ELECTRODEPOSITION OF COPPER INDIUM DISELENIDE FROM AN ACIDIC BUFFER SOLUTION (THE GLYCINE MEDIA)

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ABSRACT : Copper indium diselenide electrodeposition in thin films is studied in an electrolyte consisting of a glycine / glycinium (NH_3—CH_2—$COOH^+$ / NH_2—CH_2—$COOH$) buffer solution. Compared with the currently used sulphuric acid electrolyte, the use of a buffer makes easier the indium insertion, especially when the solution is poorly stirred. This is explained by the fixation of the pH near the electrode that impedes the hydrolysis of In^{3+} ions.

Keywords: Thin films, electrodeposition, glycine, buffer, $CuInSe_2$ (CIS) current-potential curves, atomic absorption spectroscopy.

RÉSUMÉ : L'électrodéposition du diséléniure de cuivre et d'indium en couches minces est étudiée en milieu tampon glycine/glycinium (NH_3—CH_2—$COOH^+$/ NH_2—CH_2—$COOH$). Comparée à l'utilisation habituelle d'une solution d'acide sulfurique comme électrolyte, l'utilisation du tampon permet l'insertion facile de l'indium dans le dépôt, surtout lorsque la solution est faiblement agitée. Ceci est attribué au pH de la solution qui reste inchangé au voisinage de l'électrode, ce qui empêche alors l'hydrolyse des ions In^{3+}.

Mots clés: Couches minces, électrodéposition, glycine, tampon, $CuInSe_2$ (CIS), courbes intensité-potentiel, spectroscopie d'absorption atomique.

INTRODUCTION

Most of the works dealing with $CuInSe_2$ electrodeposition make use as the electrolyte, of a dilute solution of a strong acid, like sulphuric or hydrochloric acid [1-5]. Now, the global electrodeposition reaction exhibits an H^+ ions consumption :

$$Cu^{2+} + In^{3+} + 2\,H_2SeO_3 + 8\,H^+ + 13\,e^- \longrightarrow CuInSe_2 + 6\,H_2O \qquad (1)$$

and the resulting local pH increase may change the distribution of the present chemical species and consequently change the reaction mechanism that leads to $CuInSe_2$ formation. In order to check this hypothesis, we realised a study parallel to a previous one [6], but using as electrolyte, instead of sulphuric acid, a buffer glycine (NH_2—CH_2—COOH) / sulphuric acid solution, that makes possible the fixation of pH between 1.2 and 3.6, as recently published [7]. The results show that the use of a buffer favors the indium accommodation, in particular when the solution is poorly stirred.

EXPRIMENTAL

The buffer solution is a modified version of that described by Sørensen [8]. In the buffer preparation, the 0.025 M NaCl was replaced by 0.05 M Na_2SO_4. The total glycine concentration was 0.05 M and the pH adjusted by a proper addition of sulphuric acid. The temperature (20°C), and precursor concentration were the same as the previous work ([Cu(II)] $=10^{-3}$ M, [In(III)]= 3 10^{-3} M, [Se(IV)] = 1.7 10^{-3} M). The solution volume was 900 mL, placed in a one litre beaker and stirred with a magnetic stirrer. Thus, the solution was only gently stirred.

The films were deposited upon a motionless substrate of tin oxide covered glass substrate (area :5cm^2). Current-potential curves (potential scan rate : 10 $mV.s^{-1}$) and potentiostatic film depositions were performed using a classical three electrodes equipment. The reference electrode was a mercury sulphate electrode, MSE, (+0.645 V *vs.* Standard Hydrogen electrode : SHE). The auxiliary electrode was a 5 x 5 cm^2 glass plate also covered with tin oxide.

After preparation, some films were dissolved in nitric acid and analysed for the main components. Copper and indium were determined by atomic absorption spectroscopy by means of a Perkin Elmer spectrometer model 3100 and Se by a potentiometric back titration with potassium thiosulphate after addition of an excess of KI. The accuracy of the determinations has been estimated to ± 0.8 % after execution of several titrations of known compositions.

