Five-source PVD for the deposition of Cu(In$_{1-x}$Ga$_x$)(Se$_{1-y}$S$_y$)$_2$ absorber layers

Mario Gossla[a,b,*], William N. Shafarman[a]

[a]*Institute of Energy Conversion, University of Delaware, Newark, DE 19716, USA*
[b]*Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany*

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Abstract

A new five-source PVD system was developed for the deposition of Cu(In$_{1-x}$Ga$_x$)(Se$_{1-y}$S$_y$)$_2$ (CIGSS) thin films. The system allows the independent and controlled deposition of all five elements. In the first part of this paper, we investigate CIGSS formation via a double-layer process of depositing a Cu–S or Cu–Se layer on top of an In–Ga–Se or In–Ga–S layer, respectively. Incomplete intermix of two different chalcopyrite species is observed. In one case, additionally, an enrichment of Ga at the interface between those two layers is observed. In the second part of the paper, films within the complete compositional range of $0<x<1$, and $0<y<1$ were deposited on Mo-coated soda lime glass. The incorporation of sulfur in the films depends strongly on the sulfur concentration in the vapor phase, the substrate temperature, and the Cu/In ratio. The films were analyzed by means of EDS, XRD, Rutherford backscattering spectroscopy (RBS), and AES. Solar cells were fabricated and characterized by I–V measurements. We show results for a series of solar cells deposited group-III rich on the equal-gap line $E_{\text{gap}}=1.5$ eV for various S and Ga contents. The best cells show an efficiency near 10%. The highest open circuit voltage is 854 mV at sulfur contents of S/(Se+S)=0.26.
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1. Introduction

The multinary compound semiconductor Cu(In$_{1-x}$Ga$_x$)(Se$_{1-y}$S$_y$)$_2$ is a viable option as an absorber material for thin film solar devices. Typically In-rich deposited Cu(In$_{1-x}$Ga$_x$)Se$_2$ films with band gaps of 1.2 eV [1], or Cu-rich deposited Cu(In$_{1-x}$Ga$_x$)S$_2$ films with band gaps of 1.5 eV are investigated in solar cell deposition [2]. Both of these processes use only one of the chalcogen species, either selenium, or sulfur, respectively. With respect to higher band gaps, which should lead to improved module performance and could enable the development of thin film based tandem solar cells, the use of sulfur and selenium together should be an interesting option. For thin film tandem cell photovoltaics, a top cell with a band gap in the range 1.6 eV≤E_g≤1.9 eV and

a small subband gap absorption is needed. While the selenium system is limited to 1.7 eV, the use of both selenium and sulfur offers a band gap range from 1.0 up to 2.4 eV.

For the deposition of homogeneous CIGSS, sequential processes, in which metal or binary layers were deposited at low temperatures and then reacted in mixed hydride gases or elemental vapors, were ruled out due to difficulties in attaining uniform incorporation of Ga and In [3]. For complete control of the incorporation of sulfur and selenium, an independent deposition of both species would be favorable. Therefore, in the first part of this paper, we report a double-layer deposition process with the sulfur and the selenium deposited in different layers and investigate the intermixing of the chalcogen species. The objective of these processes was to separate the S and Se depositions so the precise control of the chalcogen fluxes was not critical. In the second part of the paper, we will present results of solar cells with band gaps of 1.5 eV, deposited In-rich in a single step process varying the Ga, and S content of the absorber layers.

* Corresponding author. Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany. Tel.: +49 3641 947 357; fax: +49 3641 947 302.
E-mail address: physics@gossla.net (M. Gossla).

2. Experimental details

A new deposition system has been designed and built to deposit CIGSS films by five-source elemental thermal evaporation. An illustration showing the layout is given in Fig. 1. Boron nitride crucibles are used as sources for Cu, In, and Ga. These crucibles are heated in a boron nitride furnace using tantalum wire resistive heaters and multiple layers of thermal shielding. The sources are mounted in stainless steel jackets. While these metal sources typically operate at temperatures between 1100 and 1400 °C, the evaporation temperatures of S and Se are between 100 and 350 °C. To minimize thermal cross-talk, the distance between the hot metal sources and the much colder chalcogen sources was increased by mounting them below the metal sources. Additionally, a new design for these sources was developed to facilitate precise thermal control. The crucibles for the S and Se sources consist of stainless steel bottles connected to tubes that enable the S and Se vapor to pass between two of the metal sources. The tubes are heated radiatively by the metal sources. The S and Se sources have a tapered shape to fit snugly in the stainless steel heater, which is heated by an electrically insulated tantalum wire. A water-cooled jacket surrounds each source to decrease the thermal response time and therefore enhance control at low temperatures. The nozzles from all five sources are at the same height, 0.25 m from the substrate.

