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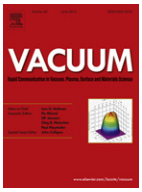

Post-selenization of stacked precursor layers for CIGS

Zs. Baji [a,*], Z. Lábadi [a], Gy. Molnár [a], B. Pécz [a], A.L. Tóth [a], J. Tóth [c], A. Csik [c], I. Bársony [a,b]

[a] Institute of Technical Physics and Matrials Science (MFA), Research Centre for Natural Sciences, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary
[b] Doctoral School of Molecular- and Nanotechnologies, Faculty of Information Technology, University of Pannonia, Egyetem u.10, H-8200 Veszprém, Hungary
[c] Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI), P.O. Box 51, H-4001 Debrecen, Hungary

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In this study the possibility of the fabrication of CIGS layers from stacked precursors with selenization is examined. Different sequences of precursor layers and two different selenization methods were applied, in order to establish the optimal order of Cu, In and Ga layers in the precursor layer stack. The obtained CIGS films were studied by different micro- and surface analysis methods (TEM, SEM, EDS, XRD, SNMS, XPS). Since the evaporation of a Se layer and post-annealing does not result in a homogeneous CIGS layer, the appropriate selenization must be accomplished in Se-vapour.

1. Introduction

Chalcopyrites are perhaps the most promising materials as absorbers in thin film solar cells. The band gap of $CuInSe_2$ is $E_g = 1$ eV, that of $CuGaSe_2$ $E_g = 1.7$ eV. Therefore, a manipulation of the band gap between these two extremes, thus the preparation of a wide variety of absorber materials is possible by simply adjusting the Ga/In ratio [1].

$CuIn_xGa_{1-x}Se_2$ (CIGS) films have been fabricated by a number of methods. The most successful, but also the most complex technique proved to be the co-deposition of all components from individual sources [2]. This approach resulted in the highest reported conversion efficiency solar cells with 20.3% [3]. On the other hand this method also implies the most complex and expensive procedure, where an economical usage of the source materials is impossible. Another disadvantage is that it requires an incredibly well controlled processing technique [4].

Post-selenization of precursors is a low cost alternative that does not require expensive apparatus. It can be achieved by the use of Se vapour, diethylselenide or H_2Se. The latter is highly toxic, therefore its use rises environmental and health concerns and it is very complicated to handle [5]. Copper, gallium and indium precursors may be selenized to create CIGS material. In that case it is of great advantage that no precise control of the parameters is needed, as the metallic precursors only absorb the amount of selenium required by the stoichiometry [6–8]. An additional advantage of the technique is that Se diffuses into the Mo back-contact of the solar cell. Thereby $MoSe_2$ is formed at the boundary of the active layer and the back-contact, which leads to an improved contact between the two materials [9].

The chemical reactions that occur during the selenization of precursors may take a number of routes, which also depend on the precursor structure. In the case of selenization of metallic copper, indium and gallium depending on time and temperature a certain order of the chemical reactions can be observed. First the binary phases form, then the CuSe phase, and finally the $CuInSe_2$ and $CuGaSe_2$ phases that react to form $Cu(InGa)Se_2$ [10–12].

It was indicated [13,14] that the morphology of the as deposited CIG layer may have a crucial role in the resulting morphology, thus the overall quality of the final CIGS film after selenization. Both evaporated and sputtered CIG layers are inhomogeneous with a rough surface, which would deteriorate the quality of the resulting films.

Another often mentioned disadvantage is that gallium tends to diffuse near the back-contact at the high temperatures during selenization, while the top layers become richer in indium. This finally results in an adverse phase separation of CIS and CIGS material, which reduces the device efficiency.

2. Motivation

The purpose of our research is to study the CIGS material and the method of post-selenization, as the detailed knowledge of the

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* Corresponding author. Tel.: +36 1 3922222; fax: +36 1 3922226.
E-mail address: baji.zsofia@ttk.mta.hu (Zs. Baji).

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processes that take place during layer preparation is prerequisite to the fabrication of device quality absorber material. In our previous studies [15] we examined flash evaporated and post-selenized layers and found that even a rough morphology of precursor metals results in homogeneous CIGS layers after selenization. On the other hand these layers showed low mechanical stability and adhesion to the substrate underneath. The aim of the present work is to analyse whether sequentially evaporated precursors could also result in homogeneous layers with perhaps improved mechanical properties.

Another disadvantage of the flash evaporation method [15] was that the thickness of the deposited precursor material was <400 nm due to the limited size of the evaporation source, which resulted in ca. 800 nm of CIGS material. In the present work we attempted to determine how thick precursor layers could be selenized reliably and what the optimal selenization method is.

3. Experimental

CIGS layers were deposited by the selenization of metallic precursors. To examine the effect of the order of the layers in the stack we deposited them in all possible deposition sequences. Si and glass substrates were used, both cleaned in cc.HNO_3 and high purity water before layer deposition.

The sputtering and evaporation took place in a flexible research tool optimized for the manufacturing of $Cu(InGa)Se_2$ based solar cell modules. Mechanical movement, gas pressure and composition, DC electric supply and additional pulse parameters are computer controlled.

