IMPACT OF THE SOLVENT PROPERTIES ON THE MORPHOLOGY OF THE SILICON SURFACE GENERATED BY LASER ABLATION UNDER A SOLVENT FILM

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ABSTRACT. An improvement in Silicon ablation by lasers is achieved when laser ablation takes place under a thin liquid film. Therefore it is necessary to investigate the effects of the liquid on the silicon surface during laser irradiation. Different types of microstructures observed on the silicon [100]-surface of a Si-wafer after nanosecond-pulsed laser irradiation under liquid films of molecular solvents are presented to complete our understanding of the Laser Chemical Processing (LCP). Water and perfluorocarbons (PFCs) are hitherto employed as liquid media due to their high thermal and chemical stability in the LCP. Here we report on results obtained with a new reactor that allows studying the stability of solvents occurring during the laser irradiation and the effects of solvents on the silicon surface during and after laser irradiation.

Keywords: Laser irradiation under solvent, nanosecond laser, microstructuring of silicon, IR spectra.

1 INTRODUCTION

The deep laser cutting is strongly affected when different solvents are employed in the LCP. Therefore a new method is necessary to characterize how the silicon surface is affected when a silicon wafer under different solvent films is irradiated by laser light. In this work we presented a new Reactor to perform these experiments and to support the understanding of the LCP.

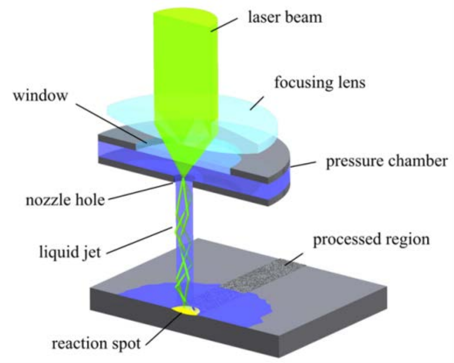

Figure 1:Schema of the LCP

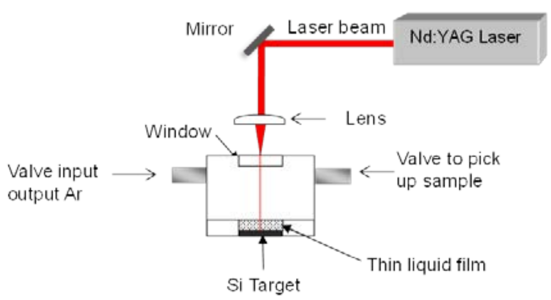

Figure 2 Schema of the Reactor

The reactor chamber contains two input-output valves providing inert gas condition inside and picking of sample. In this work a 5 ns 1064 nm nanosecond laser with a maximum peak power $8.4x10^8$ W is employed. Monocrystalline [100]-silicon targets (20 x 20 x 0.78 mm) were used, which were irradiated with different laser parameters, exposure times and different volume of solvent. The silicon targets are deposited in a small hole in the basis of the reactor (about 20x20 mm). The laser beam goes through the thin liquid film and achieves the silicon surface. According to the impact of the laser on the silicon surface a crater is generated. The silicon is molten, evaporated and ejected at the middle of the laser spot and afterwards the material is cooled by the liquid film and redeposited on the silicon surface. Different microstructures on the silicon surface are generated by laser irradiation under different solvents. In this work the morphology of two different crater zones are studied. The first zone a) represents the border area of the crater in which the material is ejected. The second zone b) is the middle of the crater directly in the spot zone. In the following pictures the different zones of the crater are shown.

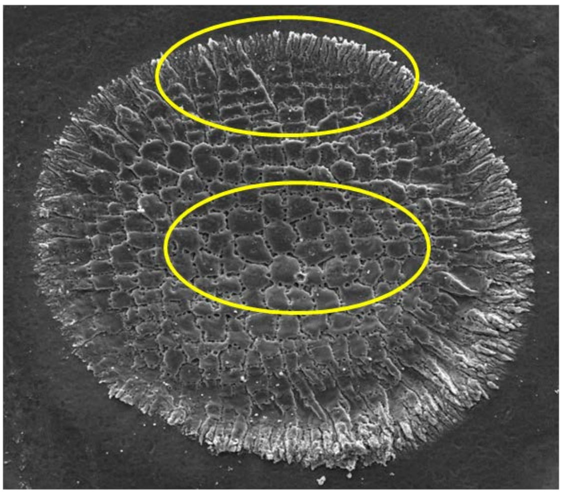

Figure 3: SEM picture of the two zone study in this work zone a) in the middle of the crater and zone b) edge.

