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ScienceDirect
Thin Solid Films 515 (2007) 6036 – 6040
www.elsevier.com/locate/tsf

Study of $CuInS_2$/*buffer*/ZnO solar cells, with chemically deposited ZnS-In_2S_3 *buffer* layers

B. Asenjo [a,*], A.M. Chaparro [a], M.T. Gutiérrez [a], J. Herrero [a], J. Klaer [b]

[a] Department of Renewable Energies, CIEMAT. Avda. Complutense, 22. 28040 Madrid, Spain
[b] Hahn-Meitner-Institut, SE3, Glienicker Str. 100, D-14109 Berlin, Germany

Available online 16 January 2007

Abstract

Thin film solar cells based on $CuInS_2$/*buffer*/ZnO have been prepared with different *buffer* layers of mixed ZnS-In_2S_3 composition. The buffer films are grown by chemical bath deposition (CBD) from acidic solutions of $InCl_3$, $ZnSO_4$ and thioacetamide (TA). A kinetics study of the growth of the *buffer* layers is carried out with the quartz crystal microbalance. The influence of bath conditions (solution, temperature and composition) on the growth rate is studied. Films are obtained with different physical, chemical and morphological properties. The absorption coefficient spectra of the films show a variation depending on the CBD conditions, with absorption edges between 2.6 and 3.35 eV. Surface morphology of the films, observed with scanning electron microscopy, reveals that the presence of Zn produces characteristic structures with microtubular form, compared with pure In_2S_3 buffer films. Solar cell results show a significant increase of Voc and FF upon introducing Zn^{2+} ion in the buffer layer.

Keywords: Buffer layer; Chemical bath deposition; Solar cells

1. Introduction

Substitution of CdS by other materials as buffer layer of $CuInS_2$, and other thin film based solar cells is a research line to obtain cells with higher efficiency and non-toxic elements. Indium sulphide and zinc sulphide prepared from chemical bath deposition (CBD) are possible candidates, because they offer enhanced properties as buffer layers, due to their higher energy gap (Eg = 2.2 eV and Eg = 3.6 eV for the indium and zinc compound, respectively [1,2]), transparency, and general good film properties (compact, adherent, conforming). Some groups have reported good solar cell results: Braunger et al. [3] obtained 11.4% efficiency with In (OH, S), and Neve et al. [4] 10.7% with ZnS thin film buffer, prepared by the CBD method [5–7]. On the other hand, films with a mixed ZnS-In_2S_3 composition may have additional possibilities as buffer layer of solar cells because they may be obtained with a range of properties in terms of light absorption properties and morphologies. There are not many works referring to the mixed ZnS-In_2S_3 system in the literature. Hashimoto [8] deposited (Zn, In) S_x with and without NH_3 aqueous solution. Bayón [9] indicated the existence of various compounds in the films prepared from acidic solution, and reported 4.5% efficiencies in $CuInS_2$ based solar cells. These films probably include, together with the

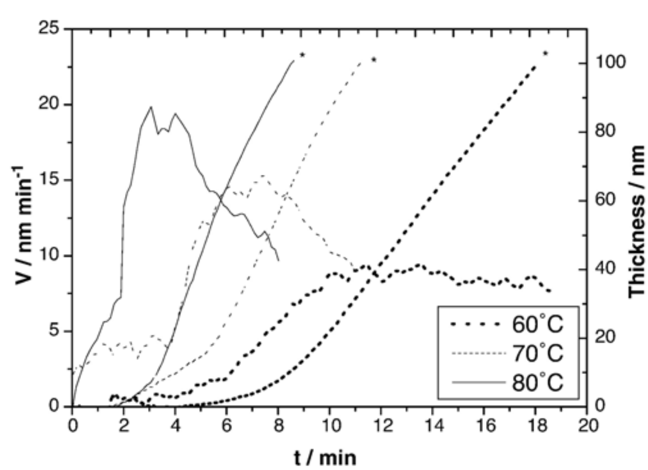

Fig. 1. Growth rate plots of ZnS-In_2S_3 thin films at three different solution temperatures. Solution composition: [TA] = 0.5 M, [$InCl_3$] = 0.025M, [ZnSO4] = 0.01 M, [HCl] = 0.01 M and [CH_3COOH] = 0.3 M. (* = deposited thickness).

* Corresponding author. Tel.: +34 913466675; fax: +34 913466037.
E-mail address: mbegona.asenjo@ciemat.es (B. Asenjo).

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doi:10.1016/j.tsf.2006.12.056

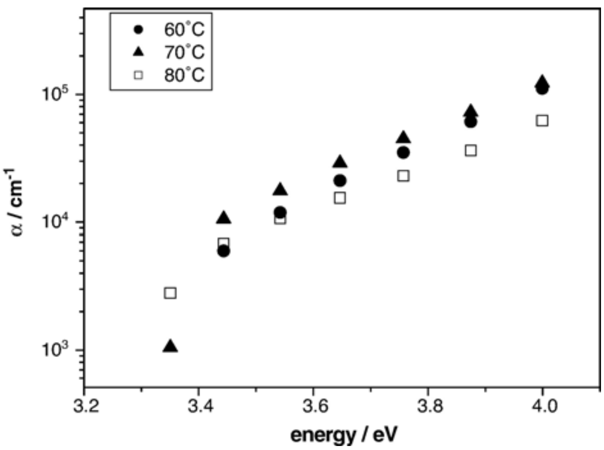

Fig. 2. Absorption coefficient spectra of films obtained at three bath temperatures. Same solution composition as in Fig. 1.

