Ripple formation with intense Gaussian femtosecond laser pulses close to the damage threshold

U Teubner 1,2, A Andreev 1,3, V Makin 4,5 and J Imgrunt 3

1 Institute for Laser and Optics, Hochschule Emden/Leer—University of Applied Sciences, Constantiaplatz 4, 26723 Emden, Germany
2 Institute of Physics, Carl von Ossietzky University, Carl-von-Ossietzky-Str. 9-11, 26111 Oldenburg, Germany
3 Saint-Petersburg State University, 199034 Universitetskaya Emb. 7-9, St. Petersburg, Russia
4 NPC OEKN Branch, Comet Corporation, St. Petersburg, 194021 Russia
5 Nuclear Energy Institute, St. Petersburg Polytechnic University, Sovnary Bor, Leningrad oblast, 188540 Russia

E-mail: ulrich.teubner@hs-emden-leer.de

Keywords: LIPPs, high intensity laser pulse, femtosecond pulse, ripple formation, energy transfer, surface plasmon polaritons, nano structure

Abstract
The formation of laser-induced periodic surface structures (LIPSS or ripples) is a topic that has been investigated for almost 60 years. More recently with the advent of ultrashort laser pulses this subject has regained interest, in particular, due to interaction regimes that have not been present so far. Consequently a lot of work has been done in that field, especially with comprehensive experimental and theoretical investigations of the scaling of ripple parameters on laser pulse duration, wavelength, applied fluence, shot number and so on. However, there are still a lot of questions. The present work addresses an important issue on that subject. In particular, ripple formation is investigated at high laser intensity, namely at an intensity sufficiently large to generate a femtosecond-laser induced plasma. Thus ripple formation occurs close to damage threshold. Experimental results and theoretical discussion of ripple formation and the interrelation to laser pulse energy deposition, energy transport and sample damage originating from the optical interaction and additional thermal effects, respectively, are discussed. Most important, a reduction of ripple formation threshold with laser intensity and fluence, respectively, has been observed which is associated by a super-linear increase of the ripple area. The scaling of this reduction with laser fluence obtained from theoretical estimates is in good agreement with the experimental data.

1. Introduction

A lot of theoretical and experimental studies of the processes of condensed matter surface behaviour when irradiated with a train of polarized laser pulses were devoted to metal surfaces [1–19]. Specifically, models based on surface plasmon polaritons (SPP) and waveguide modes excitation and their experimental verification for long laser pulses (with a duration larger than the electron-phonon relaxation time) have been reviewed in [1,2]. The extension of the SPP model for ultrashort laser pulses was suggested and verified in [3]. At present this model well describes the grating formation with ripple periods \( \lambda_r \) less, but still close to the wavelength \( \lambda_0 \) of laser radiation. It describes the orientation of the grating vector \( \mathbf{k} \), with respect to the laser pulse electric field vector \( \mathbf{E} \) and is appreciated for condensed matter with different physical properties. The applicability of this model ranges from cw to femtosecond pulse duration and from ultraviolet to sub-millimeter wavelength.

Reference [7] provides a review with details of the mechanisms of the periodic surface structure formation. The process of grating structure ‘writing’ (fixation) on the material surfaces for long laser pulses is reviewed in [1,2] and that for the ultrashort pulses in [4,7]. For low energy density regimes the most frequently realized generation mechanism is thermostripillar, which was considered in detail in [8] and more schematically in [9,10]. For higher energy densities, namely for a fluence \( F \gtrless 0.9 \text{ J cm}^{-2} \) (and a pulse duration of approximately 100 fs), Coulomb mechanisms become important at the metal-vacuum boundary. Then the electron emission

© 2022 The Author(s). Published by IOP Publishing Ltd
from the metal surface is large enough to generate an opaque plasma layer near to the surface. Moreover, the strong electrostatic field which is induced dynamically by the laser pulse, supplies spatially selective metal ions ejection from the irradiated surface area [11].

