

LiM 2011

Pump-Probe Investigations on the Laser Ablation of CIS Thin Film Solar Cells

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Abstract

A picosecond laser lift-off process of an about 0.5 μm thick Mo layer on a glass substrate can be induced by irradiating the layer from the glass side. A pump-probe setup for time- and space resolved microscopy is used to investigate the ablation process in a time domain from a few picoseconds up to 3.6 ns. The results display a bulging of Mo within 1 ns followed by a lift-off at times past 3.6 ns. Furthermore, the setup is used for in situ investigations of a multi pulse ablation through the whole layer stack (ZnO/CIS/Mo/Glass) of a CIS thin film solar cell.

Keywords: CIS; thin film; solar cell; laser; lift-off; pump-probe; time resolved microscopy

1. Introduction

Several investigations have shown, that laser lift-off processes efficiently remove and transfer thin absorbing layers from transparent substrates, being utilized e.g. in micro processing [1,2]. Furthermore, the selective removal of transparent solid thin films such as SiO_2 (silicon oxide) and SiN_x (silicon nitride) on Si substrates for the production of silicon solar cells has been demonstrated in several articles [3-6].

Our group at the Munich University of applied sciences investigates picosecond laser processes for the monolithic interconnection of CIS (Copper indium diselenide) thin film solar cells. In the first process step, called pattern 1 (P1), the p-electrode, which is a 0.5 μm thick molybdenum layer on a glass substrate, has to be galvanically separated. When the Mo layer is irradiated through the substrate with a 10 ps-laser pulse, a laser lift-off can be observed, resulting in an directly induced selective ablation free from thermal effects [7].

In the CIS system a further type of laser lift-off free from thermal effects can be observed for P3; the selective ablation of an about 1.5 μm thin transparent ZnO (zinc oxide) film, forming the n-electrode. Here, the laser ablation is indirectly induced in the absorbing and underlying substrate. Both, directly and indirectly induced ablation, are performed at laser fluence far below 1 J/cm^2 , leading to process speeds of several m/s in an industrial application, saving cost and time [8].

In this paper we focus the laser lift-off process of Mo on glass. It was already observed, that the irradiation of Mo through the glass substrate below a certain threshold fluence results in a bubble formation of the Mo layer.

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Furthermore, a variation of the laser fluence is also affecting the bubble height, as shown in Figure 1. If the laser fluence is increased above a certain threshold fluence, complete Mo caps are punched out. That threshold is called punching threshold. Microscopic pictures of the bubble formation and a punched out cap are shown in Figure 2, left side.

Energetic considerations support the theory that a laser lift-off ablation cannot be caused by a purely thermal process of subsequent heating, melting and evaporation of the complete layer. We assume that the mechanism of the process is as sketched in Figure 2, right side: The laser pulse evaporates the lower part of the metal layer and forms an ideal gas (bottom), the hot metal gas expands adiabatically (middle) to the tensile stress limit of the Mo film and punches out the metal layer (top). Finite element analysis show, that a maximum tensile stress is created at a maximum curvature of the film, occurring at one constant radius, while the film is still connected with the substrate. The subsequent shearing of the Mo disk explains why the ablation region resembles punched holes and is free from thermal effect [9]. To collect more data for this model, an imaging pump-probe setup was developed, allowing a spatially and temporally resolved observation of the ablation process.

Imaging pump-probe investigations of laser ablation have already been performed by several groups. The first investigations with photographs of silicon ablation were published by Downer et al. in 1985 [10]. Later works used a CCD Camera for image recording. Different groups studied the ablation of several bulk semiconductor materials and metals [11, 12] as well as of thin metal films on glass substrates [13]. Moreover, laser induced forward transfers [14] and laser lift-off processes of SiO₂ on Si [15] and of silicone for print plates have been studied [16]. We present for the first time to our knowledge pump-probe microscopy investigations on a direct induced laser lift-off process of thin metal films on glass substrates by irradiation through the glass substrate. Furthermore, we show for the first time to our knowledge in situ investigations of multi pulse ablation through the whole layer stack of a CIS thin film solar cell under front side illumination.