In this work we present the results obtained with deep laser cutting in a silicon block under different solvents with LCP at Fraunhofer ISE and the results obtained when a silicon target is irradiated by a nanosecond laser under different solvents in a Reactor developed at University Freiburg. Finally according to the results it is shown that the Reactor is a useful tool to better understand the LCP.

2 RESULTS OF LCP

Several laser grooves were performed on a silicon wafer (5x5x0.2 cm) with an infrared laser using a 50 µm nozzle. The LCP parameters used in this experiments for all different solvents were: 198 bar, 15 Khz, 42 W and number of scans 40. In the following picture it is shown that the grooving depth is affected by the solvent in the LCP.

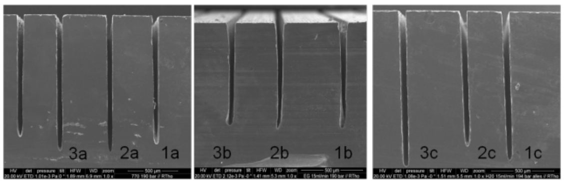

Figure 4: Different laser grooves achieved by the LCP under different solvents. Laser parameters: 40 scans, 42 W, 15 Khz and 198 bar. a) Three laser grooves (1a, 2a and 3a) obtained by FC-770 with 200 mm/s. b) Three laser grooves (1b, 2b and 3b) obtained by EG with 200 mm/s c) Three laser grooves (1c, 2c and 3c) obtained by H_2O with 200 mm/s.

To improve the depth of the grooves by the LCP a mixture of FC-770 and 0.034 M of Chlorine gas was used in previous work [1] with a liquid pressure of 103 Bar. In this work the depth of the laser grooves could be increased when the pressure was also increased, see table 1.

Table I: Laser parameter and flow conditions of the grooves of Figure 2.

Solvent	Frequency [Khz]	Power [Watt]	Scan speed [mm/s]	Pressure [Bar]	Deep [µm]
FC-770	13	69	200	103	850
FC-770 1a)	15	42	200	186	1294
FC-770 2a)	15	42	200	186	1375
FC-770 3a)	15	42	200	186	1383
EG 1b)	15	42	200	198	740
EG 2 b)	15	42	200	198	733
EG 3b)	15	42	200	198	713
H_2O 1c)	15	42	200	198	1232
H_2O 2c)	15	42	200	198	1035
H_2O 3c)	15	42	200	198	1176

3 RESULTS WITH THE REACTOR

Different microstructures on the silicon surface were generated by laser irradiation under different solvents. The silicon target was irradiated with 39 mJ and covered by a thin solvent film of 0.6 mm high. Different nucleation sites are obtained under different solvents. The nucleation sites were generated by a Phase explosion [2-4] in which the silicon is overheated beyond the spinodal temperature [5,6]. As a consequence the liquid and gas phase are in equilibrium and nucleation bubbles are generated which can be seen in the following pictures. A smooth surface was generated when the silicon target was covered by FC-770, FC-43 AND EG.

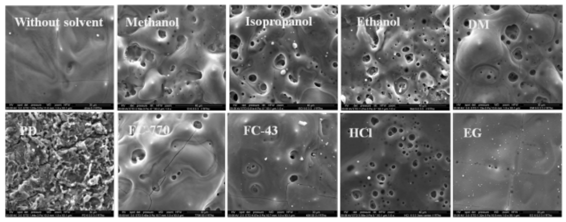

Figure 5 : SEM pictures of different silicon targets irradiated by a nanosecond laser under different solvents corresponding to the zone a: Laser parameter 39 mJ laser energy 3 second laser irradiation and 0.3 ml solvent

In addition a change in surface structure can be seen in figure 5 when the surface is irradiated with varying laser power for 3 seconds and 0.6mm liquid height.

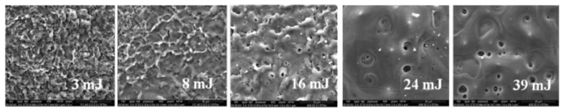

Figure 6: SEM picture of different silicon surfaces covered by FC-43 and irradiated for 3 seconds with varying laser energy.

