Experimental study of spatial frequency transition of laser induced periodic surface structures

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Abstract. This study shows the influence of laser fluence and pulse number on the spatial frequency distribution of laser induced periodic surface structures (LIPSS) on a stainless steel surface. Also the transition of LIPSS to larger self organized, periodic, cone-like structures has been investigated. The experiments were carried out using a Ti:Sapphire femtosecond laser system with 800 nm centre wavelength, a pulse duration of 30 fs and a repetition rate of 1 kHz. Experiments have been carried out on flat, cold-rolled stainless steel surfaces (1.4301) by variation of the laser output power and feed rate. It could be shown, that the transition of low spatial frequency LIPSS (LSFL) to high spatial frequency LIPSS (HSFL) is a continuous process, strongly depending on the laser single pulse fluence and the pulse number. At higher accumulated fluences the transition of LIPSS to larger self organized structures could be observed. As a result, hierarchical structures were created with micrometer-sized cones at the bottom and nanometer-sized LIPSS on top. By further increasing the accumulated fluence, the grooves between the micro structures are widened until the ablation threshold of the alloy is reached. These hierarchical structures could be of considerable value in improving wetting properties of technical surfaces.

1. Introduction

Laser induced periodic surface structures (LIPSS) are self organized nano structures that occur, when laser radiation interacts with the surface of a material near its ablation threshold for a single laser pulse [1]. They were first observed in the 1960ies after illumination of semiconductor surfaces by a pulsed ruby laser and high peak powers [2]. Since then, the initial formation mechanisms of LIPSS have been investigated using a variety of laser sources and substrate materials, but they are still subject of international research [3]. They have been applied on metals [4], semiconductors [2] as well as on dielectrics [5] and can be categorized according to their spatial period Λ or period ratio Λ/λ, with λ being the incident laser wavelength. There have been reports of various period ratios, ranging from so called supra wavelength sized LIPSS Λ/λ > 1 which were observed on fused silica [6] to high spatial frequency LIPSS Λ/λ < 0.5 [3]. The most commonly used model associates the formation of LIPSS with a coupling mechanism between the incident laser light and the surface plasmons, which results in the excitation of so called surface plasmon polaritons (SPP) [7]. Surface plasmons can be described as oscillations of free electrons (or as electron plasma). Once excited, SPPs are evanescent, longitudinal TM-waves that travel in the interface of a metal and a dielectric [7]. But because SPPs are evanescent waves, according to the model, they cannot be excited directly by a laser beam with an incident angle
of $\alpha = 0$, since the momentum of the incident light wave is orientated perpendicular to the surface plane [8]. Nevertheless and despite of this theoretical limitations, it could be shown experimentally, that LIPSS can be generated under this condition [9].

Theoretically, the excitation of SPPs is possible, if either the phase velocities of the incident light and the propagating plasmon polariton waves are matched [10] or by coupling via the surface roughness [11]. Since the dielectric prism configuration is not used in most setups for generation of LIPSS, the coupling via the surface roughness is the current theory to explain their formation. Gurevich et al. investigated the influence of initial surface conditions (pre-patterned metal samples) on the resulting LIPSS period [8]. According to the plasmonic theory, after the first laser pulse hits the surface and thereby initiates the formation of LIPSS, further applied laser pulses should decrease the LIPSS period. They were not able to verify the plasmonic theory experimentally.

In the paper presented here, we describe experiments to investigate LIPSS formation and ablation thresholds for stainless steel and a wide range of applied fluences and pulse numbers. We observed not only the formation of LIPSS with different spatial periods, but also the transition of low spatial frequency LIPSS (LSFL) to high spatial frequency LIPSS (HSFL) by splitting until a certain threshold is reached and the ablation regime is initiated. By further increasing the applied fluence, larger self-organized structures in the micro-meter-regime appear, initially with LIPSS on top, thereby forming hierarchical structures. The size and spatial separation of those larger cone structures is strongly influenced by the applied accumulated fluence. Once in the ablation regime, a higher pulse number leads to increased surface roughness due to more internal reflections and causes the micro structures to grow [12].