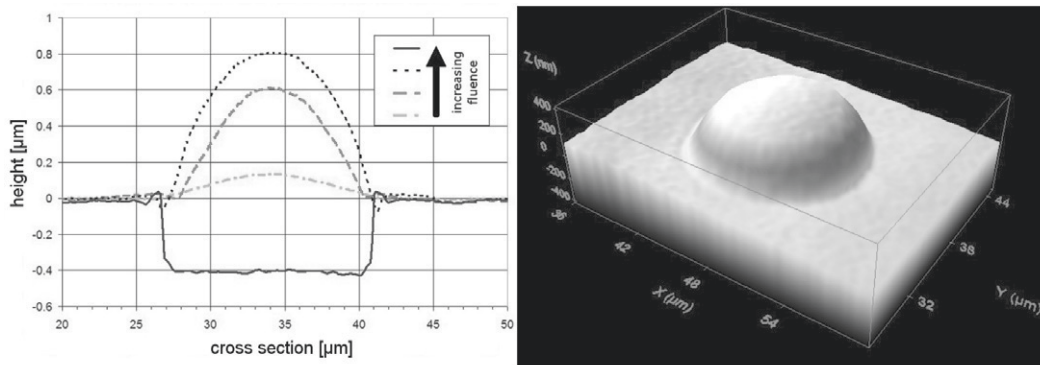


Figure 1. (a) Cross section of a 430 nm thick molybdenum film on glass irradiated from the back (glass) side with laser fluences below (dotted and dashed lines) and above (solid blue line) the punching threshold, measured with a confocal image profiler. Below the punching threshold the blister height increases with fluence, whereas above the threshold, a whole cap is punched out. (b) 3D view of a Molybdenum blister generated with a fluence close to the punching threshold.

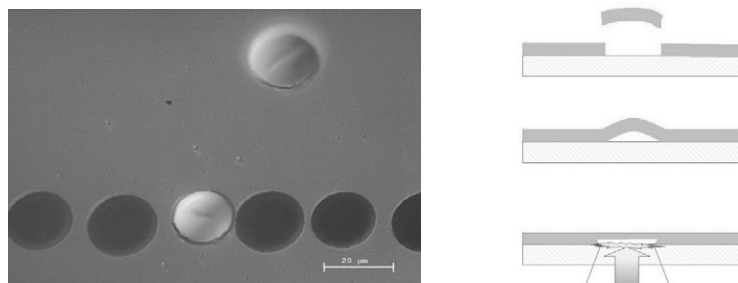


Figure 2. (a) Microscopic picture of blister formation and a collected intact Mo disc which was punched out by laser ablation through the glass substrate. (b) Schematic representation of the underlying process: The laser pulse evaporates the lower part of the metal layer (bottom), the hot metal gas expands adiabatically (middle) to the tensile stress limit of the Mo film and punches out the metal layer (top). If the laser fluence is too low the process stops during blisters formation.

2. Material and Methods

2.1. Experimental

The basic principle of a pump-probe setup is using one laser pulse for initiating ablation and a second pulse for a temporally delayed illumination of the ablation spot. We apply a High Q Laser model “picoREGEN” with a pulse duration of about 10 ps (FWHM) and a wavelength of 1064 nm. The output energy is controlled by means of an integrated half wave plate and polarizer combination. A subsequent second half wave plate and beam splitter combination behind the laser output is used to split pump- and probe beam and to adjust the pulse energy in both paths. The pump beam is focused on the sample with a spot diameter of about 80 μm . The probe beam is frequency doubled by an LBO crystal, enabling a spectral separation of pump and probe beam by a band pass in the microscope, and optimizing illumination for the higher sensitivity of a standard CCD at 532 nm compared to 1064 nm. Subsequent, the time delay between pump and probe pulse is set by an optical delay line (Micos, model “LS-180”) with a length of 300 mm. To achieve an optical delay of up to 4 ns the beam is folded twice along the delay line. For this purpose and to simplify adjustment 3 retro reflectors are used. In the next step, the probe beam irradiates the sample at an angle of about 40 degrees with respect to the pump-beam; the pump beam is perpendicularly oriented to the surface. A microscope with a CCD camera is positioned on the other side at an observation angle of about -40 degrees to the pump beam to capture an image of the ultra-short exposed region.

