyrite structure were electrodeposited on titanium substrates from an acidic sulphate solution containing citrate ions as a complexing agent. These layers were characterized by X-ray diffraction, SEM, X-ray energy dispersive analysis and spectrophotometry of reflected light. The best deposits were obtained at $E = -0.97$ V vs SSE, in a solution adjusted to pH 3.3. The deposition of the binary alloys was also investigated. It was shown that the formation of smooth layers of crystalline definite compounds is correlated with a slow surface process which induces a plateau on the polarization curves.

1. Introduction

Ternary chalcogenides CuInX₂ (X = S, Se, Te) appear to be promising semiconducting materials for use in photoelectrochemical cells. In particular, the CuInSe₂ interface with an aqueous polyiodide electrolyte is one of the most stable photoelectrochemical systems. It has been proved that a CuInSe₂ electrode in contact with an I/I⁻ redox solution is protected against photocorrosion by a solid heterojunction which is due to the formation of CuISe₃.Se⁰ polycrystalline layer [1-4].

In this case, it was demonstrated that this photoelectrochemical cell operates with a 12% solar conversion efficiency over very long times (over 800 h of continuous operation). Various methods to obtain monocrystalline or polycrystalline CuInSe₂ are employed. For several applications it is not necessary to use large and perfect single crystals which are expensive and difficult to prepare. In particular, for the conversion of solar energy by photovoltaic or photoelectrochemical cells using as absorber a direct band gap material, thin polycrystalline layers are sufficient for low-cost applications. Electrodeposition appears to be one of the cheapest methods: it does not require very pure starting materials and can be easily monitored by convenient electrical parameters.

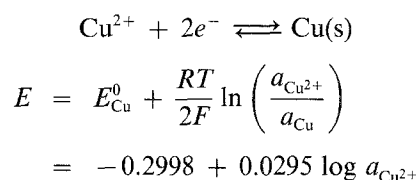
The first attempt to electrodeposit this ternary chalcopyrite compound was reported by Bhattacharya [5, 6]. He plated from an SeO₂-based bath containing InCl₃ and CuCl, complexed by triethanolamine and ammonia. However, the deposits obtained were generally rather amorphous and required heat treatment to improve their crystallinity. Attempts by Noufi *et al.* [7] and Hodes [8] to plate Cu-In-Se from aqueous electrolytes containing SeO₂, InCl₃ and CuCl, without any complexing agent, resulted in Cu-Se deposits containing no indium. Another approach consists of preparing a Cu-In film by alloy codeposition or

by alternating deposition of Cu and In layers, followed by a chemical treatment of selenization [8, 9]. Recently, Ueno *et al.* [10] have reported results of electrodeposition of CuInSe₂ films from a sulphate bath containing no complexing agent. The thin films thus obtained were microdendritic and required heat treatment to enhance their solar conversion efficiency.

Several studies concerning CuInSe₂ electrodeposition have been made in the galvanostatic mode. However a weak variation of current may induce large modifications of deposit composition, so it seems more logical to work under potentiostatic conditions. Moreover, the experimental conditions mentioned in the literature are rarely supported by a preliminary study of the electrochemical kinetics of the codeposition.

The aim of this work is to define the electrochemical conditions leading to the formation of smooth crystalline deposits of CuInSe₂, and also of the related binary compounds Cu₉In₄ and Cu₂Se, by analysing polarization curves obtained under potentiostatic conditions. Various techniques, such as X-ray diffraction, SEM, energy dispersive X-ray analysis and spectrophotometry of reflected light, are used to characterize the layers.

The direct electrodeposition of the ternary compound is rather difficult because the conditions favourable for the deposition of one of the metals differ from these necessary for the other constituents. One difficulty comes from the disparate values of equilibrium potentials. The electrochemical deposition reactions of the three metals mentioned above are:



$$\begin{aligned} \text{In}^{3+} + 3e^- &\rightleftharpoons \text{In(s)} \\ E &= E_{\text{In}}^0 + \frac{RT}{3F} \ln \left(\frac{a_{\text{In}^{3+}}}{a_{\text{In}}} \right) \\ &= -0.9800 + 0.0197 \log a_{\text{In}^{3+}} \\ \text{HSeO}_2^+ + 4\text{H}^+ + 4e^- + \text{OH}^- &\rightleftharpoons \text{H}_2\text{SeO}_3 \\ &+ 4\text{H}^+ + 4e^- \rightleftharpoons \text{Se(s)} + 3\text{H}_2\text{O} \\ E &= E_{\text{Se}}^0 + \frac{RT}{4F} \ln \left(\frac{a_{\text{HSeO}_2^+}}{a_{\text{Se}}} \right) + \frac{3RT}{4F} \ln C_{\text{H}^+} \\ &= 0.10 + 0.0148 \log a_{\text{HSeO}_2^+} - 0.043\text{pH} \end{aligned}$$

