



## Ultra-thin $\text{Cu}_2\text{ZnSnS}_4$ solar cell by pulsed laser deposition

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### ABSTRACT

We report on the fabrication of a 5.2% efficiency  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) solar cell made by pulsed laser deposition (PLD) featuring an ultra-thin absorber layer (less than 450 nm). Solutions to the issues of reproducibility and micro-particulate ejection often encountered with PLD are proposed. At the optimal laser fluence, amorphous CZTS precursors with optimal stoichiometry for solar cells are deposited from a single target. Such precursors do not result in detectable segregation of secondary phases after the subsequent annealing step. In the analysis of the solar cell device, we focus on the effects of the finite thickness of the absorber layer. Depletion region width, carrier diffusion length, and optical losses due to incomplete light absorption and back contact reflection are quantified. We conclude that material- and junction quality is comparable to that of thicker state-of-the-art CZTS devices, even though the efficiency is lower due to optical losses.

### 1. Introduction

Considerable research effort is presently devoted to alternative earth-abundant and non-toxic materials for photovoltaic applications. In this context, the p-type chalcogenide semiconductor  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) has become very popular due to its optimal direct bandgap at 1.5 eV, its high absorption coefficient  $>10^4 \text{ cm}^{-1}$ , and its rapid technological development in the last decade [1,2]. Still, the current record efficiency of 12.6% for CZTSSe [3] and of 9.1% for pure-sulfide CZTS [4] is far below the 21.7% efficiency demonstrated by the very similar CIGS technology [5] with analogous device architecture. Regarding the pure sulfide CZTS, different vacuum deposition techniques have been successfully employed, such as sputtering [4,6–8] and co-evaporation [9–12]. The most successful strategy to date consists of a two-stage process, where precursors are prepared at a substrate temperature below 300 °C, followed by a high temperature annealing ( $>500 \text{ °C}$ ) done separately at much higher pressures. Among vacuum techniques, pulsed laser deposition (PLD) was firstly studied in 2007–08 by Moriya et al. [13,14], who demonstrated a power conversion efficiency up to 1.74% with a two-stage approach consisting of room temperature

deposition of the precursors followed by high temperature annealing in a mixture of  $\text{N}_2$  and  $\text{H}_2\text{S}$ . With a similar approach, but using a quaternary oxide target, a power conversion efficiency of 4.94% was claimed very recently by Jin et al. [15].

Pulsed laser deposition is a non-equilibrium technique that enables the fabrication of high quality thin films with complex stoichiometry, particularly oxides, nitrides, and amorphous materials [16–18]. Briefly, a pulsed UV laser beam is focused onto a solid target and laser ablation occurs, which result in highly non-thermal removal of the target material. The ablated material, which is an expanding plasma cloud, is finally collected onto a substrate placed a few cm away. The fact that the energy source is outside of the vacuum chamber and decoupled from the deposition process enables one to investigate many experimental parameters (background gas pressure, substrate temperature, ablation energy density) over a wider physical range than with other vacuum techniques. Since the laser heating and subsequent plasma formation are confined in a very small region of the target, there is no risk of contaminating the growing film with materials coming from components of the chamber other than the target itself. The kinetic energy of the atoms and ions in the deposition flux is related to the

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laser fluence and is usually of few eV. Particularly relevant to this work, PLD has proven to be a very successful technique in the growth of high quality films of amorphous structure [18,19]. This ability comes from a few combined features: the possibility to keep the substrate at room temperature with relative ease, the sticking coefficient close to unity for all incoming species, and both compactness and flatness of deposited films due to the highly energetic instantaneous material flux [16,19]. However, reproducibility is often reported to be an issue, mostly because it is difficult to keep the laser ablation parameters within the desired range throughout the whole deposition process, especially in the case of strong coating on the laser viewport [20]. Droplet production and target deterioration are also issues in PLD [16]. Such problems have already been recognized as hurdles to production of high-efficiency solar cells by PLD [21].

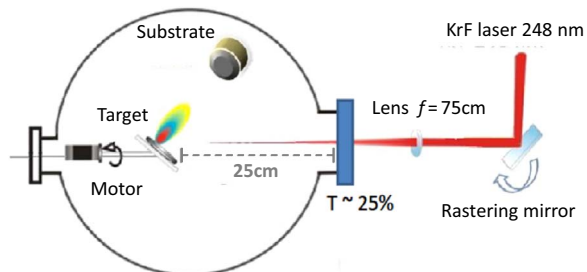
However, in this work we demonstrate that it is possible to circumvent most of the above problems and obtain a CZTS solar cell efficiency above 5%. Interestingly, this result is achieved with an “ultra-thin” absorber layer, with thickness below 450 nm.