To minimize the observation angle a 20 mm long working distance microscopic objective with a 20x magnification is used. A 532 nm band pass is located between objective and tube lens to reject reflections and scatter of the pump beam as well as ambient light. The CCD camera is an ImagingSource model “DMK 41BU02.H” with 1280x960 pixels, resulting in a field of view of 285x223 μm and a pixel resolution of 0.23 μm . The synchronization of ps-laser and CCD camera is realized with a SRS DG645 digital delay generator. Since each time delayed image affords a new ablation spot, a second motorized stage (Micos, model “LS-65”) was used to move the sample. Thus, the setup can automatically take a series of pictures at different time delays on different locations on the sample (see Figure 3).

Besides time resolved microscopy, the setup can be used for in situ multi pulse ablation studies. For this purpose, at first a single pulse is sent to the sample. Then, the pump-beam is blocked by a mechanical shutter and the ablated spot is illuminated with the probe beam and captured by the CCD camera. If this procedure is repeated without moving the sample, an in situ study of multiple single ablations can be performed. However, since the frame rate of a CCD cam is about 15 Hz the repetition rate of the laser is limited to that value.

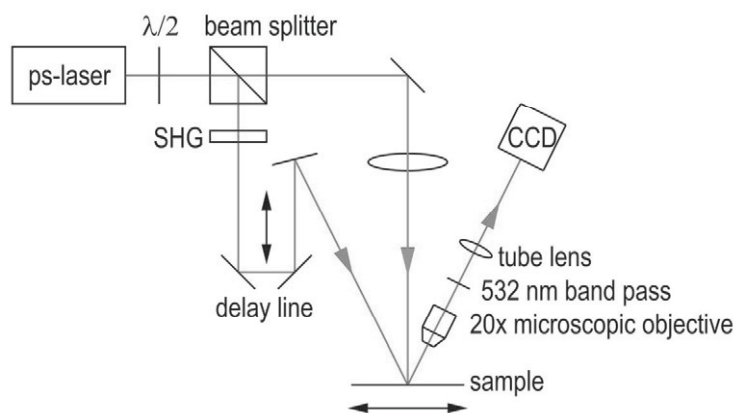


Figure 3. Schematic pump-probe setup. The beam of a 10 ps-Laser is split up by a polarizing beam splitter into pump and probe beam. The pump-beam is focused on the sample for ablation. The probe beam is frequency doubled by an LBO crystal. Then, an optical delay line defines the temporal delay of the probe beam. After this, the collimated probe beam irradiates the sample at the ablated spot under an angle of about 40°. This area is imaged by a 20x microscopic objective and a tube lens to a CCD camera. In between is a 532 nm band pass that blocks reflections of the pump beam and ambient light.

2.2. Samples

For an in situ investigation of the multi pulse ablation, a complete layer stack of a CIS thin film solar cell was used (sample courtesy of AVANCIS GmbH, Munich, Germany). The sample consists of a glass substrate carrying an about 0.5 μm thick Mo-layer followed by a 1-3 μm thick CIS-layer covered with a 1 - 2 μm ZnO-layer. The pump beam is sent perpendicularly to the covering ZnO layer, while the probe beam irradiates the sample at an angle of about 40 degrees with respect to the probe beam (see Figure 4, left side).

A time resolved investigation of a single pulse ablation was performed on samples consisting of an about 0.5 μm thick Mo layer on a glass substrate, also provided by AVANCIS. Here, the Mo layer was irradiated and observed through the glass sample (see Figure 4, right side).