When the laser beam achieves the silicon surface the material is molten. A fraction of silicon is evaporated and disappears from the reaction spot. On the other hand the molten material is moved and ejected out of the reaction spot. After the laser irradiation the overheated silicon surface cools down and the material solidifies. Depending on the used solvent the silicon morphology looks different in the border area of the craters see figure 6. The ablated silicon volume was measured with a LEXT confocal microscope. The values of the volume ablation rate were then calculated by dividing the ablated volume of the silicon by the experimental time.

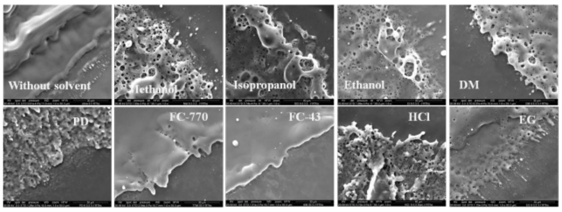

Figure 7: SEM pictures of the different solidification structures of ejected material from the reaction spot under 39 mJ laser energy 3 second laser irradiation and 0.3 ml solvent

3.1 Silicon volume ablation rate for different solvents and average laser powers

The silicon targets were covered by 0.3 ml solvent and irradiated 3 seconds experimental time under 3, 8, 18, 26, 32 and 39 mJ laser energy. In the following picture the difference in silicon volume ablation rate is shown for varying solvent films on the silicon surface using the same laser parameters.

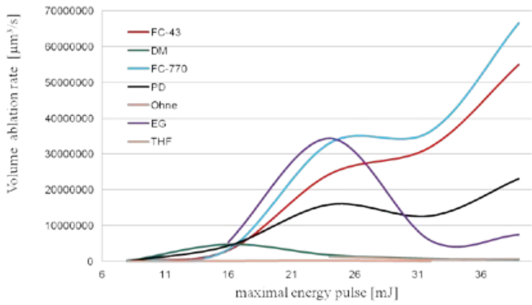

Figure 8: Values of volume rate of silicon under different pulse energy and solvents.

The best values are obtained by PFCs, FC-770, FC-43 and PD. In the following table the physical properties of solvents used in this study are listed.

Table II: Physical properties of solvents

Phy. Properties	FC-770	FC-43	PD	Met	IP	Et	EG	HCl	DM	THF
Bp (C°)	95	174	80	65	82.5	78	197	61	39.6	66
Density(Kg/m3)	1793	1860	1730	791.8	768	789	1113	424.4	1330	0.889
Viscosity (Cp)	1.359	4.7	0.87	0.59	1.96	1.2	16.1	1.9	5.85	0.48
Vp (KPa)	6.58	0.19	10.6	13.02	4.3	5.95	53	14.5	47	17.3
ΔH_v (Kj*mol^{-1})	65.33	160.3	46.19	38.57	43.98	41.68	63.9	44.64	28.4	32

As shown in figure 3 different deep laser grooves are achieved with LCP by using different solvents. However the impact of the solvent properties on the processed silicon surface cannot be investigated for LCP laser grooves due to the preparation problems.

On the other hand the stability of the solvent cannot be measured by the LCP because the atmosphere is not inert and no spectra device is coupled to measure the liquid phase after and before the laser irradiation. The physical properties of the solvents play an important role in the volume ablation rate of silicon by the LCP but unfortunately are not possible to measure in the LCP. Therefore the Reactor is a good device to complete the understanding of the LCP. According to the results the best volume ablation rate are achieved by PFCs which have a high vaporization enthalpy, a high density and boiling point.

3.2 Infrared Spectra

The silicon targets are covered by different solvents. The liquid phase before and after the laser irradiation is measured by IR spectroscopy and compared (see figure 8) The solvent can be decomposed during laser irradiation. In this case the signal of the decomposed products would be detected by the IR spectroscopy. The black line corresponds to the signal of solvent without laser irradiation, the red one corresponds to the liquid phase after 3 mJ laser energy, the blue one to 8 mJ and the green line to 16 mJ. If the solvent is decomposed during laser irradiation a foreign signal would be appear or the signal would change. It can be seen that only for DM a variation of the signal takes place. The blue line differs from the black line and the green line is higher than the red. The change in the blue line indicates decomposition or a change of the liquid phase under laser irradiation. For the other solvents no changes of the foreign signal can be observed which means that the solvent are stabile during laser irradiation.