## 2. Experimental details

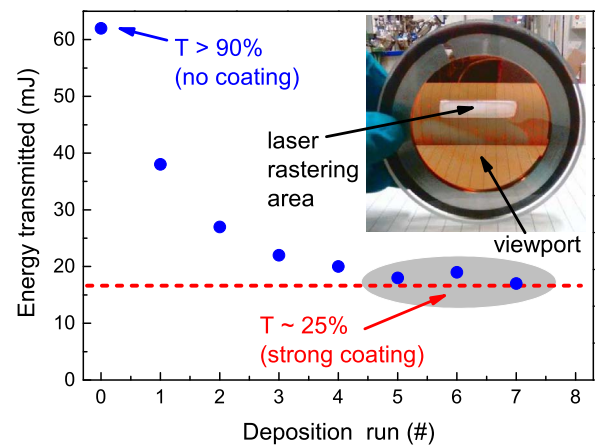
A  $10 \times 10 \text{ cm}^2$  soda lime glass (SLG) substrate was sequentially cleaned in acetone and isopropanol in an ultrasonic bath (5 min each), rinsed in deionized water, and dried with nitrogen. A Mo bilayer was deposited by DC magnetron sputtering at  $10 \text{ W/cm}^2$  power density. The first layer was 200 nm thick and deposited at a working pressure of  $1.3 \times 10^{-2}$  mbar for good adhesion to the substrate. The second layer was 300 nm thick and deposited at a working pressure of  $3.9 \times 10^{-3}$  mbar to achieve a lower sheet resistance. The sheet resistance of the Mo bilayer was  $0.7 \text{ } \Omega/\text{sq} \pm 50\%$  depending on position on the SLG substrate. The Mo-coated glass was cut into  $1.5 \times 3 \text{ cm}^2$  substrates, which were cleaned in the same way as above prior to pulsed laser deposition of CZTS precursors. Precursors were deposited with our PLD equipment, depicted schematically in Fig. 1, under high vacuum with pressure  $p < 5 \times 10^{-6}$  mbar. The KrF excimer laser beam (248 nm wavelength, 20 ns pulse-width, 15 Hz pulse repetition rate) was focused onto a sintered target with overall CZTS stoichiometry (2.5 cm diameter, 2CuS:ZnS:SnS, Testbourne Ltd) at a laser fluence of  $0.6 \text{ J/cm}^2$  and a spot size of  $4 \text{ mm}^2$ .

The laser energy on the target was measured inside the chamber to avoid errors due to strong coating of the viewport with ablated material. The depositions were done after the laser beam-viewport system had reached equilibrium, as shown in Fig. 2.

Rastering of the laser and rotation of the target were used to maximize film uniformity and target utilization. The target-substrate distance was set to 4 cm and the substrate was kept at room temperature. Morphology of the precursors, and of the finished solar cell devices, was examined with a scanning electron microscope (SEM) equipped with a field emission gun (Supra 60VP, Zeiss). The chemical composition of the precursors was measured in the same instrument by energy dispersive X-ray spectroscopy (EDX) using a silicon drift detector (X-Max<sup>N</sup> 50, Oxford Instruments) and a beam voltage of



**Fig. 1.** Sketch of the PLD setup. The laser pulses are focused on the target at  $45^\circ$  from normal incidence with a focal lens. The fluence on the target was  $0.6 \text{ J/cm}^2$  with a spot size of  $4 \text{ mm}^2$ .



**Fig. 2.** Laser energy transmitted through the viewport as a function of cumulative number of CZTS deposition runs. In the inset: photograph of the viewport after more than five deposition runs, when the transmission coefficient  $T$  has reached an equilibrium value of about 25%. The rectangular-shaped region of the viewport through which the laser is rastered is indicated by an arrow. The transmitted energy is measured inside the chamber within that region. One deposition run corresponds to a 20 min deposition at 10 Hz pulse repetition rate.

15 kV. The CZTS precursors were vacuum packed and taken to the University of New South Wales for the annealing treatment and the buffer/window layer deposition. Annealing was conducted at  $560^\circ \text{C}$  in the presence of S and SnS powder in a rapid thermal processor (AS-One 100). The CdS buffer layer (60 nm) was deposited by a standard chemical bath deposition process [22], followed by RF magnetron sputtering of a window layer consisting of 50 nm intrinsic ZnO (i-ZnO) and 200 nm indium tin oxide (ITO) having a sheet resistance around  $30 \text{ } \Omega/\text{sq}$ . A  $1.5 \text{ mm}^2$  dot-shaped silver paste contact was applied on the ITO layer, followed by evaporation of 100 nm  $\text{MgF}_2$  as an anti-reflection coating. Solar cell devices of  $0.2 \text{ cm}^2$  were defined by mechanical scribing.

Illuminated current-voltage (J-V) measurements were performed after 5 min light soaking under standard AM 1.5 solar spectrum ( $100 \text{ mW/cm}^2$ ) using a solar simulator from PV Measurements calibrated with a standard Si reference and a Keithley 2400 source meter. Due to the coarse nature of the top contact, in this work we present the active area efficiency of the solar cell instead of the total area efficiency. Dark J-V and capacitance-voltage (C-V) curves were measured with an Agilent B1500A semiconductor device analyzer. C-V scans were performed between  $-4 \text{ V}$  (reverse bias) and  $+2 \text{ V}$  at a frequency of 100 kHz and an AC voltage of 50 mV.

External quantum efficiency (EQE) curves were measured at 0 V and  $-1 \text{ V}$  dc bias in the range 300–1000 nm with a QEX10 spectral response system (PV Measurements) calibrated by the National Institute of Standards and Technology (NIST)-certified reference Si and Ge photodiodes. The band gap of CZTS was extracted from the inflection point of the EQE curve, i.e., as the photon energy at which  $-d(\text{EQE})/d\lambda$  has a maximum [26].

Steady-state photoluminescence (PL) spectra were measured on completed solar cells with an Accent RPM2000 system at an excitation wavelength of 532 nm and power density  $100 \text{ W/cm}^2$ . On the other hand, Raman spectroscopy, X-ray diffraction (XRD), and time-resolved photoluminescence (TR-PL) were performed on a bare CZTS absorber layer deposited on Mo-coated SLG. It was fabricated similarly to the absorber used for the solar cell. Raman spectra with multiple excitation wavelengths (455, 532, and 780 nm) were measured with a DXR Raman microscope (Thermo Scientific) in backscattering configuration, with a laser power of 1.6 mW and a spot size of approximately  $2 \times 2 \text{ } \mu\text{m}^2$ . X-ray diffraction (XRD) patterns were recorded with a Bruker D8 diffractometer in Bragg-Brentano configuration. TR-PL was measured using the time-correlated single photon counting

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