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Study of $CuInS_2$/ZnS/ZnO solar cells, with chemically deposited ZnS buffer layers from acidic solutions

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Abstract

Thin film solar cells based on $CuInS_2$/ZnS/ZnO have been prepared with ZnS buffer film of different thickness. ZnS films are grown by chemical bath deposition (CBD) from acidic solutions of $ZnSO_4$ and thioacetamide (TA). The change of the growth rate with time is studied by means of the quartz crystal microbalance. Films with different thickness show variable physical, chemical and morphological properties. The structure is studied with X-ray diffraction, showing different crystallinity with deposition time. The absorption coefficient depends also on the CBD deposition time, and shows absorption edges between 2.70 and 3.65 eV. The compositional analysis carried out with XPS (surface) and EDAX (bulk). Bulk composition reflects highly stoichiometric films, with Zn/S ratios close to unit. Preliminary results with $CuInS_2$-based solar cell show efficiencies around 5%, lower than usually found with standard CdS buffer films (around 9%).

Keywords: Zinc sulphide; Buffer; Chemical deposition; Thin film

1. Introduction

Zinc suphide (ZnS) is an important semiconducting material with a wide direct band gap of 3.65 eV [1]. It is of interest for replacement of CdS as buffer layer of thin film-based solar cells due to higher energy gap, good transparency, and general good film properties (compact, adherent, conforming). Several techniques can be used for thin film growth of ZnS, such as chemical vapour deposition [2], spray pyrolysis [3] and chemical bath deposition (CBD) [4–7]. Some authors have obtained good solar cell results with this buffer type; Neve et al. [8] prepared ZnS by the CBD method in basic solution and obtained 10.7% efficiency on $CuInS_2$-based cells. However, few authors prepare ZnS in acidic solutions; O'Hare et al. [9] obtained ZnS from $ZnCl_2$ between pH 2.0 and 5.0 and Makhova et al. [10] compared ZnS films obtained by acidic and basic solutions, arriving at the conclusion that thin films prepared in acidic solutions present more stoichiometric composition.

The aim of this work is to prepare by CBD-ZnS thin films of different thinckness by CBD, using thioacetamide (TA) solution and $ZnSO_4$. The growth rate of the film is monitored with a quartz crystal microbalance (QCM). Composition, optical and structural properties are studied for the films. Their properties as buffer layers of $CuInS_2$/ZnS/ZnO solar cells are also analysed.

2. Experimental

The films with ZnS composition were deposited on the different substrates (glass, Au, and $CuInS_2$) from an acidic solution (pH = 2) using 37% hydrocloric acid 0.01 M (HCl, Merck), thioacetamide 0.5 M (TA, CH_3CSNH_3, Fluka), zinc sulphate 0.01 M ($ZnSO_4$, Fluka) and acetic acid 0.3 M (CH_3COOH, Merck). Growth rate was measured in a thermostatised bath at 70 °C equipped with a QCM (Maxtek Inc.), as described elsewhere [11]. Au covered quartz substrates (unpolished, AT cut, Maxtek) were used for the QCM study.

Surface and bulk composition of the films was determined with XPS technique (Perkin-Elmer PHI 5400 spectrometer, $h\nu = 1253.6$ eV Mg K_α radiation), using

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angle-resolved X-ray photoelectron spectroscopy (ARXPS) detection. The energy position of the signals was measured with respect to the energy of adventitious carbon ($E_B = 284.8$ eV). 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 [12]:

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}, \quad (1)$$

where d is the film thickness.

For the preparation of $CuInS_2$/ZnS/ZnO solar cells, $CuInS_2$ thin films were grown on Mo substrate by a sequential sputtering-evaporation process [13]. Previous to ZnS 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 growth process. Then, the buffer film of ZnS composition is grown by CBD in a thermostatised reactor. The ZnO window layer is deposited by sputtering onto the $CuInS_2$/buffer bilayer and, finally, aluminium grid contacts are evaporated on top of the ZnO layer. The solar cell results presented here correspond to a set fabricated with $CuInS_2$ films generated in the same batch process, with identical termination of the cell (i.e., deposition of ZnO and Al contacts), in order to differentiate solely buffer layer deposition effects. The current vs voltage (I–V) curves were obtained under 100 mW cm^{-2} AM1.5 illumination at 25 °C.