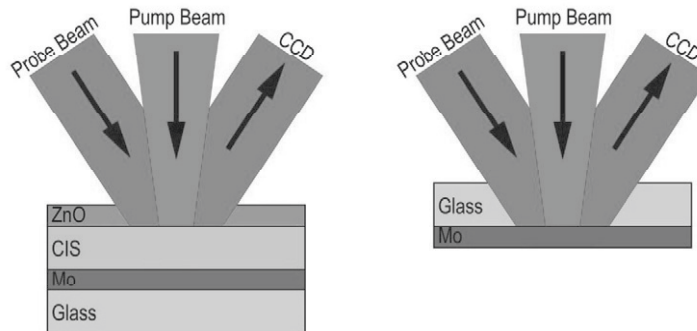


Figure 4. Sample, pump beam, probe beam and camera orientation. (a) Multi pulse ablation is studied on a ZnO/CIS/Mo/Glass Sample. Since ZnO is transparent at 532 nm and 1064 nm, the CIS layer absorbs the pump beam and reflects the probe beam. (b) Single pulse ablation studies were performed on an about 0.5 μm thick Mo layer on an about 3 mm thick glass substrate. Mo was ablated and observed through the glass sample.

3. Results

3.1. Multi pulse ablation

Multiple pulses are necessary for a selective removal of a CIS layer. The evolution of a multi pulse ablation is investigated in situ by taking pictures after each single pulse. We observe the multi pulse ablation of the whole layer stack of a CIS solar cell consisting of ZnO/CIS/Mo/Glass. Selected ablation pictures from 50 sequenced single pulses on the same position with the same fluence are shown in Figure 5, left side. The granular structure in the images displays the micro crystalline CIS surface structure. The originally round ablation spot are appearing elliptical due to the observation angle of about 40 degrees.

Recent microscopic investigations of ZnO laser ablation on CIS showed a bright region appearing after single laser pulse interaction. In this case, the laser transmits through the transparent ZnO layer and is being absorbed in the underlying CIS layer. The resulting evaporation of a fraction of the CIS layer initiates a spallation of the ZnO film. This lift-off effect is also called indirect induced ablation [8]. Thus, the bright region with a diameter of about 50 μm , which appears after the first pulse in Figure 5, is related to this effect. With each of the subsequent 20 pulses the brightness of the selectively ablated CIS layer is reduced. After 20 pulses a small bright region in the center of the ablation area appears corresponding to the uncovered Mo layer, which increases with the next pulses. After about 35 pulses the whole ablated region appears very bright, because the CIS layer is completely removed. After subsequent 5 pulses, a dark region in the center of the ablation area occurs, because the Mo layer was ablated and the bared transparent glass substrate has a low reflectivity. After 50 pulses, the area of the uncovered glass substrate is about 30 μm in diameter. The ablation region was also observed under a microscope with back side illumination for layer identification (Figure 5, right side). Here, the center of the ablation spot appears bright, because the back side illumination shines through the removed Mo region in the center.