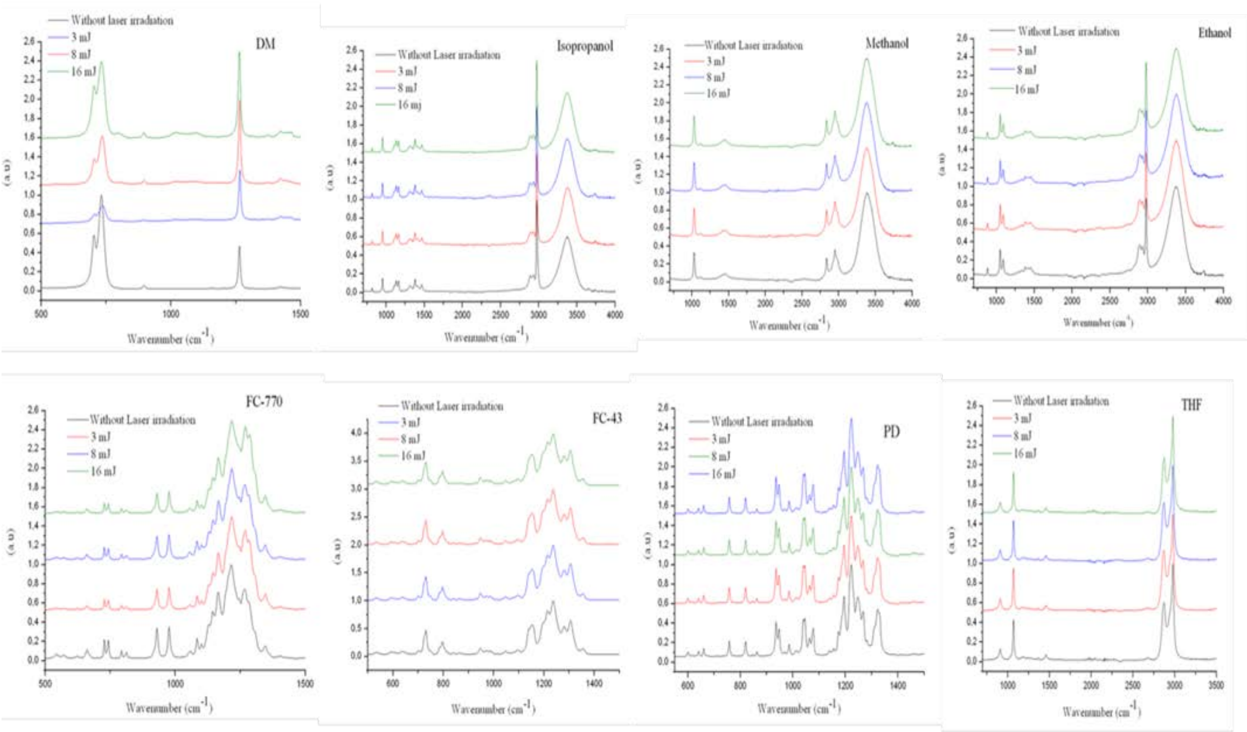

Figure 9: IR spectra of the solvents used in this study before and after laser irradiation

4 DISCUSSION

The highest volume ablation rate is achieved by PFCs and according to the physical properties we can suggest that high values of vaporization enthalpy, density and boiling point trigger an increase in the silicon volume ablation rate. The investigation of the liquid phase after and before the laser irradiation lead to the conclusion that only the DM is decomposed during laser irradiation since for the other solvents no decomposed products are generated due to absence of unknown IR signal or variation in the spectra signals. According to the SEM pictures of the silicon surface morphologies achieved for constant laser parameters and the same amount of solvent it was clearly shown that the different microstructures are due to the influence of the physical and thermodynamic properties of the solvent.

5 CONCLUSIONS

The Reactor is a good tool to characterize microstructures generated on a silicon surface during laser irradiation, which unfortunately is not possible to characterize in the LCP. Therefore the Reactor is a good tool to complete the understanding of the LCP.

The characterized IR liquid phase of the solvents has shown the chemical stability of the solvent during laser irradiation. According to the values of the calculated silicon volume ablation rate we conclude that the physical properties play a significant role in terms of achieved surface morphology. The best results are obtained by FC-770 which achieves a good deep cutting in the LCP

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