where E is the electrode potential with respect to the saturated sulphate electrode (SSE) ($\text{Hg}/\text{Hg}_2\text{SO}_4$, K_2SO_4 (sat.)); $a_{\text{Cu}^{2+}}$, $a_{\text{In}^{3+}}$, $a_{\text{HSeO}_2^+}$ are the activities of the respective ions in the solution; a_{Cu} , a_{In} , a_{Se} are the activities of the respective atoms in the electrodeposits. For a pure metal these latter are unity; in the case of alloy deposition they depend on the composition of the solid phase.

It is generally acknowledged that an alloy can be electrodeposited at a potential where each element would be deposited separately. That is true in numerous cases, especially for alloys of metals miscible in all proportions. Thus, in order to predict the conditions of formation and stability of the ternary compound, Singh *et al.* [11] superposed the three Pourbaix diagrams. The common immunity domain would lie in a narrow region around $E = -1.09$ V vs SSE. This approach does not seem to be correct because it ignores the polarization phenomena, and moreover, the fact that the thermodynamic conditions for the deposition of an element can be modified by the codeposition of another element, in particular in the case of a definite compound, as here. In order to bring the potentials of the three elements Cu, In and Se closer, it is possible to adjust the composition of the solution. A decrease of the concentration of an ion does not change the equilibrium potential greatly, but can introduce significant concentration polarization. However, the use of dilute solutions generally leads to the formation of powdery or dendritic layers which are unusable for most practical applications. To shift deposition potentials, it is also possible to add a complexing agent to the electrolyte.

2. Experimental details

On the basis of the work of Chassaing *et al.* [12] on copper electrodeposition, a sulphate solution containing citrate ions was chosen. Indeed, these authors have shown that the use of citrate ions shifts the copper deposition potential in the negative direction, lowers the plateau current and slows down the interfacial reactions.

Compound layers were deposited at room temperature on a Ti or Ni rotating disc electrode ($\Omega = 500$ rpm, $\phi = 12$ mm). A platinum grid was used as a counter electrode. The potential was monitored

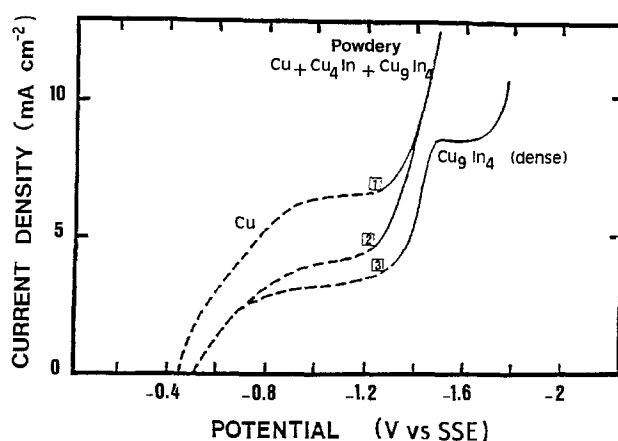


Fig. 1. Current density vs cathode voltage for Cu-In electro-deposition. (1) [cit] = 0 M; pH 2.2. (2) [cit] = 15 mM; pH 2.9. (3) [cit] = 25 mM; pH 3.7.

against a saturated sulphate electrode (SSE). X-ray diffraction data were obtained using a Philips PW 1380 diffractometer ($\text{MoK}\alpha$ source). The surface morphology of deposited films was observed with a scanning electron microscope (Cambridge Stereoscan 250). Thick layers were analysed by X-ray energy dispersive analysis (Tracor TN 1710), and the band gap was evaluated by spectrophotometry of reflected light.

3. Results

In a preliminary step, the electrodeposition of two binary alloys Cu-In and Cu-Se, was explored.

3.1. Cu-In binary alloy

The selected bath composition consisted of an aqueous solution containing 10 mM CuSO_4 , 10 mM $\text{In}_2(\text{SO}_4)_3$, 80 mM K_2SO_4 and sodium citrate ([cit] = 0–100 mM). The substrate used was made of nickel to optimize the adherence of the Cu-In deposits. Figure 1 shows the i/V curves for various citrate concentrations. In an electrolyte free of complexing agent (curve 1), pure copper is formed at first. The current tends to be limited by Cu^{2+} ion diffusion.

