Solar Energy 174 (2018) 793–802

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Influence of process parameters on the properties of pulsed laser deposited $CuIn_{0.7}Ga_{0.3}Se_2$ thin films

Christiana Nicolaou[a], Anna Zacharia[b], Grigorios Itskos[b], John Giapintzakis[a,*]

[a] Department of Mechanical and Manufacturing Engineering, University of Cyprus, 75 Kallipoleos Av., PO Box 20537, 1678 Nicosia, Cyprus
[b] Experimental Condensed Matter Physics Lab, Department of Physics, University of Cyprus, 75 Kallipoleos Av., PO Box 20537, 1678 Nicosia, Cyprus

ARTICLE INFO

Keywords:
Pulsed laser deposition
Growth of $CuIn_{0.7}Ga_{0.3}Se_2$ films
Electrical resistivity
Carrier concentration
Photoluminescence
Absorption coefficient

ABSTRACT

This work reports on the influence of pulsed laser deposition growth parameters on the properties of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films. Polycrystalline $CuIn_{0.7}Ga_{0.3}Se_2$ thin films were grown on soda-lime glass substrates under various growth conditions. Morphological, compositional, structural, electrical and optical properties of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films were investigated as a function of laser fluence, background gas and substrate temperature. A threshold of laser fluence, 0.8 J/cm^2, and background pressure, 0.01 mbar, determined through a systematic parametric investigation, for obtaining stoichiometric films. A minor secondary phase of $Cu_{2-x}Se$ was observed by X-ray diffraction, and found to gradually diminish with increasing deposition temperature. The film grown at 500 °C shows the purest $CuIn_{0.7}Ga_{0.3}Se_2$ chalcopyrite phase. The electrical properties of the films, i.e., dark resistivity, carrier concentration and mobility, are shown to be mostly affected by the $Cu_{2-x}Se$ phase and the crystal quality of the films. All films exhibit high absorption coefficients of ~2–3 * 10^4 cm^{-1} in the vicinity of the band-edge; a blue shift of the energy gap with deposition temperature is attributed to the relaxation of the lattice strain, as corroborated by the respective shift of (1 1 2) peak of the XRD patterns. The monotonic increase of the photoluminescence intensity accompanied by the concomitant decrease of the emission linewidth and Stokes shift indicate an improvement in the material quality and uniformity as deposition temperature increases in accordance with the structural and electrical measurement findings. Long PL lifetime of ~50 ns is measured in the band-edge region for the film grown at 500 °C, suggestive of a single phase material with low defect density. Our results overall indicate that high-quality, stoichiometric $CuIn_{0.7}Ga_{0.3}Se_2$ thin films can be obtained using pulsed laser deposition, a rapid single-step growth method that eliminates the need for post-selenization.

1. Introduction

$CuIn_{1-x}Ga_xSe_2$-based thin film solar cells have attracted considerable attention by the research community over the last decades due to the promising potential for the fabrication of highly efficient thin film solar cells and modules. A tremendous evolution of the efficiency has been reported through the years with an even steeper increase since 2014 (Jackson et al., 2016), reaching the record efficiency of 22.9% in laboratory scale (SolarFrontier, 2017), thus exceeding the record value of multi-crystalline Si-based solar cells.

Chalcopyrite $CuIn_{1-x}Ga_xSe_2$ (CIGS) quaternary compound is a p-type, direct semiconductor used as the absorber layer in the cell's structure. The tunable energy gap of CIGS varies from 1.04 to 1.68 eV as the Ga composition ratio x changes from 0 to 1, and lies within the maximum theoretical efficiency region of AM1.5 solar irradiation (Romeo et al., 2004). The superior absorptivity of ~10^5 cm^{-1} in the visible spectrum gives the ability of effectively reducing the thickness of the absorber (Schock and Noufi, 2000), thus reducing raw material needs and cell volume.

