Abstract

A self-induced mechanism leading to the formation of periodic microstructures has been observed during femtosecond pulsed laser ablation with a high repetition laser source. The bottom of an ablated area shows two different kinds of microstructures. A periodic ripple or a chaotic columnar structure emerges. It has been observed that the second morphology grows out of the first one dependent mainly on the amount of fired laser pulses. This transition and the influence of several parameters on it are described. Both structures have several variations in morphology. Regarding the possible applications of such structures, this is of special interest. The presented experiments give a first glimpse of the possible microstructures emerging after ultrafast laser machining. Concerning the physical background of the found phenomena, it has been observed that a liquid phase is present in the ablation process. The formation of ripples is closely linked to that fact. Existing models on ripple formation could not be linked to the ripple spacing found in the experiments.

Introduction

In nature the morphology of surfaces is used to tune material properties to the highest possible level. Self cleaning surfaces for example, like that of the lotus leaf, amplify the hydrophobic properties of wax crystals by superimposing them on a rough, microstructured surface. Fig 1 shows the effect of this on a water droplet situated on a leaf. The goal of this research is to structure the surface of a metal mold by ultrafast pulsed laser ablation. This mold will be used for a replication process like injection molding or phase separation micromolding [17] in order to fabricate polymer products that have self-cleaning abilities.

During experiments a self structuring mechanism at the bottom of the ablated areas was observed. Depending on laser parameters, a ripple pattern and a columnar pattern emerged over the total ablated area.

Hopes are high that such structures can be utilized in a mold to generate a rough surface that amplifies the hydrophobic properties of the material used in the replication process. The presented experiments are first steps towards a deeper understanding of the emergence of microstructures, the possible variations and the reproducibility thereof. The ripple structure is discussed for about 30 years, and the proposed models do not predict all experimental results. This research gives new experimental data on which the proposed models can be validated. The next section will present some of these models.

Proposed mechanisms

The periodic pattern, often referred to as laser-induced periodic structure (LIPPS), can be understood as a very general phenomenon as it is observed on many different materials, using lasers with wavelengths ranging from 0.193 – 10.6 µm and pulses from micro- to femtosecond regime. Metals [1,2], semiconductors [2-6] and insulators [7,8] showed to form periodic ripples after laser irradiation. The orientation and period of the ripples depend on the following laser parameters: polarization, angle of incidence, fluence, wavelength and number of pulses. A widely accepted model assumes an inhomogeneous energy input across the ablated spot resulting from interference of the incident beam with microscopic fields scattered by a surface roughness [9-11]. Two interference patterns are predicted with a ripple period of \( \lambda/(1 +/- \sin \beta) \) (\( \lambda \), laser wavelength in vacuum; \( \beta \) angle of incidence in respect to the surface normal) oriented perpendicular to the incident beam polarization. A third, observed pattern appeared to be oriented parallel to the beam...
polarization with a period of $\lambda/cos \beta$ [12,13]. However, some experimental results can not be fitted in this model and other mechanisms are proposed [4, 14].

Becker et al. adopted and modified an idea by Willis and Emmony [15]. They propose resonant absorption of photons by plasmons at the surface of critically sized metallic droplets [16]. The droplets would be produced by thermal fluctuations driving the excited solid locally above the melting temperature.

Maracas et al. found an extremely wide ripple spacing of ~6,5$\lambda$ and explained it by an acoustic wave pattern corresponding to the axial mode beat frequencies of the used ruby laser, resulting in a periodic melting of their GeAs samples.

Another mechanism is boson condensation in very high carrier density regions, as proposed by van Vechten [19]. Such high carrier densities are present in the interaction of an intense femtosecond laser pulse with a material. According to the hypothesis, the polarization waves of the plasmon modes begin to create and destroy electron-hole pairs in a coherent fashion. The carriers become paired carriers which behave as bosons. These condensate according to the boson condensation mechanism. The hypothesis states that by this mechanism ripples can be formed.

**Experimental setup**

All experiments were performed on 2mm cold rolled stainless steel 304 (austenitic) with industrial BA surface finish. A titanium sapphire based laser system with a central wavelength of 800nm was used for the generation of the laser pulses. A seed/oscillator combination (Coherent Vitesse Duo) together with a regenerative amplifier (Coherent RegA9000) delivered a pulse train of 250 kHz repetition rate with 1W average power. The pulse length, measured by a second order auto-correlator, was adjusted to 200 fs for all experiments. A combination of a rotary $\lambda/2$ wave plate and a beam splitting polarizing cube served as attenuator. The beam is horizontally polarized. Manipulation of the bundle over the sample was accomplished by a two mirror galvo-scanner system (Scanlab Scangine 14). A 55mm f-theta lens (fused silica) focused the beam to a spotsize of 20 µm. The fluence was determined by measuring the beam power at the exit of the scanner system with a power meter and dividing it by the repetition rate and the surface area of the laser spot. These values are averages across the irradiated area, as the energy distribution of the pulses is Gaussian.