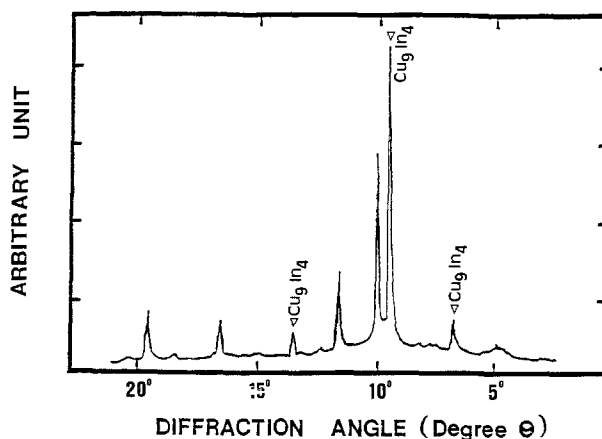


Fig. 2. X-ray pattern of copper indium thin film electrodeposited onto a Ni substrate. $E = -1.48$ V vs SSE; pH 3.7.

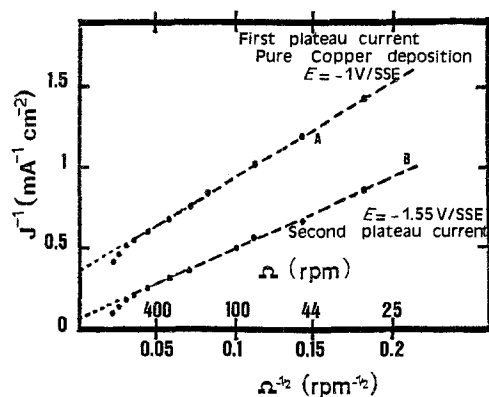


Fig. 3. Current density J vs electrode rotation speed in Koutecky-Levich plots. (a) $E = -1$ V vs SSE. Deposition of pure copper. (b) $E = -1.55$ V vs SSE. Formation of Cu_9In_4 . Only the partial current corresponding to indium deposition is here considered.

Beyond $E_{\text{In}} = -1.06$ V vs SSE the deposition of a black, poorly crystallized mixture of $\text{Cu} + \text{Cu}_4\text{In} + \text{Cu}_9\text{In}_4$ induces a rapid and irreversible rise of the current. Addition of sodium citrate (curves 2 and 3) shifts E_{Cu} towards negative values, lowers the plateau current corresponding to the diffusion of free Cu^{2+} ions, and gives rise to a new plateau beyond -1.4 V vs SSE, which corresponds to the formation of smooth and well-crystallized layers of Cu_9In_4 (Fig. 2).

In Fig. 3 are presented the relations between the plateau currents and the speed of the rotating disc electrode in a $I^{-1}/\Omega^{-1/2}$ plot. The straight lines do not pass through the origin as would be expected, according to the Levich law, for an electrochemical process fully controlled by the diffusion of active species in the electrolyte. This discrepancy indicates that a slow exchange process also contributes to limitation of the current. However, in contrast to the common case of simple mixed control kinetics the current does not increase with a more negative potential: it remains almost constant and even decreases slightly at the beginning of the plateau (Fig. 1). It is precisely at the beginning of the plateau that the obtained layers: (1) are smooth and coherent (Fig. 4), whereas the current is partially limited by mass transport; (2) have a composition close to that of the definite compound

Cu_9In_4 ; (3) are well crystallized as shown on the X-ray diagram of Fig. 2.

3.2. Cu-Se binary alloy

The electrolyte contained an aqueous solution of CuSO_4 0.01 M, SeO_2 0.01 M, K_2SO_4 0.08 M and sodium citrate as a complexing agent. The rotating disc electrode was made of titanium. For pure selenium electrodeposition, because of a very high crystallization overpotential, the current begins to increase significantly, not at $E_{\text{Se}} = -0.035$ V vs SSE, but at -0.7 V vs SSE, a potential more negative than E_{Cu} (curve 1). Figure 5 shows two polarization curves corresponding to the deposition of the binary compound. Without citrate (curve 2), copper and selenium are easily codeposited, but the layers are heterogeneous and uneven. Near -0.42 V vs SSE, the polarization curve presents a shoulder which corresponds, as in the preceding case, to the formation of smooth deposits of poorly crystallized Cu_2Se . At potentials more positive than -0.42 V vs SSE pure copper, formed of large isolated grains, is obtained and at potentials more negative than this value the current increases with time because of the dendritic formation of a mixture of Cu and rather amorphous Cu_2Se . In the presence of a small amount of citrate (curve 3), the shoulder is more marked. The corresponding layers are then smooth (Fig. 6), and the X-ray diffraction diagrams show the characteristic peaks of Cu_2Se (Fig. 7). For high concentrations of complexing agent ($[\text{cit}] > 70$ mM) the deposits become powdery.