The entire setup is mounted on a base plate in a bell jar system using a water-cooled stainless steel bell jar. All components of the system are fabricated from stainless steel or are Ni-plated to resist corrosion from the S vapor. The system is pumped by a diffusion pump (2400 l/s) equipped with a cold trap. The base pressure is 7×10^{-7} hPa. The chamber includes a chilled Meissner trap to getter excess sulfur. A crystal quartz monitor is used to monitor the overall deposition rate. The substrate holder can be heated up to 575 °C. Typically, nine substrates with dimensions 25×25 mm^2 are coated with CIGSS at the same time. One substrate has an embedded thermocouple to monitor and contro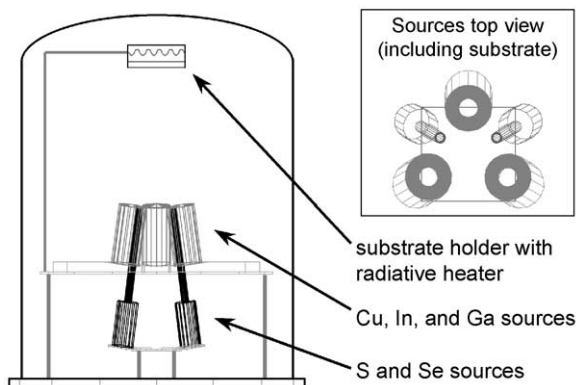l the substrate temperature. For the fabrication of solar cells, Mo-coated soda lime glass is used as the substrate. The CIGSS deposition rate was controlled by the source temperatures and monitored after each deposition by the mass loss of each evaporation crucible. Similarly, mass gain is used to estimate the thickness of each deposited film. For fabrication of devices, a CdS layer was deposited by a chemical bath process, followed by sputtered i-ZnO and ITO layers and evaporated Ni/Al grids. Cells with area 0.5 cm^2 were defined by mechanical scribing.

The CIGSS films were analyzed by means of XRD, Auger depth profiling, and Rutherford backscattering spectroscopy (RBS). For XRD measurements, a two-circle goniometer in Bragg–Brentano geometry with Cu K$_\alpha$ radiation was used. The spectra were analyzed by a Rietveld algorithm using the BGMN software [4]. The Auger depth profiling was performed at NREL. Films from the double-layer deposition were analyzed by Rutherford backscattering spectroscopy at the 3-MeV Tandetron accelerator JULIA in Jena.

3. Results and discussion

3.1. Double-layer depositions

Two different processes for a double-layer deposition were investigated. The goal was to deposit an approximately 2.5-μm-thick Cu-rich CIGSS film with uniform composition through the film. The films were deposited on Mo-coated soda lime glass. In process P1, a pure In–Ga–Se film was deposited first at 350 °C with Ga/(In+Ga) ratio of 0.29 and a Se/(In+Ga) ratio of 3. On top of this layer, a Cu–S film was deposited at a temperature of 550 °C, with a S/Cu ratio of 18. In process P2, first an In–Ga–S film was deposited at 250 °C, with Ga/(In+Ga) ratio of 0.28 and S/(In+Ga) ratio of 19. In this case, the second layer was a Cu–Se film deposited at 550 °C with a Se/Cu ratio of 2. The deposition times for the group-III containing layers was 60 min, and for the Cu-chalcogen layers, it was 90 min. Fig. 2 shows an Auger depth profile (a), and an RBS spectra (b) of a film from process P1. From both Auger depth profiling and RBS, a triple-layered structure can be derived. The Auger depth profile shows the nonuniform elemental distribution of all five elements. The sulfur on top and the selenium in the bulk of the film are clearly separated. While the Cu diffuses into the In–Ga–Se film and is distributed in this layer homogeneously, it shows a higher concentration at the surface of the film. The Ga accumulates in the interface between the S- and Se-rich layers. The RBS spectra given in Fig. 2b can be simulated by a simplified system consisting of three layers with constant composition which are partially interdiffused. The surface is covered by a 470-nm-thick Se-free $Cu_{0.30}In_{0.23}S_{0.47}$ layer, a 230-nm-thick $Cu_{0.27}In_{0.08}Ga_{0.24}Se_{0.04}S_{0.37}$ layer forms the interface between the Se-free and the following Se-rich layer with a thickness of 2170 nm and a composition of $Cu_{0.29}In_{0.16}Ga_{0.10}Se_{0.40}S_{0.05}$. Due to their similar masses, Cu and Ga are not resolvable in those inhomogeneous films by RBS,

Fig. 1. Illustration of the layout of the five-source CIGSS evaporation system.