The goal of the presented research is gaining insight in the formation of microstructures emerging at the bottom of ablated surfaces.

Four main sets of experiments were performed: a) irradiation of one spot by different numbers of pulses; b) scanning of lines, in which the scanning speed is adjusted to get an overlap that fits the number of pulses used in a); c) scanning of surfaces, here the scanning speed and the overlap between two adjacent lines determine the number of pulses that hit one unit area on the sample; and d) scanning of lines on tilted samples. All experiments were performed under atmospheric conditions. Four different fluences were used, from single pulse threshold fluence to 10 times threshold fluence. The results have been analyzed by optical and scanning electron microscopy (SEM).

**Experimental results**

**Single spot experiments**

In the fist set of experiments a single spot is irradiated with increasing number of pulses at different fluences. The threshold fluence was found to be 0.1 J/cm$^2$ for a single pulse experiment. Other fluences used in the experiments are 1.1 J/cm$^2$, 0.8 J/cm$^2$, 0.4 J/cm$^2$. The formation of the ripples starts with the first pulses, as can be seen in Fig 2. In this experiment the highest possible fluence of 1.1 J/cm$^2$ was used, limited by the maximum output power of the laser and the smallest spotsize. The ripples are perpendicular to the incident electric field and show a spacing of 620 nm. The energy of the laser pulse is significantly higher in the center of the irradiated area due to the Gaussian beam profile. This leads to a faster transition in morphology in this region, as can be clearly seen in the SEM micrographs. After about 5 pulses the ripple morphology changes into a more chaotic bumped surface. The more pulses are fired, the larger this area gets. This morphology could be a result of a liquid layer that has undergone phase explosion due to superheating. Picture f) and g) show clear evidence for a rapid expulsion of liquid droplets which then cool quickly and resolidify. The formation of a deep hole starts at 100 pulses in the center. After 800 pulses the hole extends nearly to the total irradiated area. The asymmetrical shape is a result of the asymmetrical energy distribution in the focus of the beam. The same experiments using lower fluences show similar results. The transition in morphology however is dependent on the used fluence. At lower fluences, the change will occur after more pulses. At a fluence of 0.4 J/cm$^2$ 20 pulses are needed to destroy the ripple pattern in the center of the spot. Furthermore the expulsion of
material seen in Fig 2 f) and g) is not observed for lower fluences.

The microstructures forming at the walls of the ablated holes also show transitions in morphology (Fig 3). Using 300 pulses a two-dimensional grating with feature sizes of 1µm occur, after 800 pulses this is changed into a fine structure consisting of grains of 300 nm diameter.

Line scanning experiments

Lines have been ablated using the galvo scanner with different scan speeds and fluences. The scan speed defines the overlap between two subsequent pulses. Eight different speeds have been used in order to irradiate a unit area with the same amount of pulses used in single spot experiments. At a scan speed of 500 mm/s for example, a spot is hit by 10 pulses. However, due to the Gaussian beam profile the middle of the line is not only irradiated by the highest intensities, but a considerable amount of pulses hit this area with its lower intensity outer edges. For this reason, the results shown in Fig 4 can not directly be compared to that of Fig 2. The transitions in morphologies can be very clearly seen on the pictures. The ripple pattern starts to grow from a rather irregular pattern ablated at a scan speed of 2000 mm/s to a more regular one at 250 mm/s. Especially the edges of the lines show very regular patterns in b), c) and d). At a scan speed of 100 mm/s perpendicular trenches start to break the ripples in the middle of the ablated line.

Fig 2: SEM micrographs of spot irradiated by increasing numbers of pulses at a fluence of 1.1 J/cm²: a) 3 pulses, b) 5 pulses, c) 10 pulses, d) 20 pulses, e) 50 pulses, f) 100 pulses, g) 300 pulses, h) 800 pulses

Fig 3: Morphologies of the holes at a fluence of 0.1 J/cm²: a) irradiation with 300 pulses, b) 800 pulses. Both images have the same magnification.

Fig 4: SEM micrographs of lines ablated with decreasing scan speeds a fluence of 1.1 J/cm²: a) 2000 mm/s, b) 500mm/s, c) 250mm/s, d) 100mm/s, e) 50mm/s, f) 17mm/s, g) 10mm/s, h) 7mm/s
At even lower speeds the ripples start to show defects in the out of plane direction and at 17 mm/s miniscule droplets form on top of the ripples. This process develops further until nearly the whole ablated surface is covered by droplets. Other fluences led to similar results. The observed ripples are orientated perpendicular to the incident electrical field and the spacing is 670 nm, independent on fluence and scan speeds.