3.3. Cu-In-Se ternary alloy

The electrolyte was an acidic aqueous solution ($1.5 < \text{pH} < 4.5$) of CuSO_4 (5–10 mM), $\text{In}_2(\text{SO}_4)_3$ (10–20 mM), SeO_2 (10 mM) and K_2SO_4 (60–80 mM) containing 0–80 mM of sodium citrate. The rotating disc electrode was made of titanium or nickel, titanium being preferable because its diffraction peaks do not overlap those of CuInSe_2 . Polarization curves corresponding to the deposition of the ternary com-

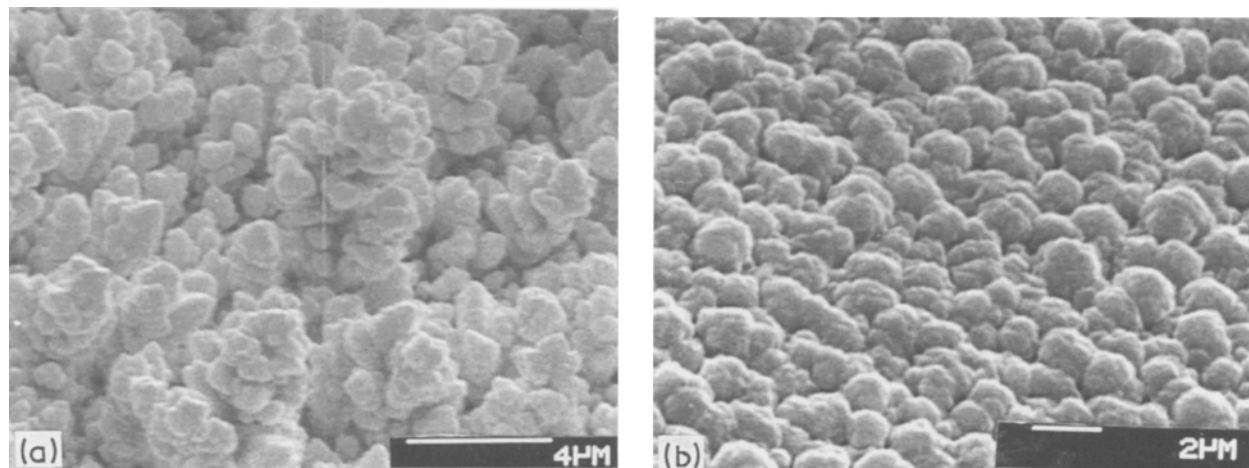


Fig. 4. SEM images of Cu-In deposits. (a) $[\text{cit}] = 0$ M; $E = -1.45$ V vs SSE. (b) $[\text{cit}] = 25$ mM; $E = -1.48$ V vs SSE.

Table 1. *CuInSe₂* X-ray diffraction data

ASTM <i>CuInSe₂</i> Chalcopyrite 23-209			<i>CuInSe₂</i> deposit obtained at $E = -0.9 V$ vs SSE $pH 3.28$: θ ($^{\circ}$)	<i>CuInSe₂</i> deposit obtained at $E = -0.97 V$ vs SSE $pH 3.28$: θ ($^{\circ}$)	<i>CuInSe₂</i> deposit obtained at $E = -1.2 V$ vs SSE $pH 3.28$: θ ($^{\circ}$)
θ ($^{\circ}$)	<i>hkl</i>	<i>I</i>			
6.09	112	70	6.07 (vw)	6.06 (m)	6.03 (vw)
10.01	204 220	100	10.05 (m)	10.04 (vs)	10.00 (w)
11.74	116 312	85	11.69 (vw)	11.67 (w)	11.69 (vw)
14.20	400	25	-	-	-
15.50	316 332	35	-	15.52 (w)	15.48 (vw)
17.47	424	60	-	-	-
18.56	336 512	25	-	-	-