3. Results and discussion

Fig. 1 shows general features of the growth rate of ZnS composition films, measured with QCM technique on Au covered substrates. Different stages for growth of ZnS can be differentiated in the acid dissolution.

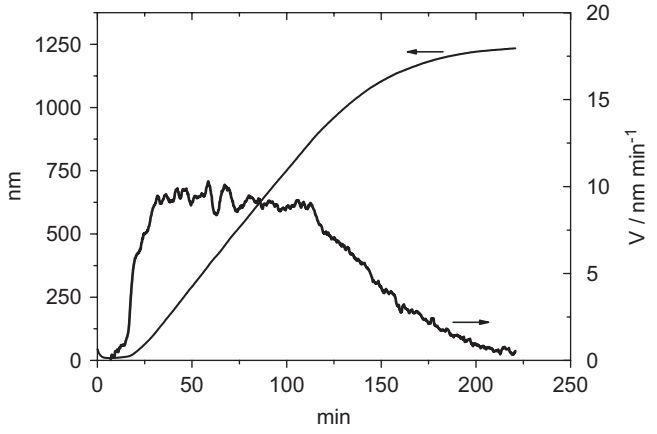

Fig. 1. Growth rate and thickness plots of ZnS thin films deposited on Au substrate. Solution composition: [TA] = 0.5 M, [$ZnSO_4$] = 0.01 M, [HCl] = 0.01 M and [CH_3COOH] = 0.3 M at 70 °C.

(1) An induction time, defined as the time interval from the addition of the last reactant (TA) to the start of film growth, is observed of about 10 min. During this time, the beginning of the decomposition of the thioacetamide (reaction (2)) and formation of the first crystalline centre takes place:

$$CH_3CSNH_2 + 2H_2O \rightarrow H_2S + NH_4^+ + CH_3COO^- \quad (2)$$

(2) A linear increase of the reaction rate, which corresponds with the growth of the most compact film. The growth of nucleation centres occurs during this period:

$$H_2S + Zn^{2+} \rightarrow ZnS\downarrow + 2H^+ \quad (3)$$

(3) A period of constant rate of growth, when a three dimensional film is growing after coalescence of the centres formed in the previous stage. There is a constant growth rate of 10 nm min^{-1}.

(4) Finally, a decrease of the growth rate. In this period, ZnS colloids are formed in the bulk of the dissolution, which does not adhere to the film so they do not contribute to its growth.

Similar succession of stages has been proposed by Eshuis et al. [14]. Other authors [15] propose reaction with two mechanisms, in the basic solution: one heterogeneous due to the reaction of the cations of Zn^{2+} adsorbed on the surface of the substrate, that gives rise to the formation of hydroxides and oxides; and a homogeneous mechanism due to deposition of aggregates of ZnS giving rise to films more stoichiometric and porous. Both mechanisms coexist in the films preparation of ZnS in the basic medium. In the acid medium, however, the formation of oxides and hydroxides is not favored by pH conditions, and the resulting films are more stoichiometric.

Crystallographic analysis of the films by X-ray diffraction (XRD) is shown in Fig. 2. The results correspond to films grown during 30 and 40 min on lime glass substrate previously activated by immersion in $SnCl_2$ (0.01 M). It is also shown the diffractogram of the second film after thermal treatment at 300 °C during 30 min in N_2 atmosphere. The results show a mixture of cubic (JCPDS 05-0566) and hexagonal (JCPDS 89-1363) phases, as observed by others [16,17]. Crystallinity of the films increases with deposition time.

Fig. 3 shows the optical spectra of the films grown after different deposition time (25, 30 and 40 min). Because the reference for these optical measurements was air, the transmittance and reflectance of the bare glass substrate have been included for comparison. Fig. 4 shows the absorption spectra of the films calculated from the data in Fig. 3, using Eq. (1). The absorption edge increases with the time of deposition, towards values close to the gap energy of ZnS (3.6 eV) [1]. For the film prepared