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Impacts of pulsed-laser assisted deposition on CIGS thin films and solar cells

Tokio Nakada [a,*], Sho Shirakata [b]

[a] Department of Electrical Engineering and Electronics, Aoyama Gakuin University, 5-10-1, Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan
[b] Department of Electric and Electronic Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan

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ABSTRACT

We have proposed a novel laser-assisted-deposition (LAD) process for improving the crystalline quality of CIGS thin films and cell performance. The influences of laser power, Ga content in CIGS, substrate temperature, and photon energy of laser on CIGS thin films and solar cells have been investigated. In the LAD process a pulsed excimer laser and a pulsed Nd:YAG laser were irradiated onto the substrate surface during CIGS deposition by the three-stage process. The crystalline quality of CIGS thin films and cell performance, particularly open-circuit-voltage, improved by LAD process for all ranges of Ga content and at substrate temperature ranges of 400–550 °C. It was also found that the laser irradiation enhanced the diffusion of Ga into CIGS even at low substrate temperatures, which strongly affects the formation of double-graded bandgap. The PL decay time of LAD–CIGS solar cells was much longer than that of the fabricated by the three-stage process, which implies the reduced defects in CIGS absorber layer. The improved thin-film quality and cell performance became noticeable only when the laser wavelength was shorter than 266 nm (4.66 eV of photon energy). This result strongly suggests that the impacts of pulsed-laser irradiation are dominated by photon-energy rather than thermal-energy.

1. Introduction

It is well-known that elemental selenium and selenides are photo-sensitive materials. Photo-crystallization of amorphous (*a*)-Se has been first reported by Dresner and Stringfellow [1] in 1968. They found that a 200 W Hg arc lamp enhances the crystallization rate of *a*-Se into hexagonal crystals. Innami and Adachi [2] also found the photo-crystallization of *a*-Se using a linearly polarized 488 nm line of Ar laser at room temperature.

Tseng et al. [3] investigated a $CulnSe_2$/GaAs heterostructure grown by a photo-assisted MBE technique using an Hg lamp, of photon energy up to 4.9 eV. They found that photo-assisted MBE process dramatically reduced the epitaxial temperature to 300 °C. In this process, the ultraviolet photons may supply an additional energy to the film surface and activate the surface diffusion and the dissociation of Se_2 and Se_4 molecules [4]. The possibility of photo-induced bond breaking in a Se_8 ring was theoretically confirmed by Shimojo et al. [5]. Hoshino et al. [6] also reported that the illumination of pulsed laser will produce many shorter Se chains by breaking bond. Moreover, the photo-assisted deposition enhances the surface migration of arrival atoms or molecules on the substrate surface and the growth of high-crystalline quality films with reduced defects [2,3]. These works have been carried out using an Hg arc lamp or a continuous wave Ar laser. On the other hand, Wang et al. studied the properties of Cu(InGa)Se_2 (CIGS) thin films and solar cells using pulsed-laser annealing approach which could modify near surface defects and related junction properties. They reported that the pulsed non-melt laser annealing has the potential to be an effective method to improve solar cell performance in an industrial setting [7].

Recently we have proposed a novel laser-assisted-deposition (LAD) technique for improving the crystallographic quality of CIGS thin films and cell performance [8]. In our LAD process, a pulsed excimer laser (λ=248 nm) and pulsed YAG laser (λ=1064, 532, 355 and 266 nm) were irradiated onto the substrate surface during CIGS deposition by the three-stage process. The crystallographic properties of CIGS thin films grown by LAD and the three-stage process were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), and photoluminescence (PL) analyses. Time-resolved photoluminescence (TRPL) measurement was also carried out in order to predict a photovoltaic potential of CIGS thin films grown by LAD process.

2. Experimental [8–12]

CIGS thin films were deposited by LAD process using a molecular beam epitaxy (MBE) system. In LAD process, a pulsed excimer laser (Lambda Phys. Co, Ltd. COMPex100, KrF: 248 nm, 100 Hz, and 30 mJ/cm^2) was irradiated onto the surface of Mo-coated soda lime glass (SLG) substrates during CIGS deposition by the conventional three-stage process. The laser spot size on the substrate surface

* Corresponding author. Tel.: +81 42 759 6251; fax: +81 42 759 6521.
E-mail address: nakada@ee.aoyama.ac.jp (T. Nakada).

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was $2 \times 4\ cm^2$. The substrates were rotated with approximately 2–10 rpm to obtain good compositional uniformity of CIGS films. The ring-shaped laser-irradiation area was easily distinguished after CIGS deposition by the different optical reflection. In this manner, CIGS thin films with the same chemical composition grown by LAD and three-stage processes were simultaneously obtained by one deposition run. Similar experiments were carried out using a pulsed YAG laser (Quantel YG982E; 10 Hz, 5 mJ/cm^2) in order to investigate the influence of laser power or photon energy on the properties of CIGS thin films and cell performance. The MBE system for LAD and three-stage process is shown in Fig. 1. The substrate temperature was measured by means of a thermocouple attached on the backside of the Mo-coated SLG substrate. The surface temperature of the deposited film was simultaneously measured by means of a thermopile.