2. Experimental Setup

In this study we used cold rolled stainless steel samples (1.4301) with a thickness of 0.05 mm without any post production surface modification. Measurements showed an arithmetical mean height of $S_a = 141.3$ nm and a maximum height of $S_z = 2.29 \mu$m (acc. to ISO 25178). The surface properties were obtained by an Alicona Infinite Fokus G5 measurement system. A Ti:Sapphire (Ti:Al$_2$O$_3$) solid state laser (Femtopower Compact Pro) was used to initiate LIPSS generation. The system operates at a repetition rate of 1 kHz, emitting 30 fs pulses at a central wavelength of $\lambda = 800$ nm and a bandwidth of $\pm 50$ nm. The laser delivers radiation with an average output power of 800 mW which leads to a single pulse energy of 0.8 mJ. Due to its internal setup, the output radiation is linearly polarized. To adjust the laser fluence on the specimens’ surface, a variable attenuator was used. Leaving the attenuator, the laser beam is then focused on the specimen by an off-axis parabolic mirror with a protected silver coating. To exclude the influence of astigmatism effects caused by the convex focusing mirror, the workpiece was not moved in direction of the incident laser beam during the experiments (angle of incidence = 0). The experiments have been conducted in a controlled environment at 21 °C in air. To study the effects of fluence and the number of pulses on the formation of LIPSS, the workpiece was mounted on a motor driven linear stage and moved with various feed rates along the horizontal axis. Since the maximum feed rate was limited to 8 mm/s, the beam diameter was adjusted to $d = 295 \mu$m to achieve the desired fluence range on the specimen. After inducing nanostructures on the surfaces, the samples were cleaned with demineralized water in an ultrasonic bath and examined by a scanning electron microscope (Jeol JCM-5000, FEI Quanta 250 FEG). To investigate the initiation of the LIPSS generation, we concentrated the analysis on those areas, where the Gaussian intensity distribution of the laser beam has its maximum. The SEM pictures were then analysed using Fast Fourier Transformation (Matlab) perpendicular to the LIPSS orientation. By using the Matlab Signal Analyser Tool, the FFTs were further investigated by searching for peaks in the frequency spectrum. Those peaks can be interpreted as the favorable spatial LIPSS periods and the amplitude gives an indication on their characteristics. To investigate the transition of LSFL to HSFL the ratio of the amplitude peak values is of interest. A raising ratio indicates that the HSFL are more favorable, which was also validated visually on the SEM images. The applied fluence was varied from $\phi = 0.02$ J/cm$^2$ to 0.90 J/cm$^2$, the number of pulses from $n = 37$ to
n = 1030. For analysis of the formed grooves and cone structures at higher pulse energies, the area fraction of the grooves and the average base diameter of the cones have been evaluated. This was done by examination of 50 µm x 50 µm SEM images of the relevant surface areas using ImageJ Software.

3. Results

According to the plasmonic theory, the spatial period of the laser induced surface structures depends on the wavelength $\lambda$ of the applied laser beam and the material properties of the interface [13]:

$$\Lambda_{\text{LIPPS}} = \frac{\lambda}{\eta \sin \theta}$$  \hspace{1cm} (1)

where $\theta$ is the laser’s angle of incidence and $\eta$ is the real part of the effective index of the surface plasmon mode. For an air/metal interface, $\eta$ is typically about 1 [13]. This implicates that only one spatial period $\Lambda \approx \lambda$ will be induced by the laser source. Ref. [3] describes, that due to the increasing structure depth and other effects like the multi-pulse feedback phenomena, equation (1) is only valid for a small number of pulses. Our experimental results show a LSFL period which varies around $\Lambda_{\text{LSFL}} = 655$ nm for a wide range of pulse numbers $37 \leq n \leq 1030$, which is significantly lower than the center laser wavelength $\lambda = 800$ nm. The LIPSS orientation on our steel samples was found to be perpendicular to the polarization direction of our linearly polarized laser source, which is in agreement with observations of other authors for different metals [3], [12], [14]. We could observe the initialization of LIPSS formation with a spatial period of 650 nm at a single pulse fluence of $\phi = 0.04$ J/cm$^2$ and $n = 37$ pulses respectively (Figure 1). Experiments were also conducted with a lower fluence of $\phi = 0.02$ J/cm$^2$, which turned out to be below the LIPSS formation threshold of steel 1.4301.

![Figure 1. Initialization phase of LIPSS formation: $\phi = 0.04$ J/cm$^2$, $n = 37$.](image1)

![Figure 2. Splitting of LSFL into HSFL: $\phi = 0.04$ J/cm$^2$, $n = 462$.](image2)

An increased pulse number of $n = 178$ while keeping the fluence level constant at $\phi = 0.04$ J/cm$^2$ resulted in a larger structured area, showing only LSFL. By further increasing the number of applied pulses, splitting of LSFL occurs (Figure 2), which leads to a simultaneous formation of HSFL with a spatial period of $\lambda/\Lambda < 0.5$. This splitting process and its dependency on fluence and pulse number has already been described by multiple authors [15], [16]. The ratio between LSFL and HSFL can be adjusted by varying the number of pulses (Figure 3).

The maximum HSFL/LSFL amplitude ratio of 78% is reached at $\phi = 0.04$ J/cm$^2$ and $n = 462$ pulses. By further increasing the applied pulse number, the ratio decreases below 60%. At a higher fluence level of $\phi = 0.10$ J/cm$^2$ the splitting process is not as distinct, but the dependency on the pulse number is evident, reaching a maximum of 55% at $n = 178$ pulses. Figure 3 shows that for a fluence of $\phi = 0.28$ J/cm$^2$ and low pulse numbers, the HSFL/LSFL ratio drops below 15%, showing the start of the LIPSS/cone transition for $n > 321$. Under even higher fluences and pulse numbers $n < 321$, HSFL will not form at all, leaving only LSFL on the sample. Looking at the influence of the pulse
number on the spatial LIPSS periods, for lower fluences ($\phi = 0.04$ to $0.28 \text{ J/cm}^2$) the results show little fluctuations around the mean value of $\Lambda_{LSFL} = 655 \text{ nm}$ with a tendency to higher spatial periods for higher pulse numbers (Figure 6). This finding does not support the theory of grating assisted surface plasmon coupling, for which the LIPSS period should decrease for higher pulse numbers [3], [17].