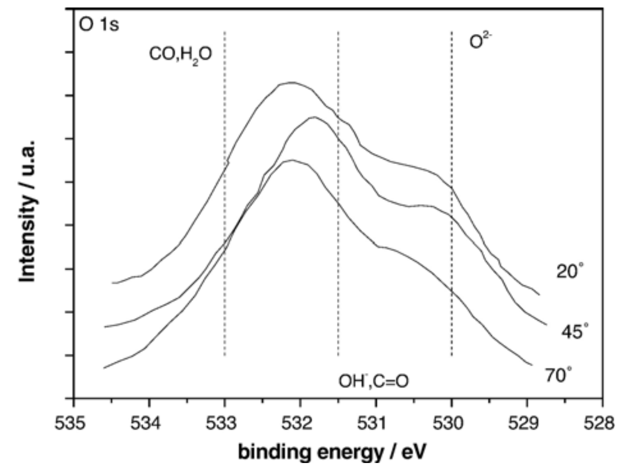

Fig. 4. XPS results corresponding to O1s signal for the same film as in Fig. 1 at 70 °C, measured at 45° detection angle.

sulphides, the respective metal oxides and hydroxides in different proportions as side compounds resulting from the CBD process.

The aim of this work is to prepare by CBD thin films with mixed ZnS-In_2S_3 composition, under different conditions in the bath. Composition, optical, structural and morphological properties are studied for the different films. Their properties as *buffer* layers of $CuInS_2$/*buffer*/ZnO solar cells are analysed.

2. Experimental

The films with ZnS-In_2S_3 composition, were deposited on the different substrates (glass, Au, and $CuInS_2$) from an acidic solution using 37% hydrochloric acid (HCl, Merck), thioacetamide (TA, CH_3CSNH_3, Fluka), indium (III) chloride ($InCl_3$, Fluka), zinc sulphate ($ZnSO_4$, Fluka) and acetic acid (CH_3COOH, Merck). Growth rate was measured in a thermostatised bath equipped with a QCM (Maxtek. Inc.), as described elsewhere [10]. Au covered quartz substrates (unpolished, AT cut, Maxtek) were used for the QCM study.

Surface and bulk composition of the films were determined with XPS technique (Perkin Elmer PHI 5400 spectrometer, $h\nu$= 1253.6 eV Mg K_α radiation), using angle resolved detection (ARXPS), and Ar^+ ion sputtering (3 kV, 63 Å min^{-1} sputtering rate measured on Ta_2O_5) for composition analysis in depth. The energy position of the signals was measured respect to the energy of adventitious carbon (E_B=284.8 eV). The parameters of the signals were obtained by fitting to a symmetric Gaussian–Lorentzian (0.8–0.2) sum function after subtracting the background by the Shirley method. Absorption coefficient (α) and band gap (E_g) of the film was determined from transmittance (T) and reflectance (R) spectra (Perkin Elmer Lambda 9 spectrometer) using the equation [11]:

$$T = (1-R)^2 e^{-\alpha d} / \left(1-R^2 e^{-2\alpha d}\right) \quad (1)$$

where d is the film thickness. SEM microscopic analysis (Hitachi S-2500) was used to study the surface morphology.

For the study of $CuInS_2$/*buffer*/ZnO solar cells, the $CuInS_2$ films were grown on Mo substrate by a sequential sputtering-evaporation process [12]. Previous to *buffer* layer deposition the surface of $CuInS_2$ is treated in 0.1 M KCN solution at 40 °C during 2 min to remove the CuS overlayer that results from the

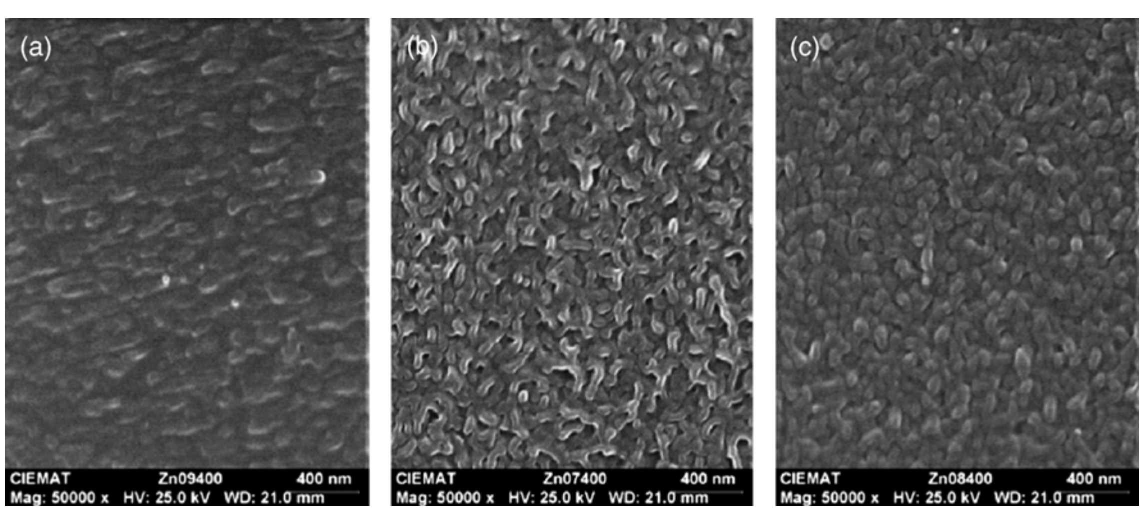

Fig. 3. SEM image of ZnS-In_2S_3 films deposited at 60 °C (a), 70 °C (b),and 80 °C (c).