Depending on the experimental conditions the ratio \( \lambda_e / \lambda_f \) may change. Such changes have been observed in experiments (slow variations of \( \lambda_e \) values result also from pulse to pulse changes) and variations of the local micro/nano-geometry and of the local dielectric permittivity (via the SPP’s dispersion relation)) are described by nonlinear models [5,6]. As a consequence, from experiments a different behaviour of \( \lambda_f / \lambda_e \) for the low and the high fluence (\( F \)) regime, respectively, was observed and, in particular a change of the sign of this derivative \([12,13,16,17]\). For the high energy density regime (i.e. large fluence) the sign of the derivative is positive, which is the indication of the opaque plasma layer formation as mentioned above \([12,18]\). For the particular case of gold and silver, this sign for was interpreted via the behaviour of a solid state metal plasma \([14,15]\).

In addition, energy transfer may play a significant role. The existence of a lateral energy transfer caused by (hot) electron diffusion in a thin gold film irradiated by a femtosecond laser pulse was discussed in \([20]\). An initially rapid diffusion of (hot) electrons during first few picoseconds was followed by a slower diffusion at longer times. The ratio of the coefficients of the (hot) electron diffusion to the phonon-limited thermal diffusion was approximately 100 (deduced from experiments).

Laser-induced micro and nano-grating structures (i.e. ripples) find a lot of applications. Particularly they are suggested for surface friction reduction, for increased surface absorptivity and an emissivity change, for biological molecules and liquid crystals orientations, for the creation of antibacterial surfaces, etc \([19]\). Another issue is the potential application in experiments performed at high laser intensity where the structured targets could be generated in situ and used for improved coupling, e.g. for X-ray or high energy particle generation \([18,21,22]\).

Although the large amount of experimental and theoretical investigations on laser-induced periodic micro and nanostructure formation, there are still a lot of questions, especially for structure generation with femtosecond laser pulses. Additionally motivated by the possibility of more tailored applications, this drives further research in this field.

The present work contributes to this process with the investigation of nanostructure formation (ripples) and morphology changes (cellular damaged surface) generated with linear polarized femtosecond laser pulses. These were focused to a rather high laser intensity (and thus large fluence), namely to a value close to the damage threshold. We may mention that here the applied intensity is 3 orders of magnitude larger than that, e.g. applied in \([20]\) which takes influence on the related interaction. The threshold for the formation process has been studied at different laser intensities and fluences, respectively, and for laser pulse trains with various shot numbers. The results clearly show that there exists a transitional area between the ripple zone and the neighboured cellular zones with hierarchical orthogonal gratings. Two regimes of ripples formation have been considered which differ for different regimes of supplied laser energy density. In case of large intensity and fluence it has been shown that there is a threshold energy density change for ripple formation. Part of the energy is associated with the lateral energy transfer from the adjacent cellular zone where most of the laser energy is dumped.

2. Experimental setup and analysis

The experiments were carried out with a Ti:sapphire chirped pulse amplification laser system coupled to an advanced setup for micro and nano structuring applications \([18,23]\). The system operated at a wavelength of \( \lambda_L = 775 \text{ nm} \) and delivered linearly polarized pulses with a duration of \( \tau_L = 153 \text{ fs} \) (FWHM). The pulses were focused with an achromatic lens of \( f = 200 \text{ mm} \) focal length to a focal spot with an average diameter of \( d_L = 50 \mu \text{m} \) (\( \pm 10\% \); FWHM), with a slightly elliptical shape (long and short axis of \( d_{\text{long}} = 56 \mu \text{m} \) and \( d_{\text{short}} = 44 \mu \text{m} \), respectively, see figure 2 in section 3; \( d_L = (d_{\text{long}} d_{\text{short}})^{1/2} \)). \( D_L \) is the corresponding \( 1/e^2 \)-width (\( \approx 1.7 \cdot d_L \)). The radial spatial intensity distribution was Gaussian.