Surface scanning experiments

In the third set of experiments areas were ablated using the galvo-scanner which manipulated the beam in a one-directional hatch pattern. Different fluences, scan speeds and distances between the hatch lines were used. Fig 5 represents a typical experiment. Here, the maximum fluence of 1.1 J/cm² and the hatch line distance of 15 µm were kept constant, the scanning speed was decreased in 7 steps from 2000 mm/s to 16 mm/s. Two adjacent scan lines overlap by 5 µm leading to an overlap percentage of 50%. It is worth noting that only the outer, lower energy regions of the pulses overlap. The SEM micrographs again show a transition in morphologies. The ripple pattern has its most regular form at a scan speed of 1000 mm/s. However, the regularity seen at the outer edges in the scan line experiments are not matched, disorientations are always present. The ripples are perpendicular to the incident electrical field and show a spacing of 600 nm. Distortions perpendicular to the ripples start to show up at 500 mm/s. These grow into trenches with decreasing scan speed. At a scan speed of 100 mm/s droplets start to form on top of the ripples. Finally, at 16 mm/s the ripple structure disappeared completely. Instead, a rough and chaotic morphology emerges, covered by submicron sized grains.

The experiments show that the structure at low scan speeds also is highly dependent on the used fluence and hatchline distance. Fig 6 shows three areas scanned with different fluences. All other parameters are kept constant. At a fluence of 0.4 J/cm² the morphology is characterized by the trenches and grain covered ripples. Increasing the fluence to 0.8 J/cm² the trenches have grown and are pronounced even more. The bumps in between have dent-like shapes, still covered with submicron grains. Increasing the fluence to 1.1 J/cm² has a dramatic result: mountain-like pillars seem to grow out of the surface. Very deep irregular trenches have formed and the emerging structures are not covered by grains but have a crystal-like appearance.

Fig 5: Areas ablated with varying scan speeds. Fluence 1.1 J/cm², hatchline distance 15µm: a) scan speed 2000 mm/s, b) 1000 mm/s, c) 500 mm/s, d)250 mm/s, e) 100 mm/s, f) 50 mm/s and g) 16 mm/s h) length scale for all micrographs of this figure.

Fig 6: Dependence of morphology on fluence. Used scan speed 16 mm/s, hatchline distance 5 µm; a) fluence of 0.4 J/cm², b) 0.8 J/cm², c) 1.1 J/cm² and d) zoomed in on micrograph c).
Keeping the fluence constant and varying the hatch line distance also leads to different results, as is depicted in Fig 7. By decreasing the distance from 20 µm to 15 µm the ripples totally disappear. Also the perpendicular trenches get less pronounced. At 10 µm little crystals seem to grow on top of the roughness. Letting the hatch lines overlap four times (distance = 5 µm) leads to the same results as shown in Fig 6 c) and d).

![Fig 7](image1)

**Fig 7:** Dependence of morphology on hatchline distance. Fluence 1.1 J/cm², scan speed 16 mm/s: a) hatchline distance 20 µm, b) 15 µm, c) 10 µm and d) 5 µm.

**Line scanning on tilted samples**

In order to investigate the possible physical background of the ripple formation, also experiments on tilted samples have been carried out. Lines have been ablated with different fluences, scan speeds and angles of incidence. The interference model predicts two ripple spacings dependent on the angle of incidence: \( \Lambda_{1,2} = \frac{\lambda}{1 \pm \sin \beta} \). The results depicted in Fig 8 show a superposition of a fine and course spacing, the fine one located at the edges and the course one in the middle of the ablated line. Different kinds of transition can be observed: a) two small ripples combining to form a large one; b) small ripples superimposed on large ripples; c) gradually transition of small to large ripples. In all cases the larger ripples are dominant in the area irradiated by the higher energy part of the pulses, the smaller ones extend over the areas irradiated by the lower energy edges of the pulse. The ripple spacings are again not consistent with the model, as can be read in Table 1.

![Fig 8](image2)

**Fig 8:** Lines ablated on tilted samples. Pulse strikes the surface on the left hand first. Fluence 1.1 J/cm², scan speed 150 mm/s. a) angle of incidence (measured between normal of surface and incident beam) 10°, b) 20°, c) 30°, d) 40° and e) 50°.