Intensity: vw: very weak; w: weak; m: medium; s: strong; vs: very strong.

pound are presented in Fig. 8. Without citrate (curve 1), the current is not steady because of the formation of a powdery deposit of a $Cu_3Se_2 + Cu$ mixture. Traces of the indium were detected by microanalysis. After addition of a complexing agent (curve 2), two plateaux appear: on the first, more or less marked depending on $[Cu^{2+}]$, heterogeneous layers of $Cu + Se$ are obtained without any indium. X-ray data indicate the $Cu_{2-x}Se$ berzelianite phase. The second plateau is relevant to the formation of smooth and dense deposits of $Cu-In-Se$ compounds (Fig. 9). As in the case of Cu_3In_4 and $CdTe$ electrodeposition [13], the variations of this plateau current versus the rotation rate (in a $I^{-1}/\Omega^{-1/2}$ plot) do not follow the Levich law, indicating that the overall deposition rate is limited by mass transport and by a slow surface process.

Figure 10 shows typical X-ray diffractograms of as-deposited specimens obtained at various cathodic potentials. The peak intensities are maximum at $E \approx -0.97 V$ vs SSE and decrease for E greater or less than this value. However, the X-ray diffraction peaks are always characteristic of the tetragonal chalcopyrite structure (Table 1), with a strong (204, 220) preferred orientation.

Table 2 shows the results of energy-dispersive X-ray analysis of deposits prepared under different conditions. Their composition varies considerably with the applied potential; in particular the Cu/In ratio

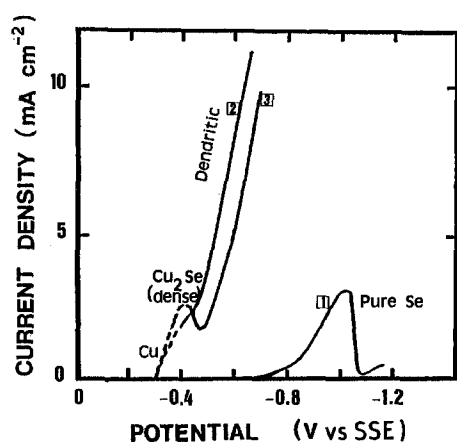


Fig. 5. Current density vs cathode voltage for $Cu-Se$ electrodeposition. (1) Pure Se ($[Cu^{2+}] = 0 M$). (2) $[cit] = 0 M$; $pH 2.39$. (3) $[cit] = 25 mM$; $pH 2.6$.

decreases when the potential becomes more negative and, according to Ueno *et al.* [10], this variation must induce a transition from p to n type.

The band gap of the deposited material was evaluated by spectrophotometry of reflected light. Figure 11 presents the total light reflectance versus the wavelength for $CuInSe_2$ deposits prepared at two different potentials. The band gaps (0.95 and 1.16 eV) evaluated from the characteristic wavelengths are close to the theoretical value (1.08 eV) for a single crystal.

4. Discussion

In the course of this experimental study we observed, in three different cases, an evident correlation between the shape of the polarization curve and the occurrence of a definite compound [22]. Effectively, Cu_3In_4 , Cu_2Se and $CuInSe_2$ were obtained in a potential range where the curve slope dI/dV is very low and, in some cases, even negative. It is evident that the mass transport by convective diffusion tends to limit the current, the active species being in relatively weak concentration in the electrolyte. Nevertheless, according to the variations of the current versus the speed of the rotating disc electrode, a slow surface reaction, in serial with the diffusion step, also contributes to the current limitation precisely in this potential range. This slow surface process has important consequences: — it tends to suppress the tendency to form non-compact morphologies as dendrites, powdery or spongy layers as often found in the case of materials electrodeposited under pure mass transport control;

Table 2. Results of energy-dispersive X-ray analysis of $Cu-In-Se$ layers obtained at different potentials in a solution at $pH 3.28$

	Composition (at. %)		
	<i>Cu</i>	<i>In</i>	<i>Se</i>
Theoretical values	25	25	50
Deposit at $E = -0.8 V$ vs SSE	42.4	21.2	36.4
Deposit at $E = -0.9 V$ vs SSE	34.4	23.1	42.5
Deposit at $E = -0.97 V$ vs SSE	26	24.2	49.8
Deposit at $E = -1.2 V$ vs SSE	21.8	25.9	52.3