Mo layers were deposited and target characteristics monitored by pulsed DC magnetron sputtering (deposition chamber manufactured by Energosolar, Hungary), with 10 μs period length and 10% duty factor from a 114×440 mm^2 sized metallic Mo target at a 60 mm working distance. Under the target of the substrate was moved at a speed of 50 mm/s bidirectionally. The electric supply unit can work both in DC and adjustable pulse mode. Before opening the Ar valves the pressure in the vacuum chamber was typically $8 \cdot 10^{-7}$ mbar. Depositions and target characterization were made at $6 \cdot 10^{-3}$ mbar working pressure (measured by Edwards WRG − S type Gauge) with a total gas inlet of 50 sccm. The target power in power controlled mode was 750 W and the target voltage 300–315 V. We applied no substrate bias and no preheating.

Cu layers were deposited from a Cu target in the same magnetron sputtering equipment under the same conditions. The target power was 250 W, the target voltage 290 V.

The temperature during In evaporation was $T = 1040$–1060 °C and the pressure $p = 2 \cdot 10^{-5}$ mbar, In the case of the Ga evaporation $T = 1115$–1141 °C and $p = 1.7 \cdot 10^{-5}$ mbar. Table 1 summarizes the prepared samples.

Two different approaches were applied for the selenization of the consecutively deposited precursors. The first consisted of evaporation of selenium on top of the layer stack and an additional annealing so that the Se could diffuse into the layers, and the precursors could transform into CIGS layer. This process took place in a vacuum chamber designed for this purpose. The background pressure was $p \sim 10^{-6}$ mbar. The Se-source was a resistivity heated W-boat. The estimated temperature of the source was $T = 800$ °C. Se pellets were completely evaporated during the ramp-up and hold period (1 minone minute each) at the final boat temperature. Thereby the thickness of the "selenium source layer" on the differently stacked precursors is expected to be constant. The substrate temperature was $T = 430$ °C during evaporation, followed by a 20 min annealing step at the same temperature.

The other method involved the sealing of the samples into glass ampoules evacuated to ca. 1 Pa and a subsequent annealing of the precursors in Se atmosphere for 15 min at $T = 500$ °C, where the partial pressure of Se is about 1 Pa.

The X-ray diffraction (XRD) measurements were performed with Cu K radiation using a Bruker AXS D8 Discover horizontal X-ray diffractometer equipped with Göbel mirror and a two dimensional GADDS detector system. The beam diameter was about 500 m.

The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements were carried out in a LEO 1540 XB microscope equipped with a Schottky field emission gun, Gemini lens system and in-lens detector.

The depth profiles were measured with an INA-X type secondary neutral mass spectroscopy (SNMS) equipment (product of Specs GmbH, Berlin). For the sample bombardment and post ionization Ar plasma was used.

Transparent specimens for transmission electron microscopy (TEM) investigations were prepared by mechanical cutting and polishing, followed by Ar + ion milling at 10 keV ion energy. Cross sectional TEM samples were inserted into special Ti discs of 3 mm, and thinned from both sides. In order to remove the thin surface layer damaged during high energy ion milling from both sides of the specimens, the process was finished at 2.5–3 keV ion energy. Further details about sample preparation can be found in [16]. Conventional electron microscopy was carried out in a Philips CM 20 microscope at 200 keV, which is equipped with a NORAN EDS.

The XPS measurements were performed using conventional excitation of non-monocromated Al X-rays. The XPS spectra originated from a few representative depth point of the CIGS layers etched in the SNMS plasma. The specimens from the SNMS measurement chamber to the XPS measurement chamber were moved in vacuum. The XPS machine (product of SPECS, Germany) was working in the fixed analyser transmission mode. The chemical states of the CIGS layers were assigned by the help of the XPS binding energy database from the National Institute of Standards and Technology (USA). The XP spectrometer energy scale was calibrated with the relative calibration method measuring Cu, Au and Ag XPS lines and using standard binding energy values determined at the National Physical Laboratory (UK).

Table 1
Summary of sample parameters.

1	Mo	In	Ga	Cu	Selenization with Se evaporation and annealing
2	Mo	Ga	In	Cu	Selenization with Se evaporation and annealing
3	Mo	Cu	In	Ga	Selenization with Se evaporation and annealing
4	Mo	Cu	Ga	In	Selenization with Se evaporation and annealing
5	Mo	In	Ga	Cu	Selenization with Se vapour
6	Mo	Ga	In	Cu	Selenization with Se vapour
7	Mo	Cu	In	Ga	Selenization with Se vapour
8	Mo	Cu	Ga	In	Selenization with Se vapour

4. Results and discussion

4.1. *Precursor morphology after evaporation*

Fig. 1 shows the SEM micrographs (left) and the Energy Dispersive Spectra, the EDS-maps of the precursors (right). It is evident on almost all samples that the precursors completely covered the substrates. The average grain size of the samples is 100–200 nm. The importance of the deposition order of the precursor metals is revealed by the comparison of the micrographs.

The first row in Fig. 1 shows the morphology of sample 1. The surface is scattered with 0.5–1 μm sized islands. On a larger scale