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In-situ optical emission spectroscopy for a better control of hybrid sputtering/evaporation process for the deposition of $Cu(In,Ga)Se_2$ layers

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ABSTRACT

In this work, we have developed a hybrid one-step co-sputtering/evaporation $Cu(In,Ga)Se_2$ (CIGS) process, where Cu, In and Ga are sputtered simultaneously with the thermal evaporation of selenium, thus avoiding the H_2Se use. An appropriate control of the selenium flux is very important to prevent the target poisoning and hence some material flux variations. Indeed, the control of the CIGS composition must be rigorous to ensure reproducible solar cell properties. In this regard, a study of the correlations between plasma species and thin film composition, structure and morphology has been performed by varying power values and Se evaporation temperature in the 170 to 230 °C range. We started by studying the plasma with a powerful technique: optical emission spectroscopy, following light emissions from different plasma species: sputtered Cu, Ga, In but also evaporated Se. Hence, we determined the Se flow threshold avoiding target poisoning and the main parameter controlling the CIGS composition. Obviously, we also focused our interest on the material. We measured film composition and thickness of the samples with X-ray fluorescence and by energy dispersive X-ray. Different phases formed during the process were identified by Raman spectroscopy and X-ray diffraction. The optoelectronic cell properties showed promising efficiency of 10.3% for an absorber with composition ratios of $[Cu]/([In] + [Ga]) = 1.02$ and $[Ga]/([In] + [Ga]) = 0.44$. Finally, this work shows that we are able to control this hybrid process and thus the structure and composition of CIGS thin film for industrial transfer in the photovoltaic field.

1. Introduction

$Cu(In,Ga)Se_2$ (CIGS) thin film solar cells are a very promising technology for high energy conversion efficiency. Several techniques are used to synthesize CIGS absorbers. Magnetron reactive sputtering is an attractive deposition technique for depositing CIGS absorbers because of its potential for providing uniform coatings over large areas, thus offering the possibility for more competitive industrial scale-up [1,2]. Though, H_2Se gas which is usually used for the existing reactive sputtering approach is a very toxic compound [3]. In this regard, we have developed a hybrid one-step co-sputtering/evaporation CIGS deposition process, where Cu, In and Ga are sputtered together with the thermal evaporation of selenium, thus avoiding H_2Se. Nevertheless, for reactive and hybrid CIGS deposition process, an appropriate control of the selenium flux is very important to prevent target poisoning. The poisoning reduces the deposition rate drastically and may also cause arcing which can result in defects in the deposited absorbers [4]. Typically, the variation of the target self-bias voltage provides information about the evolution of the target state under different sputtering conditions. Two different modes, namely the metallic mode and the reactive mode, can be very well defined. An abrupt change in the discharge voltage is characteristic of a transition from elemental sputtering mode to the compound sputtering mode [4,5]. Therefore, the measurement of discharge voltage gives only a partial view of the sputtering process and does not directly provide information on the surface chemistry. On the other hand, optical emission spectroscopy is a powerful and non-contact tool to study the sputtering atmosphere, and for monitoring of the excited species present in the plasma processes used for film deposition.

In this work, a study of the correlations between plasma species and thin film composition and structure has been performed by varying power values and Se evaporation temperature. Obviously, we have also focused our interest on the solar cell performances. Our strategic interest is to use this approach for photovoltaic applications.

2. Experimental

2.1. Deposition process and plasma analyses

The CIGS deposition system developed with Alliance Concept consists of three magnetrons of 3-inch diameter targets and a selenium effusion cell developed with RIBER, mounted in a high vacuum chamber. The Cu, In and Ga fluxes are generated by RF-magnetron sputtering of Cu

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Table 1
Spectral characteristics of the species detected.

Species	Wavelength (nm)	Probability of transitions A_{ki} (s^{-1})
Ar	696.5	$6.39 \cdot 10^5$
In	410.2	$5.0 \cdot 10^6$
Cu	324.8	$1.39 \cdot 10^7$
Ga	417.4	$9.45 \cdot 10^6$
Se	891.3	–

(99.99%), In (99.99%) and Cu–Ga (99.99%) alloy targets. The vacuum system provides a lower pressure limit of 7×10^{-6} Pa. The growth parameters like target power, deposition temperature, pressure, rotational speed and selenization temperature can be controlled during the deposition.