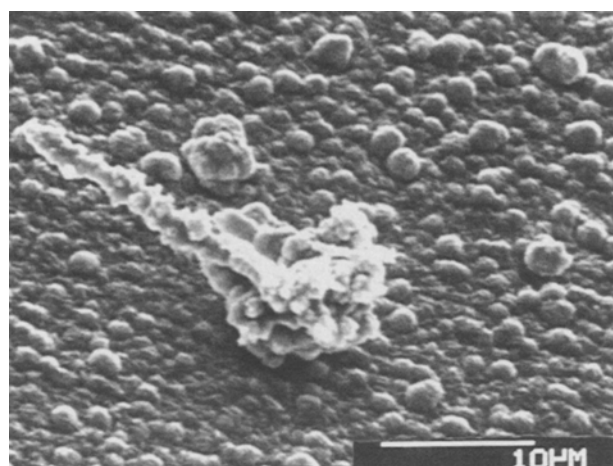


Fig. 6. SEM image of Cu₂Se deposit obtained at -0.42 V vs SSE.

— it allows a good crystallization of a material, the composition of which is close to that of a definite compound.

Conversely, the deposits prepared outside the above-mentioned potential range are poorly crystallized, microdendritic or powdery and have ill-defined compositions with, sometimes, strong heterogeneities. Moreover, in these conditions the current is rarely steady because of the continual change in the surface area of the deposit.

Citrate ions were used in order to bring E_{Cu} close to the other equilibrium potentials. But, in fact, the main function of the complexing agent is to promote the formation of crystallized definite compounds. Previous experiments on CuInSe₂, performed without any complexing agent, gave amorphous materials [7, 8, 10, 23]. Figures 1 and 5 illustrate how the addition of citrate gives a negative slope to the I/V curve in the very conditions where the transition from the amorphous to crystallized form occurs. The major effect of citrate is to cause a decrease of the plateau current of copper deposition (Figs 1 and 8) by modifying the diffusion coefficient of copper ions, but it also slows down the reduction rate through the decomplexation reaction of $(Cu\ cit\ H)^{2-}$ ions and also possibly causes an additional inhibiting effect of the

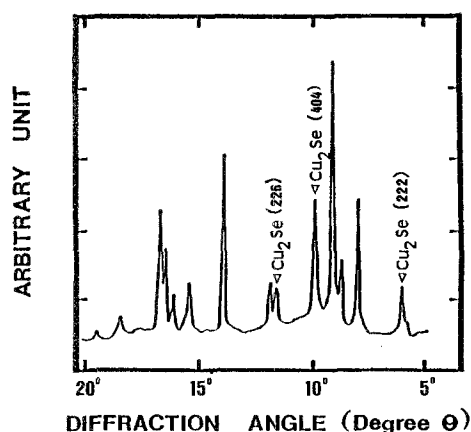


Fig. 7. X-ray pattern of an electrodeposited Cu₂Se thin film ($E = -0.42$ V vs SSE; pH 2.6). Non-indexed peaks belong to the titanium substrate.

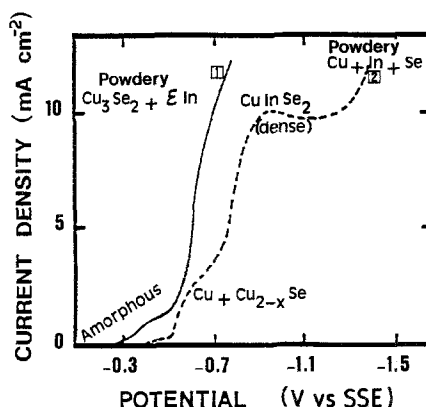


Fig. 8. Current density vs cathode voltage for Cu-In-Se electro-deposition. (1) $[cit] = 0$ M; pH 2.07. (2) $[cit] = 25$ mM; pH 3.28.

free complexing ions $[cit]^{3-}$ [12]. This reduced rate is fundamental to the spatial organization of the various elements at the atomic scale allowing a building of the three-dimensional network characteristic of the definite compound.