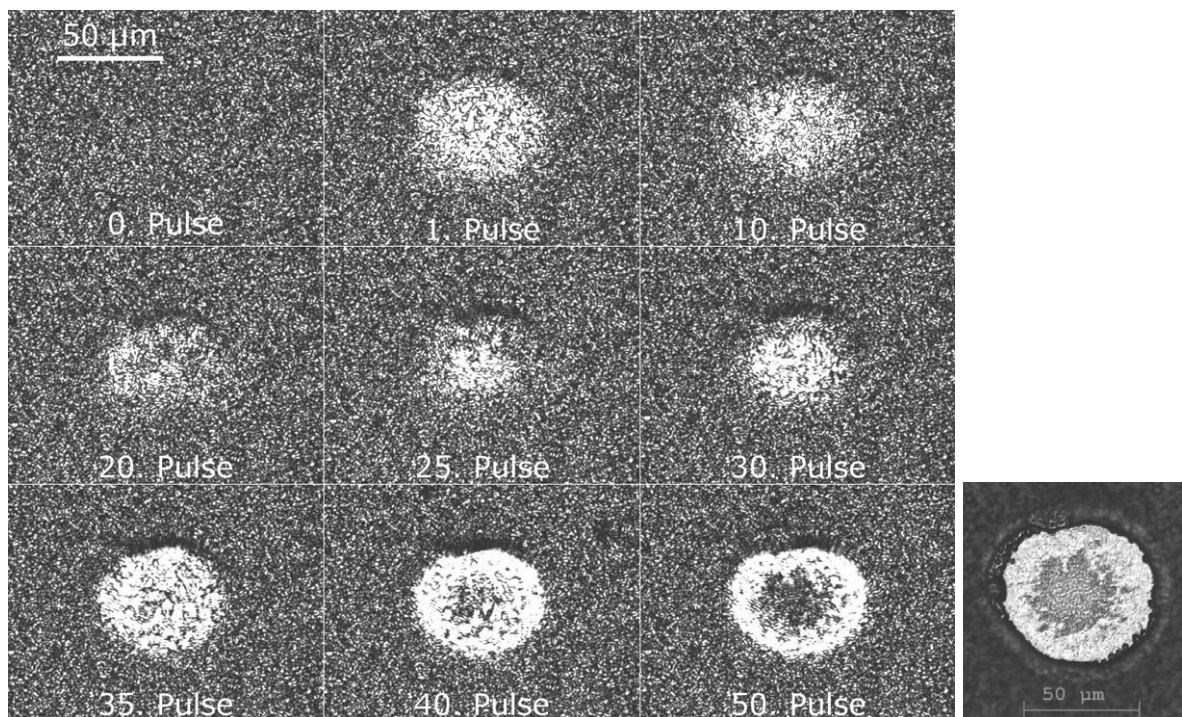


Figure 5. (a) Pump-probe microscopy images of multi pulse ablation on a ZnO/CIS/Mo/Glass sample. The images display the micro crystalline CIS surface structure. 50 single pulses were applied to the same position, while a picture was taken after each shot. The ZnO layer is removed completely with the first pulse because of a lift-off effect called indirect induced ablation [8]. During approximately the next 20 pulses the CIS layer is being selectively ablated. After 20 pulses, the subjacent Mo layer is partially uncovered. After 35 pulses the Mo layer appears to be completely free of CIS residues. After subsequent 5 pulses the laser penetrates the Mo onto the glass substrate, which can be more clearly seen after 50 pulses. (b) Microscopic picture taken from the same multi pulse ablation spot. Here, the region in the middle appears very bright because the backside illumination shines through the glass substrate and the removed Mo region in the center.

3.2. Time resolved microscopy of single pulse ablation

As recently shown in [7] the ablation or punching of the Mo layer starts at a certain laser fluence, while below this fluence the Mo layer was only bulged. In the following, we normalized the threshold fluence at which ablation starts to 100 % and call it punching fluence. To understand the mechanisms of the P1 glass side ablation, a Mo/glass sample was irradiated by a 10 ps laser at 1064 nm through the glass side with 40 %, 80 %, and 100 % of the punching fluence (see Figure 6).

Microscopic pictures from these experiments are taken through the glass substrate and from the Mo side are shown in Figure 6. It can be seen, at about 40% of the punching fluence only a small region of the Mo layer is affected. An increase to 80% of the punching fluence results in bubble formation of the Mo layer. At the punching fluence, the Mo layer is removed completely, showing punching-like behavior. The microscopic images in Figure 6 correspond to the time resolved images in Figure 7, recorded in the final state after several seconds (bottom line of Figure 7).

Figure 7 shows the temporal evolution of bulging and ablation of the Mo layer up to 3.6 ns after the impact of the pump beam. As a consequence of the observation angle, the ablation spot and the focal plane of the microscope intersect only in the horizontal center line of the ablation spot. Furthermore, almost round and elliptical spots in Figure 6 are imaged more elliptically by the pump-probe setup in Figure 7.

The temporal evolution of the slight bulging process at 40% of the punching threshold is shown in Figure 7, left column. A bright region surrounded by a dark rim appears already after 0.7 ns. The contrast of the inner ellipse and its outer rim increases with time. However, in the final state the contrast is getting weaker, but its shape and diameter remain constant.

