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Material analysis of PVD-grown indium sulphide buffer layers for Cu(In,Ga)Se$_2$-based solar cells

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Abstract

This paper is devoted to an X-ray photoelectron spectroscopy (XPS) study of Cu(In,Ga)Se$_2$ (CIGSe)/In$_2$S$_3$ structures. The indium sulphide layers are grown by physical vapor deposition (PVD) in which indium and sulfur are evaporated on the substrates at a temperature T_s. This as-deposited thin films are then heated at 200 °C for 1 min. A 12.4% efficiency champion cell has been achieved using this process. The XPS study reveals that copper diffuses from the chalcopyrite absorber towards the indium sulphide layer during this synthesis process. The amount of copper strongly depends on T_s; the higher T_s, the more copper is diffused. This observation is then correlated with the solar cell performance to conclude that a significant Cu-diffusion inhibits the formation of a high-quality junction between the Cu(In,Ga)Se$_2$ and the buffer layer.

Keywords: Indium sulphide layer; X-ray photoelectron spectroscopy; Physical vapor deposition

1. Introduction

The development of cadmium-free buffer layers grown by vacuum processes for Cu(In,Ga)Se$_2$ (CIGSe) solar cells is interesting with respect to environmental aspects and to the implementation in industrial production [1,2]. Indium sulphide is among the promising candidates to substitute the standard cadmium sulphide buffer layer grown by chemical bath deposition (CBD-CdS). Recently, it has been shown that the use of indium sulphide buffer layers grown by atomic layer deposition (ALD) leads to solar cell performances comparable to those with CBD-CdS [3,4]. During the last 3 years, our group has been developing a process to grow indium sulphide by physical vapor deposition (PVD). This process consists in the thermal evaporation of indium and sulphur onto the substrate kept at the substrate temperature T_s. These as-deposited structures are then in situ annealed at 200 °C. The solar cells realised with such indium sulphide buffer layers reach conversion efficiencies which are still lower than those reached with standard CBD-CdS. In order to improve the cell quality, it is necessary to progress in the understanding of the junction formation between the buffer and the absorber layer. We have observed that the solar cell performances are strongly dependent on T_s. In this paper, the attention is thus focused on the study, from the material point of view, of CIGSe/In$_2$S$_3$ structures grown at different values of T_s. The chemical nature of these interfaces is studied by X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. The CIGSe thin films

The CIGSe thin films (thickness~1.5 μm) are prepared by coevaporation of copper, indium, gallium and selenium on Mo-coated (thickness~0.5 μm) glass substrates at the Angstrom Solar Center, Uppsala, Sweden. They are grown on 12.5×12.5 cm^2 substrates, which are then cut down into smaller pieces (2.5×2.5 cm^2).

2.2. The indium sulfide thin films

The deposition of the two components of the buffer layer, indium and sulphur, takes place in a vacuum chamber at a

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pressure of 10^{-3} Pa. Indium is evaporated from a tungsten boat and sulphur from a Pyrex crucible. The thickness and deposition rates of the layers are controlled in situ by a quartz monitor. For the present study, the substrate temperature during the indium sulphide deposition is chosen to be T_s=130 °C and T_s=200 °C, all of the other conditions, such as the thickness of the buffer (50 nm) and the postdeposition annealing (200 °C for 1 min), are fixed.

2.3. XPS characterization

Depth profiles are performed using an LHS 12 Leybold XPS system (CNRS, University of Nantes). The experimental conditions are: Mg Kα1 X-ray excitation (10 kV accelerating voltage); constant pass energy of 50 eV; etching conditions: Ar^+ ion gun; pressure: 3×10^{-3} Pa; accelerating voltage: 9 kV. Using these conditions, the ion current density is 15 $\mu A \cdot cm^{-2}$.

As the S2p and the Se3p signals are superimposed, additional constraints are needed for the fitting program to separate the contributions of $S2p_{1/2}$, $S2p_{3/2}$, $Se3p_{1/2}$ and $Se3p_{3/2}$ and allow the quantification of sulfur and selenium. The S2p signal is considered as a single contribution with two peaks, separated by 1.2 eV. The area ratio between these two peaks is fixed equal to 0.5, corresponding to a 3/2:1/2 double level. The Se3p peak is treated following the same process and is considered as a single contribution with two peaks, separated by 6 eV. The value of the full width at half maximum (FWHM) of Se $3p_{3/2}$ and Se $3p_{1/2}$ core level signals is fixed as 2.1 eV [5]. Once the contributions of S2p and Se3p are well separated using these fitting constrains, sulphur and selenium can be quantified, as well as all the other elements.

