Quartz crystal microbalance study of the chemical deposition of indium (III) sulphide

B.Asenjo, A.M.Chaparro, M.T.Gutiérrez, J.Herrero
Dep. Energías Renovables, CIEMAT
Avda. Complutense, 22. 28040-Madrid

The growth of thin films from bath solutions is interesting for its simple and cheap technology, requiring temperatures below 100 °C. This technique, as well as electrodeposition, may contribute to lower the production costs of new thin film solar cells [1]. Essential to this objective is a good knowledge of the deposition process, usually not well understood. One key information to characterize the kinetics of the deposition is the rate of growth of the film, which can be measured in situ with a quartz crystal microbalance (QCM) [2]. Here we present a study of indium sulfide (In_2S_3) deposition.

In_2S_3 is a direct n-type semiconductor with variable energy gap (2.0-2.7eV) depending on synthesis conditions [3]. Thin films are useful as buffer layer of thin film solar cells [4]. They also may have an interest in photocatalysis and photoelectrochemical energy conversion [3]. In_2S_3 deposition can be carried out by decomposition of thioacetamide (TA) in acidic solution and presence of In(III) cations. The process consists, in principle, in the slow release of sulfide anions in solution and precipitation of In_2S_3 ($k_s=6 \times 10^{-74}$). Important amounts of the indium oxide and hydroxide have been detected in the film [5], although the pure sulfide and sulfur rich can also be obtained [3]. In our study, different experimental variables are analyzed with QCM to get information of the deposition kinetics.

Fig.1 shows growth rate plots of indium sulphide on Au-unpolished substrate, and three different TA concentrations. Details of the experimental set-up are given in ref.[6]. The solution was unstirred, and thermostatised at 60 °C. It is shown that the initial growth rate increases with [TA], attaining above 9 nm min^{-1} at 0.7M. Constant or slow decaying rate is observed during the first 30-40 minutes of growth. The film produced in this period is gray-yellow and very adherent. Afterwards, growth rate increases steeply, giving rise to the deposit of an orange-yellow film, porous and poorly adherent. This final increase may be ascribed to an autocatalytic effect by protons generated in the synthesis of In_2S_3 [3]:

$$2In^{3+} + 3CH_3CSNH_2 + 6H_2O \text{ --> } \mathbf{In_2S_3} + 3NH_4^+ + 3CH_3COOH + 3H^+ \qquad (1)$$

Protons accelerate the acidic decomposition of TA. Parallel pH measurements confirm this autocatalysis (not shown).

We observed that the rate of the deposition process is different on stirred solutions. That is reflected by the growth curves of Fig.2. The induction time is longer on stirred solution. If stirring is moderate (curve b), the highest growth rate are observed, 14nm min^{-1}. On the other hand, if stirring is severe (curve c), for instance by bubbling a gas in the solution, the growth is slower, or even stops. These results indicate non-trivial effect of hydrodynamics on the deposition process. It seems clear that a moderate stirring must favor the diffusion of particles in solution, hence allowing for higher growth rates, as in curve B. However, the negative effect of intense stirring indicates that nucleation and/or growth of In_2S_3 is difficulted. One possibility is that the formation of the typical needle like particles of In_2S_3 may be impeded by a fast flow of solution. More experiments are being conducted with QCM to clarify this and other characteristics of the growth of In_2S_3 thin films.

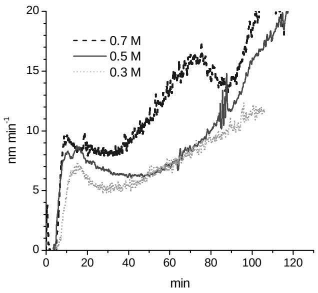

Fig.1. Growth rate of In_2S_3 films at 60 °C bath. temperature, and three concentrations of TA.

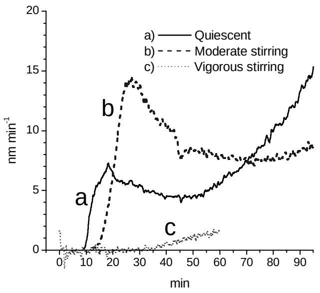

Fig.2. Growth rate of In_2S_3 films at 60 °C, under quiescent solution (a), moderate (b) and vigorous (c) stirring.

REFERENCES

[1] O.Savadogo. Sol. Ener. Mat. Sol. Cells. **52,** 361(1998)
[2] R.Ortega-Borges, D.Lincot. J.Electrochem.Soc. **140**, 3464 (1993)
[3] T.Yoshida, K.Yamaguchi, H.Toyoda, K.Akao, T.Sigiura, H.Minoura. The Electrochemical Society, proc. vol.97-20. 1997.
[4] D.Braunger, D.Hariskos, T.Walter, H.-W.Schock. Sol.Ener.Mat.Sol.Cells. **41-42**, 345 (1996)
[5] R.Bayón, C.Guillén, M.A. Martínez, M.T.Gutiérrez, J.Herrero. J.Electrochem.Soc. **145**, 2775(1998)
[6] A.M.Chaparro, M.T.Gutiérrez, J.Herrero. Electrochim.Acta **47**, 977 (2001)