RESULTS

Figure 1 shows two voltammograms corresponding to the reduction of a Cu(II) 10^{-3} M + Se(IV) 1.7 10^{-3} M solution, respectively in pH = 2.4 glycine buffer (curve 1) and sulphuric acid (curve 2) solutions. In citrate [9] and sulphate [10] solutions, the first wave has been attributed to the formation of Cu_xSe and the peak to the reduction of this compound into Cu_2Se and Se(-II), followed by a plateau coming from the direct formation of Cu_2Se and Se(-II) from the precursors in the solution. The current density is lower in the glycine medium and the cathodic current onset occurs at about the same potential.

On Figure 2 are shown three voltammograms obtained from a solution of the precursors in glycine buffers at pH = 1.8, 2.4 and 3. At pH =3, a white precipitate appears in the solution, due to the formation of indium hydroxide.

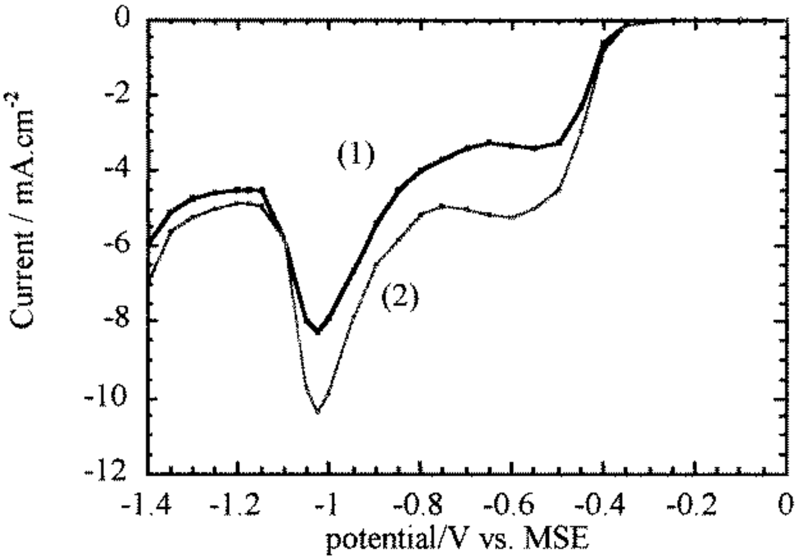

Figure 1. Voltammograms obtained in pH = 2.4 solutions containing 10^{-3}M Cu(II) and 1.7 10^{-3}M Se (IV) : (1) in glycine buffer; (2) in sulphuric acid.

The voltammogram, were we have only two picks, is similar to that obtained in absence of indium (Figure 1, curve 1). Thus, at this pH, In(III) is totally precipitated or partially present in solution as hydroxo complexes. The curve at pH = 2.4 is slightly more shifted than the curve at pH = 1.8, showing some complexation effect on the copper deposition that initiates the selenide deposition. On both these curves, the peak **A** at -0.74 V *vs.* MSE and the shift of the second peak **B** towards less negative potentials are characteristics of the $CuInSe_2$ formation [5].

Films were prepared in various condition of duration, pH and Se(IV) concentrations, at -1.08 V *vs.* MSE and chemically analysed for Cu, In and Se. On Table I are presented data obtained, at pH = 2.4, for various deposition times.

The mass increases linearly with time but slower than in sulphate medium, at the same pH (Figure 3) in relation with the difference in the current densities (Figure 1). On the other hand, the In/Cu ratio appears independent of the deposited mass : the mean of the eight values of the Table I is equal to 1.06, with a confidence interval of ± 0.017 (95 % probability level), very close to that estimated from the accuracy of the analysis (0.02). In Table I, all the ratio In/Cu are greater than 1. Thus, assuming that all the deposited copper is present in the film as $CuInSe_2$, it is possible to derive the film composition in terms of mol % of $CuInSe_2$, In_2Se_3 CuSe and Se (Table II).