![Figure 3](image3.png)

**Figure 3.** Top: Transition from LIPSS to cone structures; Bottom: HSFL/LSFL ratio dependence on the laser pulse fluence and the pulse number.

![Figure 4](image4.png)

**Figure 4.** Grooves are formed: $\phi = 0.78 \text{ J/cm}^2$, $n=178$.

![Figure 5](image5.png)

**Figure 5.** Hierarchical Structures: Cones with LIPSS on top: $\phi = 0.53 \text{ J/cm}^2$, $n = 321$.

The results shown in Figure 6, do not indicate any significant deviation from the mean HSFL period of $\Lambda_{HSFL} = 300 \text{ nm}$ ($\sigma = 21 \text{ nm}$) over a wide range of pulse numbers, but for higher pulse numbers the peaks in the FFT spectra are not as concise. Besides the formation of LSFL and HSFL the SEM images reveal the initialization and constant growth of so called grooves [18], which are ablated areas in between the LIPSS, orientated parallel to the polarization of the laser light (figure 4). Their growth is directly linked to the applied fluence and pulse number and results in the formation of cones (Figure 7). Our experimental results show, that at fluences above $\phi = 0.28 \text{ J/cm}^2$ and pulse numbers $n > 178$, the formation of cones is initiated (Figure 3). As the transition from grooves to cones continues, LIPSS are still visible. By further increasing the fluence and pulse number, the LIPSS fade and the frequency amplitudes in the FFT spectrum are attenuated until they cannot be separated from noise. The average grain size or base diameter of the cones is not only related to the single pulse fluence or the pulse number, but proportional to their product - the accumulated fluence (Figure 7). It can be
seen, that the correlation is not linear and the grain size saturates at about 11 µm for accumulated fluences above $\Phi_{\text{Acc}} = 600 \text{ J/cm}^2$. The formation or self organization of the observed structures could be a consequence of higher ablation rates at grain boundaries of the laser treated 1.4301 alloy [19]. At a critical accumulated fluence of $\Phi_{\text{Acc, crit}} \approx 1400 \text{ J/cm}^2$ ablation is dominant and erases all surface structures leaving only a clean cut in the metal sheet. It is possible to continue investigations using diffractive optical elements [20, 21].

Figure 6. Spatial LIPSS period over a variety of laser fluences and pulse numbers.

Figure 7. Correlation between groove area, cone size and the accumulated laser fluence.

4. Conclusion
In this study, we have experimentally investigated the processes, which lead to the formation of LSFL, HSFL, grooves and cone structures and found that continuous transitions between the observed structures occur and no abrupt changes could be detected. Nevertheless we were able to determine certain threshold levels for fluences and pulse numbers, at which the transitions are initiated (Table 1).
Table 1. Threshold levels for structure transitions on stainless steel 1.4301

| Transition                        | Fluence threshold $\phi$ [J/cm$^2$] | Pulse number threshold $n$ |
|-----------------------------------|-------------------------------------|--------------------------|
| Initialization of LIPSS formation | 0.04                                | 37                       |
| HSFL formation                    | 0.04                                | 178                      |
| Peak HSFL/LSFL ratio              | 0.04                                | 462                      |
| Formation of small grooves        | 0.04                                | 888                      |
| Ablation leads to cone formation  | 0.28                                | 604                      |
| Ablation leads to cut             | 0.94                                | 1500                     |

The analysis of the obtained data shows that low and high spatial frequency LIPSS can be induced in parallel by a splitting process. The LSFL/HSFL ratio is influenced by the laser parameters and can thereby be tuned in a certain range. At low fluence levels, only small areas of the specimens’ surface are covered by LIPSS, which is caused by the Gaussian intensity distribution of the used laser beam. The application of higher fluences will increase the area covered by LIPSS, but at the same time the HSFL/LSFL ratio declines. Considering this effect, the structuring of large areas with HSFL will result in long processing times, unless it would be compensated for by modifying the laser intensity distribution from Gaussian to a top hat.

A spatial frequency inversion of LIPSS could not be observed in this work. Further investigations might show a certain parameter range, where LSFL splitting occurs at a high efficiency and only HSFL are formed. Considering the growth of grooves and cones, the structure depth could be a suitable indicator to study the ablation process in more detail. Also the grain boundaries of the material should be taken into account. The topology of the induced structures could be of great use to improve the wetting properties of technical surfaces. Because of their high surface to area ratio, the rough and deep cone-shaped structures show similarities to Lotus leaves and are therefore likely to cause hydrophobic behaviour. The continuation of studies with the use of diffractive optical elements is promising.

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