A variety of methods have been employed to deposit CIGS films, such as electrodeposition (Kang et al., 2010), pulsed electron deposition (PED) (Rampino et al., 2013; Pattini et al., 2013). (Mazzer et al., 2016), thermal co-evaporation (Marudachalam et al., 1997; Zhang et al., 2012, 2009) and sputtering (Yu et al., 2013; Liu et al., 2012; Yan et al., 2014), with the latter two being the most widespread methods for obtaining high-performance solar cells. These methods often require a post-selenization treatment and precise control of the growth conditions in order to achieve the desirable composition of CIGS film. However, handling toxic Se-containing vapors raises concerns about production safety and environmental effects.

Pulsed laser deposition (PLD) is well established as an efficient deposition method for multi-component films due to the stoichiometric

* Corresponding author.
E-mail address: giapintz@ucy.ac.cy (J. Giapintzakis).

https://doi.org/10.1016/j.solener.2018.09.027
Received 25 May 2018; Received in revised form 4 September 2018; Accepted 12 September 2018

transfer of the target material to the deposited film (Schou, 2009). In the case of the quaternary Cu(In,Ga)Se_2 material, PLD stands out from other deposition techniques as stoichiometric films can be obtained without post-selenization. Furthermore, crystalline films can be produced at low deposition temperatures, due to the non-equilibrium process occurring during PLD growth. Along with the high deposition rates and its simplicity of use, PLD can be considered a fast, simple and low cost method for depositing CIGS films. A single-step, fast process is vital for the thin film photovoltaic industry, as this would reduce the manufacturing time and cost. The advantageous figures of PLD could bring the technique in the forefront as an excellent tool to fabricate CIGS solar cells. Recent developments on the scalability of PLD systems have reached the potential of large-area deposition with thickness uniformity, thus enabling the fabrication of mini-modules. State-of-the-art PLD systems, that are now commercially available, enable the deposition of high-quality thin films on various substrates, up to wafer diameter of 200 mm (Blank et al., 2013).

Despite the advantages of PLD over other deposition techniques, few published reports exist on the growth of CIGS films using PLD (Levoska et al., 1994; Kindyak et al., 1996) and only a handful of those have studied the correlation between the growth parameters and the properties of PLD-grown CIGS films, towards their rational optimization in order to achieve high-quality CIGS films (Jo et al., 2010a, 2010b; Tsai et al., 2013). This work reports on the systematic investigation of the effect of PLD growth parameters on the properties of $CuIn_{0.7}Ga_{0.3}Se_2$ thin films deposited on soda-lime glass substrates. The influence of the growth conditions of CIGS films is investigated through a comprehensive characterization of structure, composition and morphology. In addition, electrical and optical measurements of CIGS films have been performed in order to study the transport and optical properties of the films. The optimum PLD growth conditions for CIGS films are identified based on an overall assessment of film characteristics.

2. Experimental

CIGS films were deposited on soda-lime glass (SLG) substrates by PLD using a KrF excimer laser source ($\lambda = 248$ nm, $\tau \leq 25$ ns) in a high-vacuum chamber. The laser beam was driven through an arrangement of mirrors and focused by a focal lens on a polycrystalline $CuIn_{0.7}Ga_{0.3}Se_2$ (*Testbourne, England*) target at an incident angle of 45° inside the chamber. The target rotation during the irradiation ensured a uniform ablation of the target surface. The substrate was placed parallel to the surface target at a fixed distance of 4.5 cm. The deposition was carried out in the presence of background gas after the chamber was evacuated at a base pressure of 4×10^{-6} mbar. Argon (Ar) was used as background gas to confine the plume. The number of pulses and the repetition rate were kept constant at 6000 and 10 Hz respectively, for all depositions. Laser fluence, Ar background pressure and substrate temperature were systematically investigated in order to achieve the optimum growth conditions for high quality CIGS films. Prior to deposition, the substrates were ultrasonically cleaned with a sequence of organic solvents.