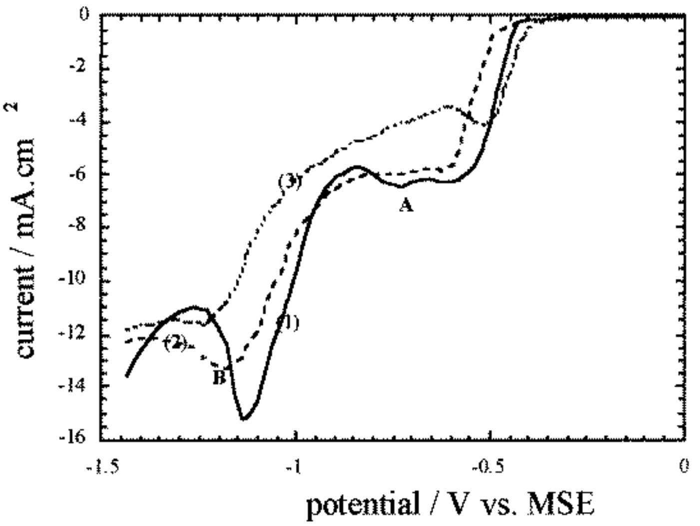

Figure 2. Voltammograms obtained from solutions of 10^{-3} M Cu(II), 3 10^{-3}M In(III) and 1.7 10^{-3}M Se(IV) solutions in glycine buffer of : (1) : pH = 1.8 ; (2) : pH = 2.4 and (3) pH = 3.

Table I : Variations, vs. time, of the deposited mass and chemical composition of the deposited films (pH = 2.4, E_{dep} = -1.08 V *vs.* SME).

Deposition time / min	Deposited mass /μg.cm^{-2}	Cu mol %	In mol %	Se mol %	In/Cu
5	1.4	18.6 ± 0.3	20.3 ± 0.3	61.0 ± 1	1.08 ± 0.02
10	2.6	22.0 ± 0.3	22.9 ± 0.3	56.2 ±1	1.01 ± 0.02
15	-	21.9 ± 0.4	23.1 ± 0.4	55.0 ± 0.9	1.05 ± 0.02
18	3.2	22.6 ± 0.4	24.0 ± 0.4	53.7 ± 0.9	1.04 ± 0.02
20	4.2	23.4 ± 0.4	24.6 ± 0.4	51.9 ± 0.8	1.04± 0.02
30	6.2	23.4 ± 0.4	24.3 ± 0.4	52.3 ± 0.8	1.03 ± 0.02
40	7.8	23.9 ± 0.4	25.3 ± 0.4	50.8 ± 0.8	1.05 ± 0.02
67	13.2	23.6 ± 0.4	25.6 ± 0.4	50.8 ± 0.8	1.08 ± 0.02

On Figure 4, it is shown that the initial Se content is quite high, but decreases with deposition time.On the other hand, the proportion of $CuInSe_2$ and In_2Se_3 increases and tends towards a constant value.

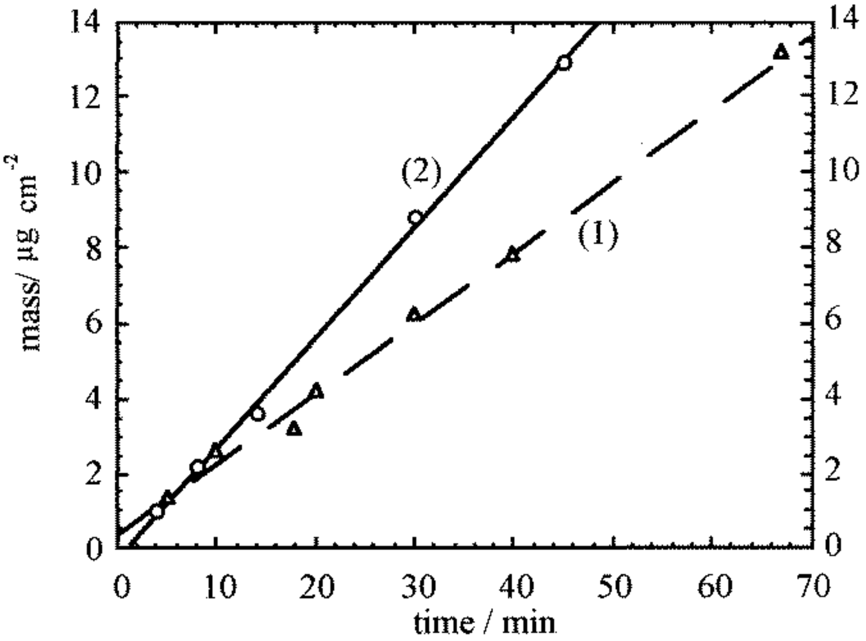

Figure 3. Variation, vs.time, of the deposited mass. glycine buffer and (2), sulfuric acid media pH= 2.4, E_{dep} = -1.08 V.

