FEMTOSECOND LASER PULSES FOR PHOTOVOLTAIC BOTTOM-UP STRATEGIES

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A promising technology in photovoltaics is based on micro-concentrator solar cells, where the photovoltaic active area is realized as an array of sub-millimeter sized cells onto which the incident light is focused via microlenses. This approach allows to increase the cell efficiency and to realize much more compact modules compared to macroscopic concentrator devices. At the same time, expensive raw materials can be saved, which is of interest, for example, with respect to indium in the case of copper-indium-gallium-diselenide (CIGSe) thin film solar cells. Two methods to produce micro-sized precursors of CIGSe absorbers on molybdenum are presented using 30-fs laser pulses at 790 nm wavelength. On the one hand, a multi pulse surface structuring of the molybdenum film or the underlying glass substrate and a subsequent physical vapor deposition were used for a site-selective aggregation of indium droplets. On the other hand, a single pulse laser-induced forward transfer was utilized to selectively deposit combined copper-indium precursor pixels on the molybdenum back contact of the solar cell. Post-processing (selenization, isolation, contacting) of the laser-generated micro-sized precursors results in functional CIGSe solar cells.

1. Introduction

In photovoltaics, a rapid progress towards new absorber materials and more sophisticated solar cell designs is being made in pursuing the aim of increasing cell efficiency and reducing production costs. Amongst others, the micro-concentrator solar cell concept is a promising new approach [1,2]. Figure 1 depicts a scheme of a micro-concentrator solar cell arrangement. It combines the potential for saving of the solar micro absorber material, an improved heat dissipation resulting in reduced thermal losses compared to macroscopic concentrators, and an increase of the solar cell efficiency under concentrated illumination using microlenses.

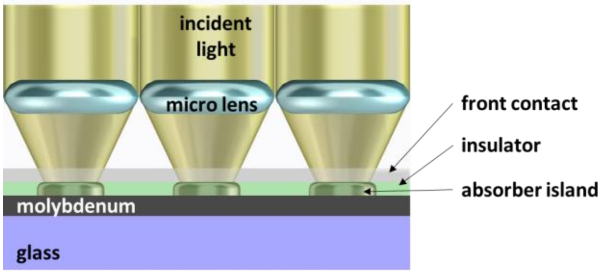

Fig. 1: Scheme of micro-concentrator solar cell concept

Copper-indium-gallium-diselenide ($Cu(In,Ga)Se_2$, CIGSe) is a direct semiconductor, an excellent solar absorber, and a well established material in thin film photovoltaic technology with current record cell efficiencies of 22.6 % [3]. This value was obtained using a cell with an area of about 0.5 cm^2. Starting from this high level, CIGSe appears very promising for micro-concentrator applications, which allow to save especially the rare and costly indium and to further increase the cell efficiency by light concentration.

In this paper, two technologically applicable processes to produce site-selective micro absorber islands on molybdenum-coated glass using femtosecond laser pulses are described. In a *direct focussing* geometry, either the underlying glass substrate or the back contact material molybdenum are locally roughened by a multi pulse 30-fs laser treatment at 790 nm wavelength. In a following physical vapor deposition (PVD) process, indium islands can be grown at the laser-defined ablation spots, serving as precursors for the production of micro absorbers [4,5]. A single pulse *laser-induced forward transfer* (LIFT) is used to selectively deposit copper and/or indium precursor pixels on the molybdenum back contact of the solar cell [6] which can be further processed to micro absorbers as parts of micro solar cells [7]. Both laser-based processes open up a new material saving bottom-up strategy for the production of CIGSe micro-concentrator solar cells.

2. Experimental

A Ti:sapphire laser (Femtolasers, Compact Pro) with a pulse duration of 30 fs at 790 nm wavelength was used for the experiments. Operating at 1 kHz repetition rate, a defined number of pulses (per spot) was selected by gating the laser electronics. The laser beam was directed onto the sample by means of a spherical mirror with a focal length of 50 cm. The focused Gaussian beam radius ($1/e^2$) was determined to be of the order of 100 µm.

