Lasers in Manufacturing Conference 2013

Picosecond laser induced selective removal of functional layers on CIGS thin film solar cells

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Abstract

Picosecond laser pulses provide a controlled laser based removal used for micro structuring of functional layers, such as copper-indium-gallium-diselenide (CIGS), due to a reduced thermal penetration depth, compared to nanosecond pulses. It is shown that with 7 ps pulse width at a wavelength of 532 nm the P2 and P3 processing of thin film solar cells on glass substrates and flexible polyimide substrates is possible. A Gaussian as well as a top-hat energy distribution were utilized for the experiments. With adjusted laser and processing parameters they allow for the fabrication of precise isolation trenches (width $\ll 100 \mu m$), without damaging the adjacent layers due to mechanical stress or thermal stress.

Keywords: ultra short laser pulses; laser ablation; layer removal; top-hat; thin film; solar cells; CIGS; TCO

1. Motivation

Copper-indium-gallium-diselenide (CIGS) based thin film solar cells are currently in the focus of research, due to their high cell efficiency \cite{1} and at the same time low production cost. For thin film photovoltaics the fabrication of isolating channels is performed in three processing steps \cite{2}, typically after deposition of the appropriate layers, as depicted in Fig. 1:

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E-mail address: a.lemke@lmtb.de.
• **P1 step:** removal of a sole molybdenum layer (Mo) from the substrate
• **P2 step:** removal of the copper-indium-gallium-diselenide layer (CIGS) and the thin cadmium sulfide (CdS) buffer layer from the Mo layer
• **P3 step:** removal of the transparent conducting oxide layer (TCO), consisting of an undoped zinc oxide layer (i-ZnO) and an aluminum-doped zinc oxide layer (ZnO:Al) [3], from the CIGS layer.

Needlescribing of isolation trenches on thin film solar cells, particularly for the P2 and P3 processes, is still state of the art. The drawback of needle scribing is the increased channel width due to random chipping of the CIGS and TCO layers along the edges, depicted in Fig. 2. This leads to reduced effective functional areas on the cells and thus a reduced total power. A channel width of smaller than 100 µm is desirable. Aside from that, the needle scribing lacks the selectivity, i.e. in the P3 process the CIGS layer is removed as well and the Mo layer is exposed unnecessarily.

The P1 process is known and already partially implemented using nanosecond (ns) laser systems [4]. Because the ablation threshold for a Mo layer (≤ 1 µm) is usually much smaller than for the substrate, e.g. glass, the layer removal can be achieved with the lesser selective ns laser pulses.

![Fig. 1. Schematic of a CIGS thin film solar cell module [Solteccture GmbH]](image1)

![Fig. 2. Needle scribed isolation trench (P3 process), chipping of CIGS/TCO layer and damage to Mo layer.](image2)

The contactless laser removal allows for the fabrication of precise isolation trenches (width << 100 µm), without damaging the adjacent layers due to mechanical stress. In laser machining the energy distribution during and after photonic excitation is of importance. It is characterized by several factors, such as pulse width and spatial beam profile on the work piece. With nanosecond pulses, quality and selectivity of the ablation is limited due to the strong thermal penetration depth, which is especially problematic for selective removal of thin films. The ultra-short energy input of picosecond laser pulses provides a much better control of laser based removal for micro structuring of functional layers, such as CIGS, due to the reduced thermal penetration depth. Picosecond laser removal of CIGS thin films is therefore in the focus of current research [2, 5].

2. Experimental

A diode-pumped solid-state laser (DPSSL) with 7 ps pulse width at 532 nm is utilized for investigating the P2 and P3 processing of thin film solar cells on glass substrates and on flexible polyimide substrates. The experiments are conducted with scanner systems as well as fixed optics and a 3-axis translation stage. The
influence of single pulse energies and the spatial and temporal pulse distribution on the ablation process and quality is investigated for two different pulse shapes: a Gaussian energy distribution is used as well as a top-hat profile (also combined with scanner). In addition, the influence of these processing parameters on the distribution and composition of the ablated material is investigated. The examination of the substrates and the ablation products is carried out with optical microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX). Furthermore, spectroscopic analysis of the generated plasma has been implemented and shows promising results for an on-line monitoring of the removal process.