CIGS thin film solar cells with a ZnO:Al/CdS/CIGS/Mo/SLG structure were fabricated as follows. First, a 1 μm-thick Mo back-contact film was deposited by DC-magnetron sputtering on 2.1 mm-thick SLG substrates at room temperature. A CIGS absorber layer was then deposited by the three-stage process using a MBE system onto Mo-coated SLG substrates at elevated substrate temperatures. The average film composition was then measured using inductively-coupled plasma spectroscopy (ICP). 60–80 nm-thick CdS buffer layers were deposited onto the CIGS layers using chemical bath deposition (CBD) with a $CdSO_4$ (0.015 M)-ammonia (2.0 M)-thiourea (1.5 M) aqueous solution at room temperature ~65 °C. Subsequently 300 nm-thick ZnO:Al (2 wt% Al_2O_3-doped ZnO) thin films were deposited by rf magnetron sputtering at room temperature. The solar cells were completed by the vacuum evaporation of an Al/Ni front-electrode. The current–voltage (J–V) characteristics of the finished cells were measured by means of a solar simulator calibrated by a Si standard cell under AM 1.5, 100 mW/cm^2 illumination at 25 °C.

The crystallographic properties of CIGS thin films were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. Time-resolved photoluminescence (TRPL) measurement was also carried out in order to predict a photovoltaic potential of CIGS thin films grown by LAD.

3. Laser-power dependence of cell performance

In our previous report [13], we discussed the influences of a pulsed-laser annealing of CIGS thin films and device performance. It was found that the surface of CIGS thin film was melted and formed many voids due to the re-evaporation of In and Se if the laser power density was too high. Therefore we have first carried out a preliminary experiment to find an optimum laser-power density to investigate the effects of pulsed-laser irradiation on CIGS thin films and solar cells [10]. The CIGS films were deposited by ;LAD process with different laser power densities at a substrate temperature of 540 °C. A pulsed excimer laser with a wavelength of 248 nm was used in this experiment. The Ga/(In+Ga) and Cu/(In+Ga) atomic ratios were maintained to be in the ranges 0.38–0.45 and 0.84–0.98, respectively.

Fig. 2 shows SEM photographs of CIGS thin films deposited by (a) LAD with a laser power density of 30 mJ/cm^2 and (b) three-stage process. As can be seen in this figure, the surface morphology became relatively flat and dense by laser irradiation. XRD analysis (not shown here) revealed that the (1 1 2) preferred orientation also became predominant due to the enhanced migration of arrival atoms or molecules onto the substrate surface. Fig. 3 shows the

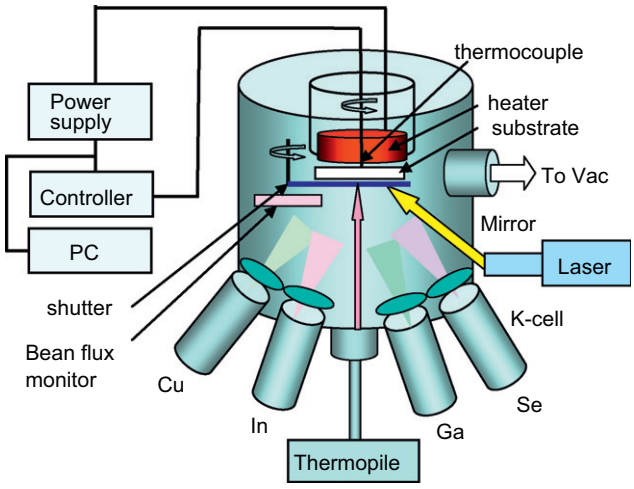

Fig. 1. MBE system for LAD and three-stage process.

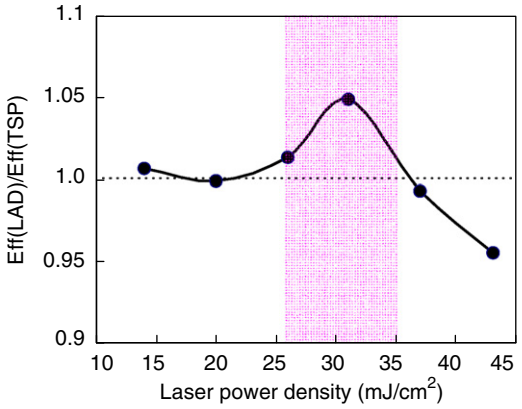

Fig. 3. The efficiency ratios of CIGS solar cells fabricated by LAD and three-stage process (TSP) as a function of the laser power density irradiated onto the substrate surface.

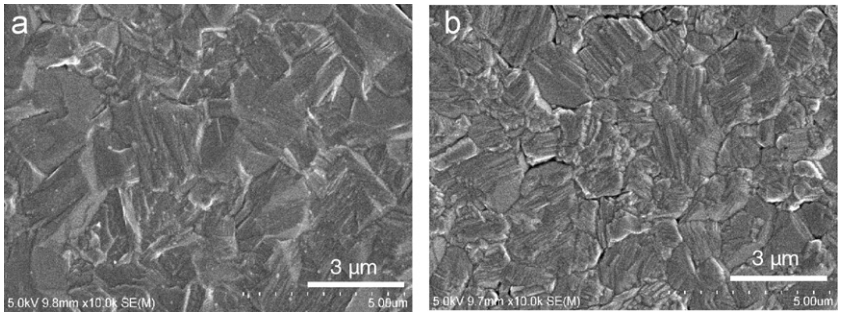

Fig. 2. SEM photographs of CIGS thin films deposited by (a) LAD with a laser power density of 30 mJ/cm^2 and (b) three-stage process.