**Table 1:** Predicted and measured ripple spacings in experiments on inclined samples. Predictions according to \( \Lambda_{1,2} = \frac{\lambda}{1 \pm \sin \beta} \) with \( \lambda = 800 \text{nm} \).

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<th>( \beta )</th>
<th>Predicted ( \Lambda_1 ) [nm]</th>
<th>Predicted ( \Lambda_2 ) [nm]</th>
<th>Measured ( \Lambda_1 ) [nm]</th>
<th>Measured ( \Lambda_2 ) [nm]</th>
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<td>1000</td>
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**Discussion**

**Ripple formation**

The formation of ripples in all four experiments is discussed in more detail. It is observed that the growth of a regular pattern needs a certain amount of pulses irradiating the same area. Regular ripple patterns that extend over larger areas have formed after irradiation with about 10 pulses. However, the irradiating fluence has to be constant. This can be seen in the experiments depicted in Fig 4, the outer regions are irradiated only with the lower energy edges of the pulses. Here, very regular patterns have formed. The incident fluence in the middle of the line changes due to the Gaussian beam profile, which obviously leads to irregularities and dislocations in the pattern. Also the scanned areas
do not show regular line patterns over larger areas. Transitions and dislocations occur in all experiments. In [18] instabilities of sand ripples are described. Here the same phenomena can be observed. For sand ripples these are linked to a change in water wavelength, which is the driving force and determining factor for sand ripple formation and spacing. This means that instabilities occur when the ripple spacing starts to change due to varying conditions. Linked to the experiments described here, it can mean that the ripple formation is fluence dependent, because only that regions stay stable where the irradiated fluence is constant. On the other hand, no change in ripple spacing due to fluence change is observed in the experiments on flat samples. Tilting the sample however leads to two different spacings that evolve into each other. The dominance of one spacing over the other is steered by the incident fluence, since the larger spacing appears in the areas with higher fluences and the smaller in low fluence regions. Obviously the fluence is an important factor in the formation and selection of the dominant ripple spacing, but does not have direct influence on the spacing itself.

The investigations of the samples revealed the presence of a liquid phase during the formation of the ripples, as is depicted in Fig 9. Note the little fingers perpendicular to the ripples in picture a), which indicate a flow of molten material towards the ripples. This observation is consistent with the explanation of ripple formation driven by the surface tension of a liquid layer [11]. Such layer would have a non homogeneous temperature distribution. Material is displaced from hotter to cooler regions due to the gradient in the surface tension. After quick resolidification the ripple pattern is formed.

![Fig 9: Ripples formed by surface ablation at a fluence of 1.1 J/cm², scan speed 2000 mm/s, hatch line distance 20 µm: a) high magnification b) low magnification.](image)

The remaining question is what kind of mechanism leads to the periodic temperature distribution in the first place. No spacing found in the described experiments matches the predictions of the interference model. A further possible parameter of influence could be the pulse repetition rate of the laser source. No other experimental results with such a high repetition rate femtosecond pulsed laser have been reported yet. Heat accumulation in the bulk material could be a factor of importance. Another parameter that has not been varied in the described experiments is the pulse length. Experiments are planned to investigate the influence of both parameters.

**Transition**

An understanding of the transition of the ripple pattern to a more chaotic structure can possibly reveal the secrets of the ripple formation itself. It is observed that the breakdown of the ripples mainly depends on the number of fired pulses. Variation of other parameters like fluence could only delay the onset, but never prevent it. A possible decisive factor could be the depth of the ripples. As soon as the ripples depth equals the laser wavelength, further pulses could cause their deterioration. However, further research has to validate this hypothesis.

**Conclusion**

Experiments of femtosecond pulsed laser ablation showed a transition of a periodic ripple structure into a chaotic columnar structure on the bottom of an ablated area. The onset of this transition is mainly dependent on the number of pulses used to irradiate a unit area. The fluence and the overlap between pulses and lines ablated with the galvo scanner had influence on this number. As predicted by the interference model, the ripple patterns were found to be perpendicular to the incident electric field. The ripple spacings found could not be linked to the theoretical values. However, some insights have been gained that can lead towards a new understanding of ripple formation: a) a liquid phase is present during formation, b) if the angle of incidence allows two different spacings, the dominance is controlled by the laser fluence, c) there must be a specific link between the ripple properties and the onset of deteriorations. The depth is the most likely parameter.

The ripple patterns showed similar morphologies in all experiments, whereas the chaotic structure appeared to adapt very different morphologies highly dependent on little parameter changes. In this respect, it seems possible to tune the structure to a specific need. The first application will be the fabrication of a mold with a microstructured surface. The negative of this morphology will be copied to a polymer replica in order to amplify it’s hydrophobicity to self-cleaning abilities.
References