3. Results and Discussion

The results show that a selective layer removal at 532 nm, 7 ps, 10 kHz repetition rate and moderate single pulse energies of 5 μJ is achievable. The choice of focal length and thus spot size of the focusing optic determines the channel width, 30 to 50 μm are possible. Fig. 3 depicts a SEM/EDX image of such an isolation channel (P3) obtained with a 50 μm top-hat profile. The EDX shows the different elements in the processed sample, one sees a clean and undamaged Mo layer in the middle of the channel and narrow edges of CIGS followed by the undamaged TCO layer. These results were obtained at a repetition rate of 10 kHz and a spatial pulse overlap of ≥ 95%, which only can be achieved with very low processing speeds of a few mm per second.

To realize the required high processing speeds for industrial application, higher laser repetition rates are necessary. However, at repetition rates above 10 kHz, with adapted processing speed for a constant pulse overlap, we observe a heat accumulation that leads to damage or removal of the Mo layer as well as fusing of the CIGS in the adjacent areas up to 100 μm from the channel. The time between succeeding laser pulses at higher repetition rates is too short for the heat energy to diffuse out of the radiated volume. In spite of the short pulse duration of 7 ps this results in heat accumulation, known from ns laser pulses, and a growing heat affected zone (HAZ). To avoid this heat accumulation at high repetition rates processing speed was further increased, and thus spatial pulse overlap reduced. At the same time the number of processing cycles was increased to compensate for the lower energy fluence rate and also leading to a higher temporal pulse distance.

Fig. 3. SEM/EDX picture of a laser fabricated isolation channel on a CIGS solar cell (P3). The different colors represent the different elements in the sample.

Fig. 4. Plasma spectra during the removal of a CIGS layer with multiple cycles. Shown are microscopic images of the second and the sixth cycle and the appertaining spectra.
This step by step way of layer removal also yields the possibility for an on-line control of the removal process by plasma analysis, as shown in Fig. 4. The plasma spectra for the different cycles correspond to the layer removal process. Vanishing Indium lines and appearing Mo lines indicate the complete removal of the CIGS layer [6-8]. The results obtained are promising and show an application spectrum for selective laser induced ablation of any multi-layer systems.

In the spectroscopic analysis of the layer removal process individual components of CIGS, CdS and Mo could be detected. The Zn of the ZnO layer was not detected in any analysis. EDX analysis of the ablation products yields a clue to this observation. The ablation products were collected by positioning of a glass wafer a few 100 μm above the isolation channel during ablation. The glass wafer was then examined in a SEM/EDX. An EDX mapping of such a glass wafer is presented in Fig. 5 and demonstrates the sizes and distribution of the ablated particles.

![EDX mapping of a glass wafer containing ablation products of a P3 step by laser irradiation at 532 nm. Laser parameters: distance between sample and glass wafer = 340 μm, pulse distance = 0.4 μm, processing speed = 4 mm/s, single pulse energy = 8 μJ.](image)

Molybdenum and indium evaporate during the removal process and can be found dispersed over a large area of the glass wafer, with particle sizes of less than 1 μm. Copper, selenium and cadmium form clusters of up to 2 μm in size. Due to the larger mass they are not as widely distributed across the glass wafer as Mo and In. However, the zinc forms fragments of up to 5 μm in size, which cannot be caused by direct removal, but indirectly through spalling from the underlying CIGS layer, thus no ZnO can be found in the plasma.

To further investigate the differences between CIGS and ZnO ablation the P3 step was conducted in two different ways. On the one hand by ablation of the ZnO layer only and on the other hand by ablation of the ZnO and CIGS layers down to the Mo, as done by needle scribing. Both samples then were analyzed for their electrical characteristics such as open circuit voltage (V_OC), short circuit current (I_SC) and fill factor (FF). Table 1 shows the results for four samples. Sample 1 and 2 were processed to the CIGS and sample 3 and 4 to the Mo layer.
Table 1. Electrical characteristics for CIGS solar cells and modules after conducting the P3 step by laser ablation at 532 nm.

