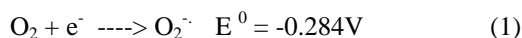


Characterisation of Zn(Se,O) thin films deposited by an electroless-chemical process

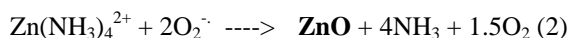
A.M.Chaparro, M.T.Gutiérrez, J.Herrero
 Dep. Energías Renovables, CIEMAT
 Avda. Complutense, 22. 28040-Madrid

Thin film semiconductors are used in new photovoltaic and photoelectrochemical cells. One of the most interesting techniques for thin film deposition is the chemical bath deposition [1]. Its main advantage is the requirement of temperatures, below 100°C, leaving the substrate structure almost unaltered after the deposition process. It is probably due to this property that chemical bath deposition gives the best results for the formation of solar cell quality heterojunctions like the CIS/buffer, where a p-n junction is formed by deposition of an n-type semiconducting thin film (buffer) onto a p-type absorber (CIS=CuInS₂, CuInS₂).

One material of interest as buffer layer for CIS based photovoltaic cells is Zn(Se,O). This material is proposed as an alternative to the commonly used CdS. Zn(Se,O) is deposited from an aqueous ammonia solution of the Zn²⁺ cations, the selenide precursor (selenourea) and a reducer agent (hydrazine). The process that gives rise to the growth of Zn(Se,O) has been characterised as an electroless-chemical process, in which hydrazine oxidation on the substrate surface induces the reduction of solution species, mainly dissolved oxygen [2]. The most probable reaction is the one electron reduction until the superoxide radical (O₂⁻):



Reaction of this radical with Zn²⁺ cations gives rise to the deposition of ZnO:



In parallel to ZnO deposition, ZnSe is chemically deposited by reaction of selenide anions (Se²⁻), from the decomposition of selenourea, with Zn²⁺, yielding a film formed by nanocrystal aggregates of ZnSe and ZnO. Experimental evidences show that, in fact, the molecule of selenourea plays a dual role, first as Se²⁻ precursor, and second as a catalyst for the redox reactions.

Fig.1 shows the growth rate and film thickness of a Zn(Se,O) film during deposition on a Au substrate, measured in situ with a quartz crystal microbalance. During the first 20 minutes the electroless-chemical growth prevails, until a film of about 100nm. It is the low conductivity of this film and probably also the consumption of selenourea molecules, which gives rise to a deceleration of the electroless reaction, prevailing a pure chemical deposition reaction of ZnSe after 20 minutes.

This films can be characterised in photoelectrochemical cells. Fig.2 shows voltammograms under chopped white light of Zn(Se,O) films grown during 20 minutes (electroless-chemical) and 120 minutes (chemical), in contact with aqueous 10⁻²M KI solution. For electroless-chemical Zn(Se,O) the photoresponse is predominantly p-type, whereas for chemical Zn(Se,O) it is n-type. These differences may reflect a variation in the bulk of the films (composition or doping character), or in the surface kinetics of photogenerated carriers. It is

interesting to note that the heterojunctions formed by electroless-chemical Zn(Se,O) buffer layers in contact with p-CuInS₂ (CuInS₂/electroless-chemical-Zn(Se,O)) give rise to significantly lower photovoltage values than p-CuInS₂/chemical-Zn(Se,O) [3]. This result may reflect the lower p-n junction quality that arises from the electroless-chemical Zn(Se,O). However the chemical Zn(Se,O) film is less stable material. More photoelectrochemical experiments are being conducted to characterise Zn(Se,O) as a function of chemical bath synthesis conditions.

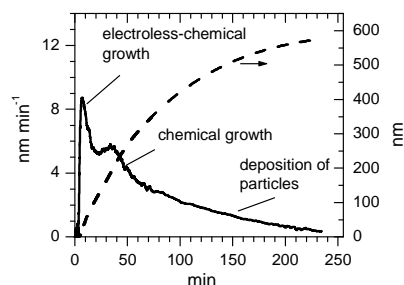


Fig.1. Growth rate of a Zn(Se,O) films at 50 °C bath temperature.

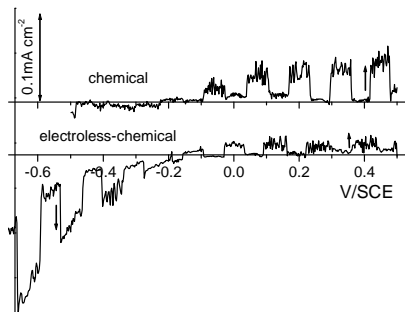


Fig.2. Voltammograms under chopped white light of two Zn(Se,O) thin films grown at different kinetics regimes.

REFERENCES

- [1] D.Lincot, M.Froment and H.Cachet, in 'Advances in Electrochemical Science and Engineering', R.C.Alkire and D.M.Kolb (Eds.). Wiley, 1999, pp.165-388.
- [2] A.M.Chaparro, M.T.Gutiérrez, J.Herrero. *Electrochim. Acta* **47** 977-986 (2001)
- [3] A. M. Chaparro, M. T. Gutiérrez, J. Herrero, J. Klaer, M. J. Romero, M. M. Al-Jassim. *Prog. Photovolt. Res. Appl.* **10** 465-480 (2002)