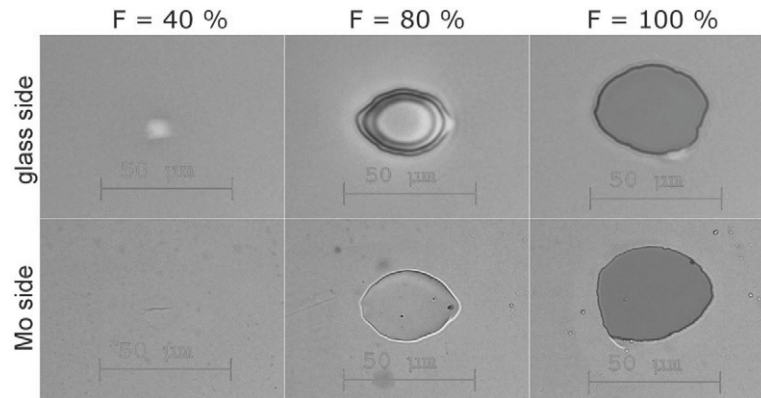


Figure 6. Microscopic pictures of single pulse ablation spots irradiated with 40 %, 80 %, and 100 % of the punching fluence taken through the glass substrate and from the front side. At the lowest fluence only a small region of the Mo layer was affected by the laser. The front view shows that the Mo layer has a small crack. At 80 % of the punching fluence Mo was bulged but not ablated, whereas at 100 % a Mo cap was ablated.

The temporal evolution of bulging at 80 % of the punching fluence is shown in Figure 7, center column. A vertical bright line appears instead of a bright ellipse with horizontal major axis. Furthermore, the brightness of the line increases with time. In the final state, the bar disappears and a distinct interference pattern occurs.

The temporal evolution of ablation at the punching fluence is shown in Figure 7, right column. Here, the contrast also increases with time, but the profile of the bright region displays another different shape. Furthermore, interference rings are getting visible around the ablation region at 1.6 ns, which remain even in the final state. Regarding the transition from 3.6 ns to the final state, a distant interference pattern appears at 80 % of the punching fluence, whereas at the punching fluence only the bright spot disappears without additional interference formations. In the final state, the region appears dark because the Mo layer is completely removed.

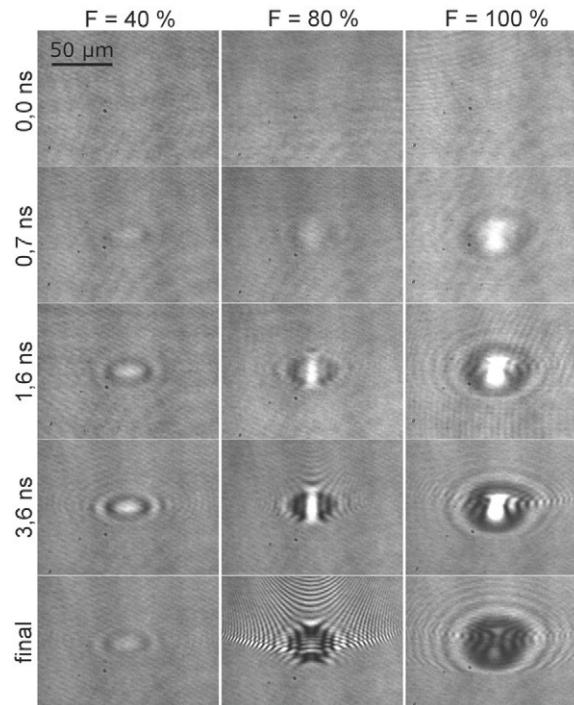


Figure 7. Pump-probe microscopy images of backside Mo film ablation initiated with 40 %, 80 % and 100 % of the punching threshold recorded through the glass substrate at an observation angle of about 40° to the pump beam. The columns show the temporal evolution of the affected area from 0.0 ns up to 3.6 ns and the final result several seconds (last line) after the initiation. Cracking and bulging occurred at 40 % and 80 % of the punching fluence, respectively, whereas a Mo cap was punched out at the punching fluence.