It is interesting to compare the results presented in this paper with those obtained on CdTe, another semiconducting definite compound the electrodeposition of which has been the subject of numerous experimental and theoretical investigations [13-16]. For example we found that the selenium-containing alloys Cu₂Se and CuInSe₂ are electrodeposited at potentials more negative than the deposition potential of the less noble element as in the case of CdTe. This phenomenon of anomalous codeposition was attributed by Kröger [17] to a potential shift due to the gain of Gibbs free energy, ΔG , provided by the crystallization of the definite compound. The partially covalent nature of the interatomic bonds of the elements Se and Te gives rise to high negative values of ΔG and is also responsible for the semiconducting properties of many of their compounds. In the case of CdTe, ΔG is $-25.5\text{ cal mol}^{-1}$ giving a theoretical shift of the Cd potential $-\Delta G/2F = 0.55$ V. Experimentally, cadmium is codeposited with tellurium in a potential range of about 0.45 V more positive than E_{Cd} and stoichiometric CdTe is obtained at a potential 0.05 V

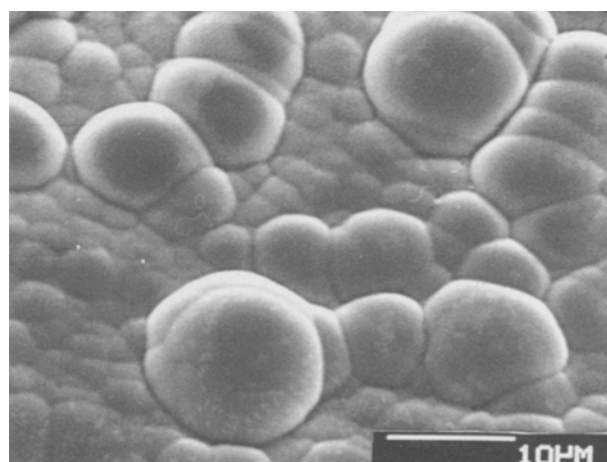


Fig. 9. SEM image of CuInSe₂ deposit obtained at $E = -0.975$ V vs SSE.

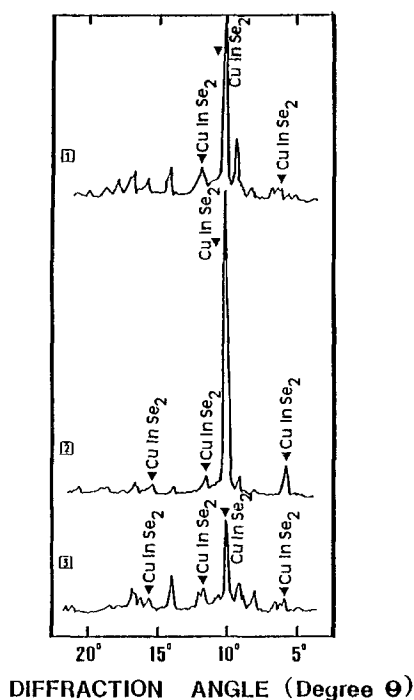


Fig. 10. X-ray pattern of three electrodeposited copper-indium-selenium thin films at pH 3.28. (1) $E = -0.9$ V vs SSE. (2) $E = -0.97$ V vs SSE. (3) $E = -1.2$ V vs SSE. Non-indexed peaks belong to the titanium substrate.

more positive than the deposition potential of pure Cd [15]. According to Cahen *et al.* [24] the formation of one mole of CuInSe_2 from the isolated elements provides -48 kcal. Thus, the corresponding theoretical potential shift of indium is -0.6 V. Experimentally, traces of indium were found at a potential 0.5 V more positive than E_{In} and crystalline CuInSe_2 was obtained at $E_{\text{In}} + 0.2$ V. It is interesting to emphasize that Kröger's theory, which is relative to binary definite compounds such as CdTe and CdSe , also appears valid for the ternary compound CuInSe_2 . Conversely, the electrodeposition of a purely bimetallic compound such as Cu_9In_4 does not involve any significant positive potential shift.

These thermodynamic phenomena have effects on the electrodeposition kinetics of semiconducting definite compounds and, particularly, on the elementary reduction reaction rate. In the case of CdTe Engelken, taking a solid state reaction into account, proposed a complex model allowing simulation of the polarization curve [18]: Vedel *et al.* [19] assumed a surface competition between absorbed species, where cadmium exhibits an inhibiting effect. In the exact conditions of stoichiometric CdTe formation, electrochemical as well as electrohydrodynamical impedance diagrams exhibit some features characteristic of an inhibiting surface process [20, 21]. Such investigations have to be extended to the case of CuInSe_2 , and other electrodeposited semiconductors, to verify the general character of these results.