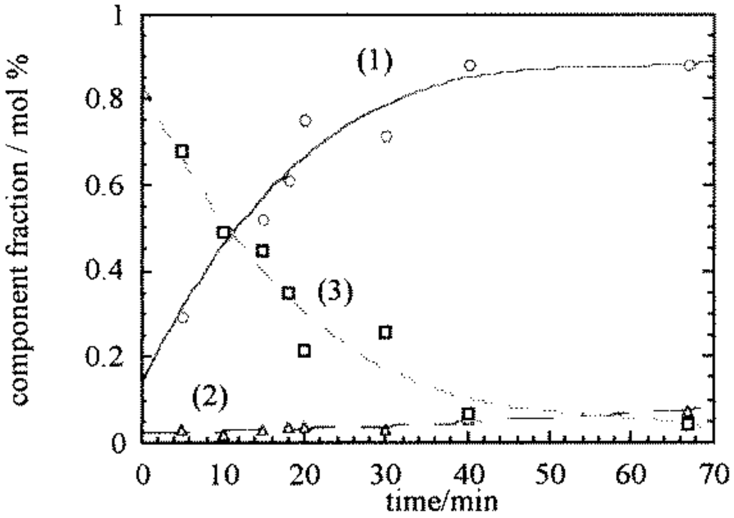

Figure 4. Variation, *vs.* the deposition time, of the $CuInSe_2$ (1), In_2Se_3 (2) and Se (3) in the films deposited at pH = 2.4 and E = -1.08 V *vs.* MSE

Remark : the compositions given in Figure 4 correspond to mean compositions that integrates, at time t, all the selenium excess deposited before. In fact, the composition of the deposit made at this time tends faster towards a limit. For instance, in Figure 5 it was assumed that the instantaneous indium content c_{inst} (/%) the film is given by equation :

$$c_{inst} = c_{\infty}(1 - \exp(-\alpha . t)) \qquad (2)$$

and the mean indium content, by integration of expression (3) :

$$c_{mean} = \frac{1}{t}\int_0^t c_{inst}\,dt \qquad (3)$$

The curve (2) of Figure 5 represents the variation of c_{mean} *vs.* t for $c_{\infty} = 26$ % and $\alpha = 0.8$. It fits quite well the observed variation of the mean indium content (1) and the variation of c_{inst}, represented by curve (3) shows that, very quickly, the indium content in the depositing material tends towards a constant value. Thus, after the formation of a Se rich layer, the film composition remains constant.

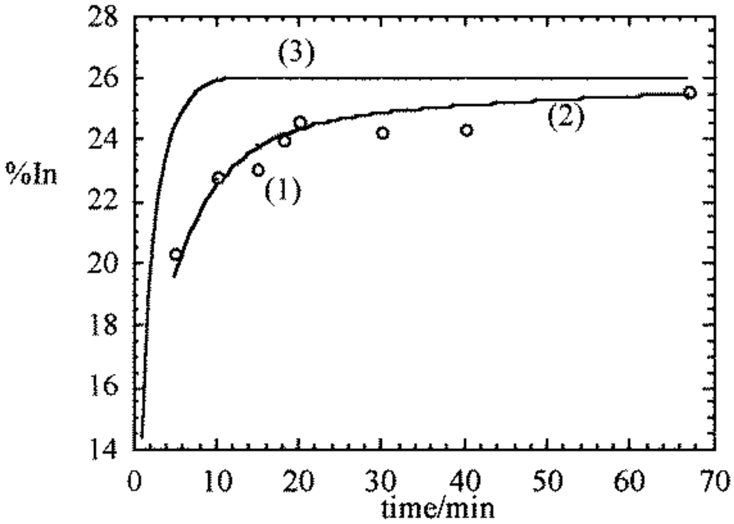

Figure 5. Variation, vs. time of the indium content of the films : (1) : observed mean indium content ; (2) : variation of the mean In content, and (3) : variation of the indium content of the depositing material, calculated using expression (3) and (2), resp., with $c_{\infty} = 26$ % and $\alpha = 0.8$.