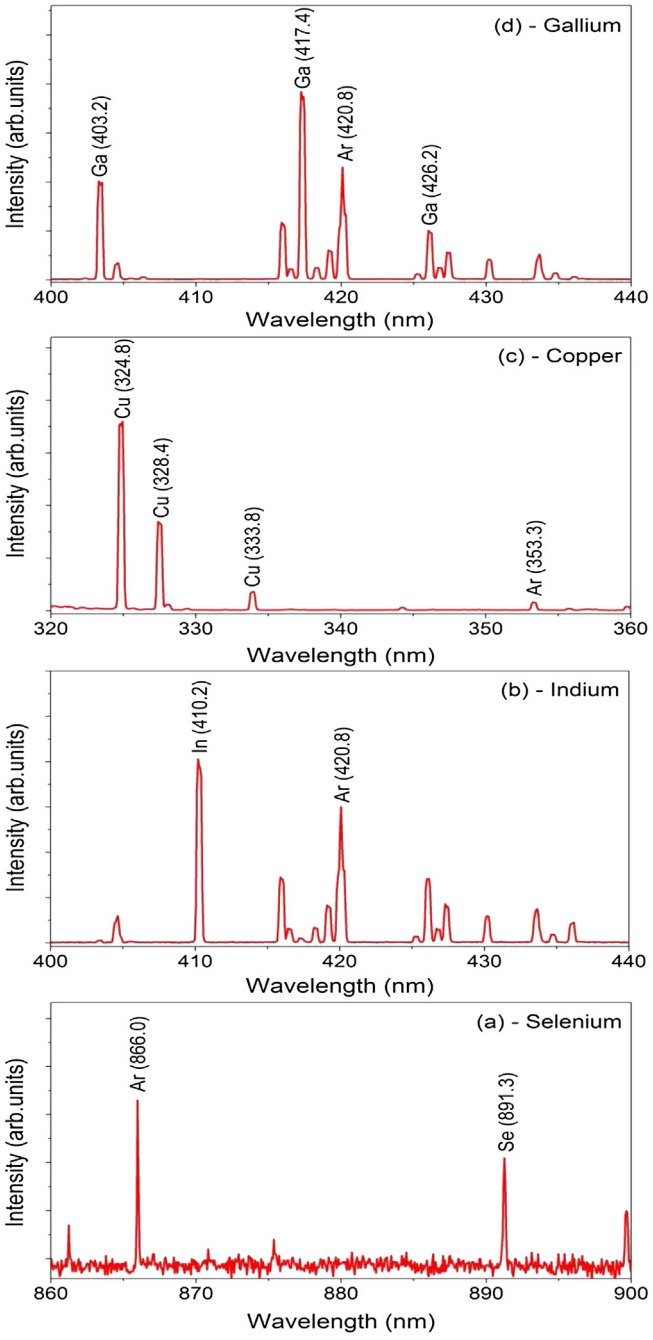

Fig. 1. Typical optical emission spectrum of Se at 200 °C (a). Typical optical emission spectrum of In (b), Cu (c) and Ga (d) in our conditions at room temperature.

Firstly, for each metallic target, a different experiment was performed. Cu, In and Cu–Ga targets have been sputtered separately with 60, 85 and 40 W of constant discharge power respectively. For all the experiments, the sputter pressure was held at 0.7 Pa while simultaneously evaporating Se. Temperature of selenium effusion cell has been increased intentionally in the 170–230 °C range during the process. Equally, different plasma species have been studied following light emissions with an optical emission spectroscopy (OES) system (Jobin-Yvon 270M spectrometer). The light was collected using an optical fiber situated outside a quartz window of the sputtering chamber and fixed in such a way that we detect the maximum of light emission. The spectra were recorded in the range of 200–900 nm and the spectral response of the detector was calibrated using a reference standard lamp.

Secondly, we have deposited CIGS absorbers with different [Cu]/([In] + [Ga]) ratios. The substrates were prepared by coating 5×5 cm^2 soda lime glass with 0.8 μm thick Mo layers by DC magnetron sputtering device using rectangular Mo target. These substrates were then introduced in CIGS deposition reactor and heated to a set-point temperature of 590 °C. This temperature was regulated by three thermocouples located above the substrate holder. After Cu, In and Cu–Ga targets have been sputtered simultaneously with the thermal evaporation of selenium. Indium and copper–gallium powers have remained fixed at 85 and 42 W respectively and Cu power has been increased intentionally in the 25–32 W range, in order to tune the $Cu(In_{1-x},Ga_x)Se_2$ layer composition. Temperature of selenium effusion cell has been fixed at 190 °C during the process. Typical growth rates were 1 μm/h and the thicknesses of layers were above 2 μm. Finally, we completed the cells with 50 nm of chemical bath deposited CdS buffer layer, and 400 nm of sputtered iZnO/ZnO:Al layers. The cells of 0.1 cm^2 were defined by mechanical scribing.

2.2. Material and device characterization

The composition of the CIGS layers was examined by X-ray fluorescence using a XRF-Fisherscope. These measurements were performed on several different parts of the samples in order to confirm that the results do not depend on a specific part of the sample and confirmed by energy dispersive X-ray (EDX) (Zeiss Ultra 55). EDX measurements were carried out at 20 keV operating voltage and the Cu, In, Ga and Se lines were used for quantification. Structural changes of the absorbers were characterized by X-ray diffraction (XRD) measurements using the classical Bragg–Brentano setup at a PANalytical Empyrean X-ray diffractometer, using Cu-$K_{\alpha 1}$ (0.1541 nm) radiation operated at 40 kV (40 mA) and by Raman spectroscopy using a Horiba Jobin Yvon LabRam instrument with a 532 nm laser and an ×100 objective. Optoelectronic properties of the solar cells have been measured using a solar simulator with AM 1.5, 100 mW/cm^2 light intensity and at room temperature.

3. Results and discussion

3.1. Plasma analyses by optical emission spectroscopy

For reactive magnetron sputtering and hybrid one-step co-sputtering/evaporation process, the evaporated selenium might react with growing film but also this sputtered targets. The formation of a compound at target surface, called target poisoning, can modify the electrical characteristics of the discharge, which commonly lead to drop of deposition rate and loss of film composition control. The compound sputtering mode should then to be avoided. Since this also affects the emission intensities of excited species from the plasma [4], we characterize the hybrid process used for CIGS solar cell deposition, by following characteristics emission lines of different species present in the plasma. We distinguished at least one line per element and selected the most intense and isolated ones. The different lines followed in this study are taken from NIST database [6] and reported in Table 1. Typical optical emission spectrum for the four elements is shown in Fig. 1.

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