3. Results

Fig. 1 shows the current–voltage curves of illuminated solar cells using PVD-In_2S_3 buffer layers deposited at T_s=130 °C (solid line) and at T_s=200 °C (dashed line). This graph shows the strong dependence of the solar cell parameters on the substrate temperature T_s. The increase of T_s from 130 to 200 °C leads to the decrease of the solar cell efficiency from 12.4% to 6.3% and affects all solar cell parameters [open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF)]. In order to gain knowledge about the origin of this phenomenon from the material point of view, the corresponding CIGSe/In_2S_3 structures were analysed by XPS.

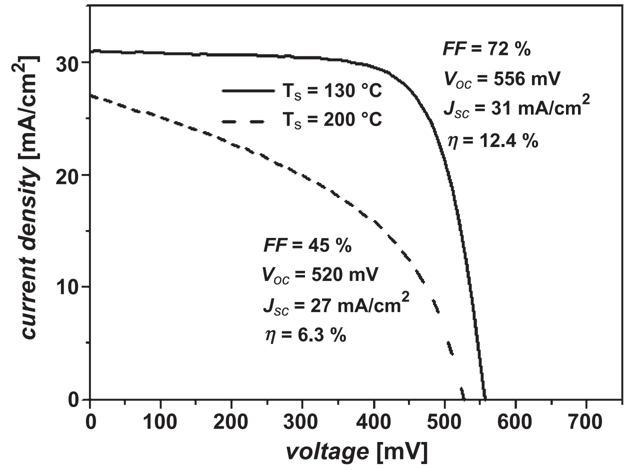

Fig. 1. Illuminated *J–V* charateristics of the solar cells with PVD indium sulfide buffer layers grown at T_s=130 °C (solid line) and at T_s=200 °C (dashed line).

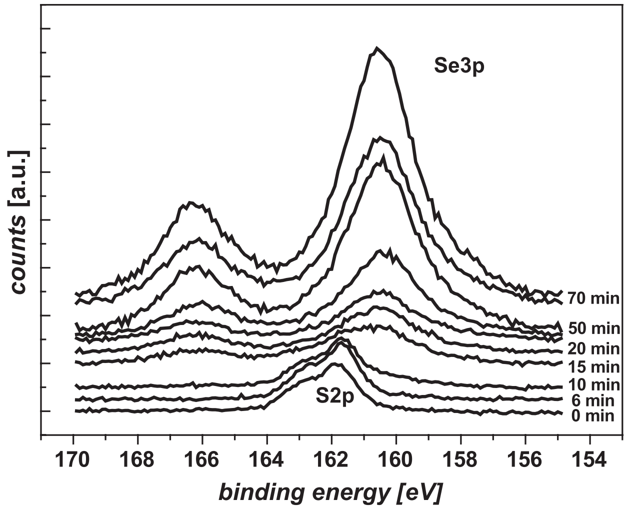

Fig. 2. XPS spectra of the S2p and the Se3p core level peaks before and after gradual etching of the CIGSe/In_2S_3 structure.

In Fig. 2, the spectra of the S2p and the Se3p core level signals after gradual sputtering of the CIGSe/In_2S_3 structure deposited at T_s=130 °C are plotted. Similar results are found for T_s=200 °C. During the first 6 min of etching, the only peaks appearing in the spectra are relative to the $S2p_{1/2}$ and $S2p_{3/2}$ levels at 163.1 eV and 161.9 eV, respectively. In the following stages of the etching, one can observe the increase of the $Se3p_{1/2}$ and $Se3p_{3/2}$ core level signatures at 166.3 and 160.3 eV, respectively. This evolution during the etching shows that the only chalcogen detected at the surface of the

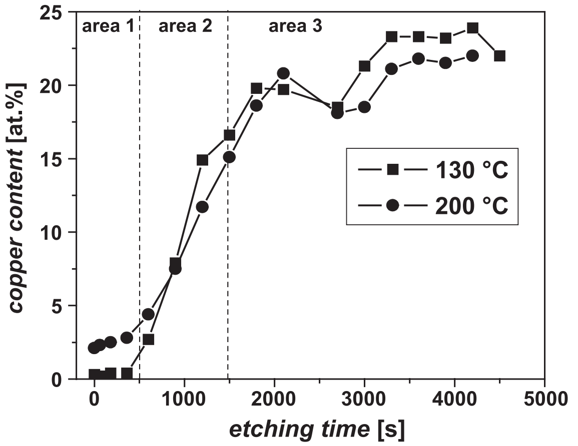

Fig. 3. Evolution of the copper content during the etching of CIGSe/In_2S_3 structures grown with T_s=130 °C (■) and T_s=200 °C (●).