For the laser experiments employing direct focussing, soda-lime floatglass samples (50×50×2 mm^3, Weidner Glas) served as substrates. Deposition of molybdenum and indium was carried out by PVD in a high vacuum chamber with a base pressure of 10^{-6} mbar at a substrate temperature of 510°C (for details, see [4]). Molybdenum films had a thickness of a few 100 nm. The indium “film thickness” of 100 nm has merely a nominal meaning, since indium forms islands during the deposition.

Laser-induced forward transfer (LIFT) was performed with single laser pulses which were focused through a glass substrate onto the donor layer. Figure 2 provides a scheme of the LIFT experimental setup. The donor films were produced by PVD of indium and/or copper layers on 150 µm thick microscopic cover slips. Depending on the laser energy density (fluence), a part of the donor layer can be transferred from the donor glass to the receiver substrate. Here, a glass substrate covered by a molybdenum film (intended as back contact of the solar cell) acted as acceptor. The spacing between donor and acceptor was set to 150 µm.

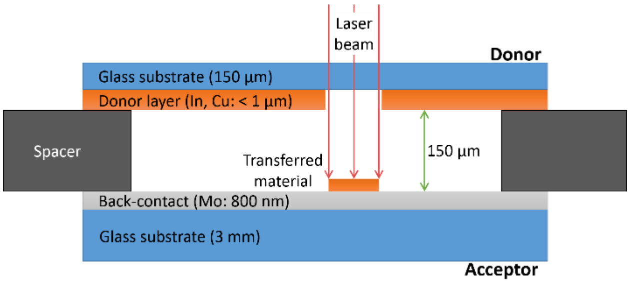

Fig. 2: Scheme of LIFT experimental setup

Arrays of precursors of micro absorbers can be produced by moving the sample relative to the fixed laser beam. These arrangements of absorbing pixels can be adapted to the geometry of the microlens array (Fig. 1) allowing optimum concentration conditions for the working micro solar cells. All laser experiments were done in ambient air.

Optical microscopy (OM) and scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDX) served for sample characterization.

3. Results and discussion

Direct focussing

Figure 3 shows two alternative pathes for a substrate structuring followed by a PVD of indium to grow indium islands at the laser-irradiated spots.

Figure 3, left, depicts laser-structuring of the glass substrate before a molybdenum film and indium were both deposited by PVD. On the right side of Fig. 3, a molybdenum layer is deposited on the pristine glass substrate by PVD followed by laser treatment of the molybdenum layer and a subsequent PVD of indium. Both approaches according to Fig. 3 lead to technologically relevant results. As an example, Fig. 4 shows SEM pictures of a single fs-laser ablation spot on glass (Fig. 4a) and the same spot after deposition of molybdenum and indium (Fig. 4b).

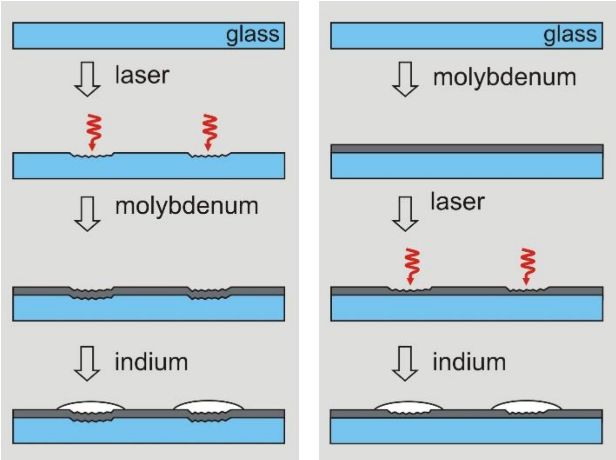

Fig. 3: Laser ablation of glass (left) or molybdenum on glass (right) for a subsequent growth of indium islands (adapted from [4])

Figure 4 demonstrates that indium islands as precursors for CIGSe solar cells can be grown at a laser-predefined position (Fig. 4a) on molybdenum as the standard back contact (Fig. 4b). A roughening of the surface without significant ablation of the glass substrate (Fig. 4a) or the back contact molybdenum (not shown here) is sufficient to act as a material trap for indium. The indium deposition parameters were optimized to manufacture island heights of about 2 – 3 µm and diameters in the 50 µm range meeting the geometrical requirements of micro-concentrator solar cells.