5. Conclusion

The electrodeposition technique from aqueous medium was successfully used to prepare smooth and crystal-

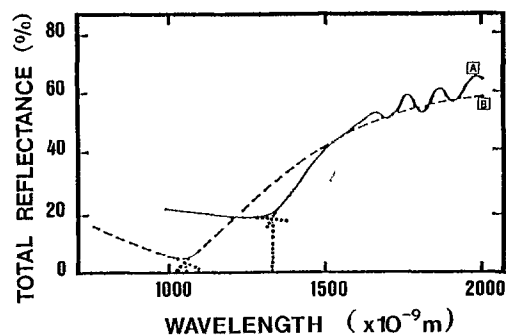


Fig. 11. Total light reflectance vs wavelength for deposits prepared at: (A) $E = -0.9$ V vs SSE; $E_g = 0.95$ eV; (B) $E = -1.1$ V vs SSE; $E_g = 1.16$ eV.

lized layers of the ternary semiconducting definite compound CuInSe_2 and of the binary compounds Cu_9In_4 and Cu_2Se using citrate ions as complexing agent. The stoichiometry of CuInSe_2 thin films depends upon the solution composition, applied potential and pH of the electrolyte. The best films thus obtained have a slight excess of copper and present the tetragonal chalcopyrite structure with a band gap of ca 1.1 eV. In every case, we observed that the definite compounds were formed in a potential range corresponding to a weak (or negative) slope of the polarization curve. This phenomenon seems to be general.

Thus, a careful analysis of the polarization curves appears to be a method to detect the ideal experimental conditions of preparation of various definite compounds by electrolytic codeposition.

References

- [1] G. Razzini, L. Peraldo Bicelli, B. Scrosati and L. Zanotti, *J. Electrochem. Soc.* **133** (1986) 351.
- [2] S. Menezes, *Solar Cells* **16** (1986) 255.
- [3] D. Cahen, Y. Chen, R. Noufi, R. Ahrenkiel, M. Tomkiewicz, W. M. Chen and R. Matson, *Solar Cells* **16** (1986) 529.
- [4] J. Szot and D. Haneman, *J. Appl. Phys.* **59** (1986) 2249.
- [5] R. N. Bhattacharya, *J. Electrochem. Soc.* **130** (1983) 2040.
- [6] R. N. Bhattacharya and K. Rajeshwar, *Solar Cells* **16** (1986) 237.
- [7] R. Noufi, R. Powell, R. Axton, Y. Chen and T. Datta, 1984 Annual Report Solid State Photovoltaic Research Branch, SERI/PR-212-2601 DE85008812, April 1985.
- [8] G. Hodes and D. Cahen, *Solar Cells* **16** (1986) 245.
- [9] V. K. Kapur, B. M. Basol and E. S. Tseng, Comm. Meeting of Electrochem. Soc., Boston (1986) Abstract No. 312.
- [10] Y. Ueno, H. Kawai, T. Sugiura and H. Minoura, *Thin Solid Films* **157** (1988) 159.
- [11] R. P. Singh, S. L. Singh and S. Chandra, *J. Phys. D. Appl. Phys.* **19** (1986) 1299.
- [12] E. Chassaing, K. Vu Quang and R. Wiat, *J. Appl. Electrochem.* **16** (1986) 591.
- [13] M. Froment and G. Maurin, 31st IUPAC Meeting, Sofia (1987).
- [14] M. P. R. Panicker, M. Knaster and F. A. Kröger, *J. Electrochem. Soc.* **125** (1978) 566.
- [15] G. Maurin and J. T. Li, *Le vide, les couches minces* **232** (1981) 99.
- [16] M. Froment, J. T. Li, G. Maurin and O. Solorza, Comm. Meeting of Electrochem. Soc., Boston (1986) Abstract No. 326.
- [17] F. A. Kröger, *J. Electrochem. Soc.* **125** (1978) 2028.
- [18] R. D. Engelken, Ph.D Thesis, University of Missouri-Rolla.
- [19] C. Sella, P. Boncorps and J. Vedel, *J. Electrochem. Soc.* **133** (1986) 2043.

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- [20] G. Maurin, O. Solorza and H. Takenouti, *J. Electroanal. Chem.* **202** (1986) 323.
- [21] C. Deslouis, G. Maurin, D. Pottier and B. Tribollet, 36th ISE Meeting, Maastricht (1987) Abstract No. 338.
- [22] G. Maurin and D. Pottier, Comm. Meeting of Electrochem. Soc., Chicago (1988) Abstract No 368.
- [23] F. J. Pern, J. Goral, R. J. Matson, T. A. Gessert and R. Noufi, *Solar Cells* **24** (1988) 81.
- [24] D. Cahen and Y. Mirovsky, *J. Phys. Chem.* **89** (1985) 2818.