Table II shows the compositions, in mol % of the elements and in mol % of the constituting materials for various pH values. At pH = 2.6, the In/Cu ratio is less then unity and the Se content sharply increases, indicating a higher difficulty to accommodate indium in the film (recall that at pH = 3, there is no accommodation at all). The distribution of the elements in the constitutive materials shows that, for pH ≤ 2.4, the mean film composition remains about the same. On the other hand, at pH = 2.6, the presence of a CuSe excess is noticed, together with a large selenium excess.

Table II. Variation of the composition of films deposited at -1.08 V vs. MSE for various pH, in mol % of the elements and in mol % of the constituting materials.

pH	%Cu	%In	%Se	%$CuInSe_2$	%In_2Se_3	% CuSe	% Se
1.8	23.9	24.8	51.3	90.2	1.70	-	8.11
2.0	23.2	25.5	51.3	89.9	4.46	-	5.62
2.4	23.5	25.6	50.8	93.3	4.17	-	2.58
2.6	24.0	21.5	54.5	65.2	-	7.58	27.3

DISCUSSION

In recent works dealing with the electrodeposition of $CuInSe_2$, we observed that the final composition of the film did not depend on the Se(IV) and Cu(II) fluxes, as previously shown in citrate and sulphuric media. An analysis of the experimental conditions showed that the stirring conditions were different : in the first studies the deposition was performed either upon a rotating disk electrode or in a small cell (100 cm^3) stirred with a magnetic stirrer. In a more recent work, a large volume of solution (900 cm^3) was used, and the magnetic stirring was comparatively weaker. Contrary to what was expected from the flux ratio ($J_{Se}/J_{Cu} > 1$), an excess of copper (In/Cu < 1) was always found. In the glycine buffer, an excess of indium is observed in the deposit, except at the highest pH used. The reaction mechanism corresponding to the global deposition reaction (1) may schematically be represented as follows :

(1) : formation of a copper-selenium compound :

$$Cu^{2+} + 2\ H_2SeO_3 + 8\ H^+ + 10\ e^- \longrightarrow CuSe_2 + 6\ H_2O \qquad (4)$$

(2) : reduction of the Se excess, made easier due to the presence of In^{3+} ions :

$$CuSe_2 + In^{3+} + 3\ e^- \longrightarrow CuInSe_2 \qquad (5)$$

If, in the sulphuric acid solution, the stirring is not strong enough to balance the pH change in the electrode vicinity due to reaction (4), the In^{3+} ions may locally undergo an hydrolysis like

$$In^{3+} + OH^- \rightarrow InOH^{2+} \qquad (6)$$

Reaction (5) needs indium ions free from hydroxyl complexation. These free ions are given by a reaction reverse from reaction (6) that like most of the similar reactions, is slow and makes more difficult the indium insertion in the solid. Thus, reaction (5) cannot take place at a rate high enough to accommodate all the $CuSe_2$ produced by reaction (4). Consequently, the elemental selenium accumulates and the deposit is not as indium rich as anticipated from the J_{Se} / J_{Cu} flux ratio and is too much selenium rich, the deviation from the rule decreasing with the stirring increase. A buffered solution compensates the H^+ loss and annihilates reaction (6), except for the highest investigated pH value.

CONCLUSION

In this work, it has been shown that it is easier to obtain indium rich $CuInSe_2$ in a buffered acidic solution. This is tentatively explained assuming the masking of the formation of an indium-hydroxocomplex and dependence on the stirring conditions. When the solution is strongly stirred, or when the deposits are made upon a rotating electrode, the deposit composition depends only on the ratio of the Se(IV) and Cu(II) fluxes. On the contrary, if the substrate is motionless in quiet or poorly stirred solutions, the deposit exhibits an Indium content and an In/Cu ratio lower than those anticipated by the above rule.

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