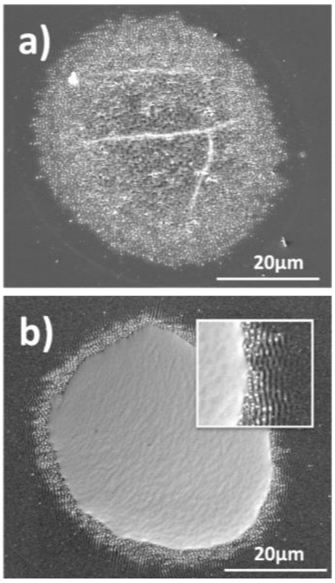

Fig. 4: Scanning electron micrographs of a laser-roughened spot on glass before (a) and after (b) indium island growth (inset: magnified island edge). Laser fluence: 1.6 J/cm^2. Pulse number per spot diameter: 100

An array of laser processed spots with subsequent indium deposition is depicted in Fig. 5. The bright spots correspond to indium islands.

Obviously, indium islands grow exclusively at the laser-induced modification spots. No indium islands can be found at intermediate positions.

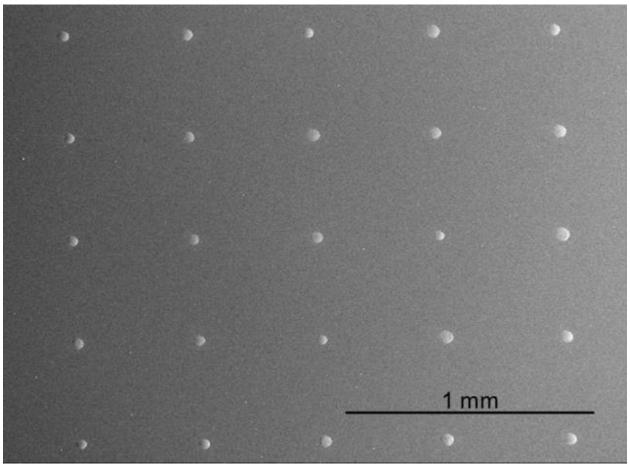

Fig. 5: Optical micrograph of an array of indium islands on molybdenum-coated glass

Laser-induced forward transfer

Laser-induced forward transfer (LIFT) was performed with various donor samples. Single layers of copper (10 - 100 nm thickness) or indium (150 – 1000 nm) as well as combined copper-indium layers (210 – 1010 nm) were used.

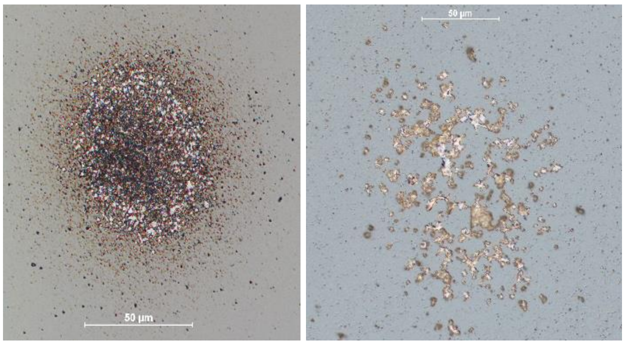

Fig. 6: Optical micrographs of indium LIFT deposits on molybdenum-coated glass. Donor layer thicknesses 150 nm (left) and 300 nm (right). Laser fluence: 7.8 J/cm^2

Figure 6 shows OM pictures of transferred material on the acceptor side for two thicknesses of the indium donor film. For the 150 nm film, the indium deposit consists mainly of small nano-/micro particles but it looks almost homogeneous (Fig. 6, left). In contrast the deposit of a 300 nm thick indium layer consists of discontinuous fragments (Fig. 6, right). The fragmentation of pure indium films as a result of the LIFT process seems not to be appropriate for a subsequent processing to micro absorbers. Therefore, LIFT of combined copper-indium films was investigated with varying thicknesses of the single films. For all combined donor layers, copper was deposited first, due to its significantly higher melting point compared to indium.