<table>
<thead>
<tr>
<th></th>
<th>P3 step, ZnO layer only</th>
<th>P3 step, ZnO and CIGS layer removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sample 1</td>
<td>sample 2</td>
</tr>
<tr>
<td>Open circuit voltage</td>
<td>VOC module [V]</td>
<td>3,012</td>
</tr>
<tr>
<td></td>
<td>VOC cell [mV]</td>
<td>604,2</td>
</tr>
<tr>
<td>Short circuit current</td>
<td>ISc [A]</td>
<td>5,53E-02</td>
</tr>
<tr>
<td>Fill factor FF [%]</td>
<td>67,24</td>
<td>68,35</td>
</tr>
</tbody>
</table>

The results for the samples 1 and 2 correspond to the values to be expected of a cell that has been processed using the conventional needle scribing method. For both the samples 3 and 4 the resulting values are too small for an efficient solar cell. The large differences between sample 3 and 4 also suggest a poor reproducibility of the isolation channels. The ablation process for CIGS at 532 nm is obviously not a reliable method although the surface analysis by means of optical microscopy, SEM and EDX (Fig. 3 and 4) at first glance suggest promising processing parameters for the completion of isolation channels.

For the selective ablation of monolayers on a transparent substrate material the "lift-off" method by rear side laser irradiation has been used for quite some time [9], e.g. for the P1 step. By appropriate choice of wavelength and pulse duration, this method can obviously be transferred to the ablation of multilayer systems, using front-side laser irradiation. More recently, several research groups worldwide are engaged in this topic [2,5,10].

The spectroscopic and EDX analysis illustrate that for CIGS, respectively ZnO removal two different ablation processes come into effect. The CIGS removal at 532 nm takes place by heating, melting and
evaporation of the CIGS layer. The melting of the CIGS apparently leads to a metallization along the edges of the isolation channels. This results in a short circuit between the ZnO front contact and the Mo rear contact and thus a decrease in cell efficiency.

ZnO removal at 532 nm happens by evaporation of CdS and CIGS at the ZnO-CdS/CIGS interface which leads to spalling of the ZnO layer by the pressure of the evaporated CdS/CIGS. A microscopic image of such an isolation channel is shown in Fig. 6a. No negative effect of the CIGS evaporation on the cell efficiency was observed. A schematic of the ablation process is shown in Fig. 6b. Rekow et al. observed and interpreted this effect already for the P2 step at 1064 nm and called it “brittle fracture ablation”[2].

Other recent publications [2,5,10] have shown that at 1064 nm the spalling ablation is achievable for the P2 step, similar to the P3 step at 532 nm. The “brittle fracture ablation“ of ZnO in the P3 process at 532 nm and in the P2 process of CIGS at 1064 nm is therefore a promising method for the implementation of the laser ablation in the manufacturing of CIGS thin film solar cells.

In addition, the analysis of the ablation products revealed the importance of a proper extraction unit for the removal process to avoid inhalation of generated nanoparticles and potentially toxic materials. A decisive influence of the substrate material on the ablation process was not observed.

4. Conclusion

Picosecond laser pulses were applied for creating isolation channels on CIGS thin films solar cells on glass and polyimide substrates. The selective removal of ZnO and CIGS layers was achieved at a laser wavelength of 532 nm and a pulse width of 7 ps without damaging the Mo rear contact.

The chosen wavelength of 532 nm proved favorably for the ablation of ZnO from the underlying CIGS layer due to “brittle fracture ablation“. Ablation of CIGS at 532 nm occurs by melting and evaporation, leaving metallized CIGS along the edges of the isolation channels leading to electrical characteristics that did not meet the demand for efficient solar cell modules.

The EDX analysis showed no residues of the ablation products on the cells. EDX analysis of the ablation products themselves confirmed the different ablation processes for ZnO and CIGS removal and revealed the importance of a proper extraction unit for laser processing of CIGS thin film solar cells.

Acknowledgement

The authors would like to thank Dr. Hodoroaba and Ms. Benemann from the Bundesanstalt für Materialforschung und –prüfung (BAM) in Berlin, for the EDX-Analysis and helpful insights. Part of this study was supported by an AiF/IGF program, project number 16376 N/1.

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