4. Discussion

Applying time and space resolved pump-probe microscopy to the multi pulse ablation of a CIS/Mo/glass layer system demonstrates the capability of ps-laser pulses for a selective ablation (see Figure 5). This method is very useful to find an optimal number of pulses per position (PPP) for the P2 and the P3 process (ZnO/CIS onto Mo) for monolithic interconnection during CIS thin film solar cell production, because the influence of each single pulse can be observed and studied individually. Nevertheless, investigating the influence of the laser repetition rate is limited by the frame rate of the used standard CCD camera. Future investigations by measuring the depth of the ablation after different numbers of pulses with a confocal microscope will also show the evolution of the depth profile over the applied pulse number. Moreover, in situ investigations of trench scribing at slow speeds can also be performed.

Time resolved results of the bulging and ablation of Mo from the glass side with different fluences are shown in Figure 7. Bright ellipses or lines appear in the middle of the affected area probably because the bulging Mo layer forms a reflecting concave surface. Figure 1 shows, increasing the fluence also increases the bulging height, and thus decreases the radius of the formed concave mirror.

The pictures of the bulging process at 40 % of the punching fluence, which are taken after 3.6 ns delay time and from the final state, show only a difference in contrast but not in shape (Figure 7, left column). Hence, the slight bulging process is almost finished within 3.6 ns.

At 80 % of the punching fluence the same comparison shows a significant difference (Figure 7, center column). At 3.6 ns a bright line is visible, whereas in the final state distinct interference effects occur. Thus, the bulging process at 80 % of the punching fluence is not completed within 3.6 ns.

In contrast, the picture, taken after 3.6 ns at the punching fluence, showed reflections in the center of the ablation region, whereas in the final state only a dark region is visible (Figure 7, right column). In conclusion, the Mo layer is still bulging after 3.6 ns and the Mo disk will lift-off at later times.

For a better understanding of the lift-off process, the time domain has to be increased in future to delay times higher than 3.6 ns. Thus, a second laser will be synchronized to the ps-laser by an electronical delay generator to observe the time domain from 4 ns to some seconds. Furthermore in future experiments, bulging and ablation will be observed from different viewing angles or by coaxial illumination. Thus, it will be possible to measure the bulging speed and the speed of the flying cap observing the ablation from the side. [15]

5. Conclusion

For the first time, a pump-probe microscopy setup was used to investigate laser ablation processes related to the monolithic interconnection of CIS thin film solar cells. The setup was used for a time and space resolved investigation of a directly induced laser lift-off effect, occurring when a Mo thin film is ablated by irradiation through the glass substrate. Furthermore, the setup was also used for in situ investigations of a multi pulse ablation through the whole layer stack (ZnO/CIS/Mo/Glass) of a CIS thin film solar cell.

Each single pulse of the multi pulse ablation had the same fluence, a wavelength of 1064 nm and pulse duration of 10 ps. It was shown that after the first pulse the ZnO layer was completely removed by a lift-off effect which was indirectly induced by the CIS layer. Further 20 pulses were necessary to ablate the CIS layer until the Mo layer was uncovered. After 35 pulses the Mo layer was completely freed from CIS. The glass substrate was uncovered after 40 pulses. In this manner, for the first time the selective structuring of thin film systems consisting of multiple layers with ps-laser pulses has been resolved. Furthermore, this method can be used to precisely determine process windows for thin film structuring.

Time- and space resolved investigations of the glass side ablation of Mo on glass showed the evolution of bulging during the first 3.6 ns after the impact of the pump pulse. It was shown that slight bulging occurred at 40 % of the punching fluence, and that the process did not further evolve after 3.6 ns. Increasing the fluence to 80 % showed that the bulging process takes more than 3.6 ns. Furthermore, at the punching fluence the Mo film was still intact, showed only bulging, but no cap removal after 3.6 ns. Thus, for a better observation and understanding of the complete bulging and ablation process, the time domain and the viewing angles of the setup have to be extended.

Acknowledgements

This work was partly funded by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety within the project “SECIS”.

We would like to express our special thanks to vice president Christiane Fritze and Juergen Meier of Munich University of Applied Sciences for supporting our work financially.

The authors would like to thank Helmut Herberg and Michael Kaiser from Munich University of Applied Sciences for the help with confocal image profiling.

We also would like to thank Avancis GmbH & Co. KG for providing the investigated samples.

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