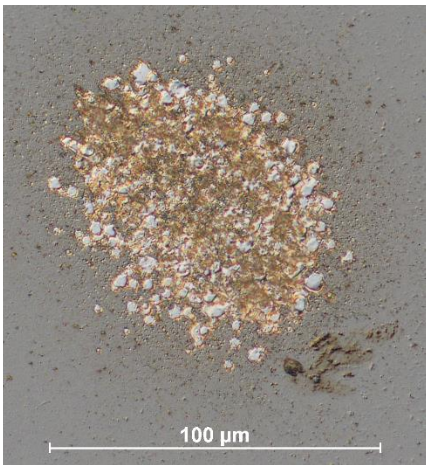

Fig. 7: Optical micrograph of a copper-indium LIFT deposit on molybdenum-coated glass. Donor: 20 nm copper, 200 nm indium. Laser fluence: 7.8 J/cm^2

Figure 7 depicts a result of a LIFT process of a combined copper-indium donor layer. In contrast to pure indium films (Fig. 6), homogeneous and compact deposits are formed on the acceptor for the combined copper-indium donor layer.

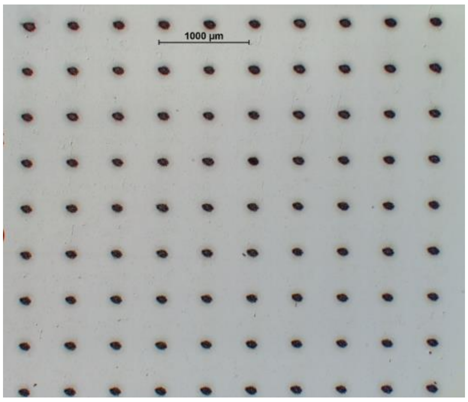

Fig. 8: Optical micrograph of an array of LIFT copper-indium deposits on molybdenum-coated glass. Donor: 20 nm copper, 200 nm indium. Laser fluence per spot: 7.8 J/cm^2

Figure 8 displays an array of copper-indium deposits on molybdenum employing the same laser parameters as in Fig. 7. The reliability of the LIFT process for the production of regular arrangements of precursors of micro absorbers is demonstrated.

Processing to micro absorbers

The precursor material from both approaches, i.e. the direct focusing technique and the laser-induced forward transfer, can be processed to absorber material for solar cell applications. The deposition of gallium on samples with indium islands arranged by the direct laser focussing method yields In-Ga precursors. Subsequent deposition of copper followed by selenization in a rapid thermal processing step leads to CIGSe micro absorber islands. Originating from layer deposition of copper, ubiquitously grown copper selenides must be removed by a selective etching step afterwards.

The selenization via rapid thermal processing can be applied analogously to the Cu-In samples from the LIFT technique resulting in $CuInSe_2$ absorber islands. However, due to the local deposition of all constituents, no chemical etching step is necessary. The opto-electronic properties of the resulting absorbers were investigated by photoluminescence mapping. The emission of both CIGSe and $CuInSe_2$ islands indicated band gap energies, which are characteristic for the respective materials, across the entire island area. In addition, the phase composition was confirmed by X-ray diffraction measurements.

Processing to solar cells and characterization

The final processing of absorber islands to solar cells was realized by the introduction of an insulating layer, which separates back and front contact (see Fig. 1). For this purpose, the photo resist SU-8 was deposited via spincoating. Subsequently, its uppermost layer was removed in a mild etching step to reveal the top of the the absorber islands for creating the p-n junction by wet chemical depostion of CdS and sputtering of intrinsic and Al-doped ZnO. Characterization by SEM/EDX measurements at cross sections of the resulting cells confirmed that the applied process steps created the desired cell structure. After electrical contacting, I-V measurements recorded at one sun illumination under a sun simulator yielded efficiencies in the range of 1.4 - 2.9% for all cells from both the LIFT approach and the indium islands grown on laser-patterned substrates.

4. Conclusions

Femtosecond-laser-based, material-efficient bottom-up approaches for the production of CIGSe micro-concentrator solar cells are reviewed. Both a local, laser-induced surface roughening of glass substrate or molybdenum back contact followed by PVD of indium as well as a LIFT process of combined copper-indium donor films result in selectively deposited precursor materials for micro solar absorbers. Working micro solar cells can be produced with efficiencies reaching 2.9 % for 1 sun illumination and showing enhancement under light concentration.

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