Structural properties and crystallinity of the films were studied by X-ray diffraction (*SmartLab RIGAKU, Cu Kα, λ = 1.5405 Å*). Morphology and chemical composition of the films were determined by scanning electron microscopy (*SEM Tescan Vega LSU*) and energy dispersive X-ray spectroscopy (*Jeol Bruker Nano 129 eV, XFlash 5010 detector*), respectively. The electron accelerating voltage of the EDS source was adjusted at 20 kV, corresponding to a penetration depth of 1.5 μm, which was larger than the thickness of the films. The thickness of the films was measured with a stylus profilometer. Topography and surface roughness were probed via atomic force microscopy (*AFM, Agilent Technologies*) scanning a $20 \times 20\ \mu m^2$ area within the film's surface. The electrical resistivity ρ, and carrier concentration n, of the films were measured at room temperature using the Van der Pauw method and Hall Effect measurement. Au wires were directly attached on the films' surface using conductive silver paste. A current of 20 μA and a magnetic field of 6 T were applied for the electrical measurements. Hall mobility was calculated by the following equation:

$$\mu = \frac{1}{\rho n e}. \tag{1}$$

Optical transmission was recorded using a triple-detector spectrophotometer (*Perkin Elmer, Lamda 1050*) covering the 200–3000 nm spectral range. The measurements allow the determination of the transmissivity T of the films as the ratio of the transmitted light intensity I_T to that of the incident intensity I_0:

$$T = \frac{I_T}{I_0} \tag{2}$$

Reflectivity experiments were performed using the output of a 450 W Xe Arc broadband lamp spectrally filtered by a double monochromator and detected by a photolumultiplier tube.

The absorption coefficient α of the films can then be estimated (Fox, 2010) through the relationship:

$$T = (1-R)^2 e^{-\alpha l}, \tag{3}$$

where T is the transmissivity and R is the reflectivity, measured by the aforementioned optical experiments, and ℓ is the film thickness.

Steady-state photoluminescence (PL) was excited via a 785 nm laser diode module (*Coherent StingRay*) with a power density of ~50 mW-cm^{-2} and detected by a high resolution spectrometer (*0.75 m Acton750i Princeton*) equipped with a liquid-nitrogen-cooled InGaAs array detector. Time resolved PL was recorded on a FluoroLog FL3 Horiba Jobin Yvon spectrofluorimeter using a time correlated single photon counting (TCSPC) method. The PL was excited by a 785 nm pulsed laser diode (DeltaDiode-785L) with a pulse width of ~80 ps. The average PL lifetime t_{avg} of the PL decays was calculated from the relation:

$$t_{avg} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}, \tag{4}$$

where τ_i are the decay times extracted from multi-exponential fits of the PL transients and A_i the corresponding decay amplitudes.

3. Results and discussion

3.1. Impact of laser fluence

The fluence of the irradiation was regulated by the laser energy and the spot size to obtain values from 0.4 to 1.4 J/cm^2. Fig. 1 shows the compositional ratios of the films deposited at 300 °C in Ar atmosphere of 0.01 mbar obtained by EDS measurements. The compositional ratios of a stoichiometric transfer from the target to the film are denoted on Fig. 1 with the dashed lines and are the following: CGI = Cu/(Ga + In) = 1, GGI = Ga/(Ga + In) = 0.3, IGI = In/(Ga + In) = 0.7 and Se/M = Se/(Cu + Ga + In) = 1. As the figure shows, all films are slightly In-rich and Ga-poor with respect to the target stoichiometry. The GGI ratio of the films is ~0.26, which lies within the range of high-efficiency cells (Contreras et al., 2005). Nearly stoichiometric films are obtained as the fluence increases with a lower threshold at 0.8 J/cm^2. The films grown at lower fluences (0.4 and 0.6 J/cm^2) are Se-rich and Cu-poor. The magnitude of the ablation yield is determined by the cohesive energy of an element (Schou, 2009) and tends to be higher for elements with low cohesive energy. In this case, Se is more readily extracted from the target as it has the lowest cohesive energy (2.46 eV/atom), while Cu having the highest cohesive energy (3.49 eV/atom) is much less volatile. Low fluence leads to pure evaporation of the elements (Schou, 2009) with preferential evaporation of Se and unfavorable evaporation of Cu, resulting in Se-rich and Cu-poor films. Similar results have also been observed for Cu_2ZnSnS_4 (CZTS) absorber, which consists of earth-abundant elements (Cazzaniga et al., 2017). Generally,