The measurements were restricted to a range of fluences close to the damage threshold of \( F_{\text{dam}} \approx 0.8 \text{ J cm}^{-2} \) (this value has been obtained for the present conditions, see \([18]\)), namely between fluences at the central peak \( F_0 \approx 0.5 \text{ J cm}^{-2} \) and \( F_0 \approx 1.5 \text{ J cm}^{-2} \). Thus the corresponding peak intensity \( I_0 \) was always larger than \( 10^{12} \text{ W cm}^{-2} \) (at the spatial central peak and averaged over the \( \tau_L \)).

Fluences much above \( F_{\text{dam}} \) were avoided due to the well-known associated effects, in particular, the contamination and potentially the damage of the focusing optics resulting from target debris. Moreover, this prevents of a significant burl on target which would make the deduction of the diameter \( D_{\text{dam}} \) of the damage region difficult.

The flat polished Copper targets were irradiated at normal incidence and mounted on motorized \( xyz \)- and rotation holder. In order to have well defined conditions, the present investigations concentrated on ripple
formation in vacuum ($10^{-4}$ mbar, $10^{-2}$ Pa). Thus chemical reactions that would have accompanied the formation process in ambient gases or air were excluded.

The targets were irradiated with a fixed fluence $F_0$ and a fixed number of shots $N$ on the same target surface at a laser repetition rate of 1 kHz. Before any change of $F_0$ and $N$ were applied, the target was shifted laterally to a new position with an unaffected surface. While keeping the target always at the same focal position, the fluence was changed by changing the laser energy by means of calibrated attenuation filters. This procedure is essential, because in contrast to other measurements where the fluence is changed by a change of the focal position, in the present experiments the target stayed always in far field where the interaction conditions are well defined. Thus the laser light was kept always purely $s$-polarized and contributions from $p$-polarizations were avoided, which would have present in focal scan experiments when the target is moved outside the focal position (note: outside the focal position, the fluence is reduced, but $p$-polarized components get better absorbed and the mixture of different polarization components leads to a seemingly lower damage threshold).

Before analysis of the irradiated targets, they were cleaned in an ultrasonic bath. Examination was made with an optical light microscope (LM; Leica DM4000 B/M) and a scanning electron microscope (SEM; Zeiss EVO® MA10).

Depending on the fluence region, namely (i) $F_0 < F_{th}$, where $F_{th}$ is the threshold for ripple formation, (ii) $F_{th} < F_0 < F_{dam}$, (iii) $F_{th} < F_{dam} < F_0$, and (iv) $F_0$ well above $F_{dam}$, four different situations may be discriminated. The first one is not of interest here and the other 3 are displayed in figure 1, where (a) to (c) correspond to (ii) to (iv).

The diameter of the ripple region $D_{th}$ (average diameter of the slightly elliptical profile) could be easily obtained from the SEM images, where one could observe that the boundary between the ripple region and the unaffected region is extremely sharp and thus well detectable (see figures 3(c) and (d) in section 3). In a similar way the diameter of the damage crater $D_{dam}$ could be determined from the images captured with the optical microscope and the SEM, respectively (note that $D_{dam}$ is also equivalent to the inner diameter of the ripple region in figures 1(b) and (c)).

### 3. Experimental results

For very low fluence and intensity ($F_0 < 0.5 \text{ J cm}^{-2}; I_0 < 2.5 \times 10^{12} \text{ W cm}^{-2}$) and a small number of shots (a couple of 10 or less), there is just an onset of ripple formation with a very inhomogeneous ripple distribution and even for large $N$ the threshold fluence for ripple formation is not much reduced, namely $F_{th} \approx 0.4 \text{ J cm}^{-2} (2 \times 10^{12} \text{ W cm}^{-2})$; see discussion below). Ripple formation starts preferentially at positions where surface scratches are present, in particular, such ones with an orientation perpendicular to the electric field. However, it also starts if
there is a small angular mismatch (see 2a). This onset is consistent with the well-known descriptions of ripple formation as a multi-shot effect \[1, 4, 7\]. At this near threshold fluence the laser pulse train produces isolated areas as local tracks of SPP propagation in the direction $E$ (see figure 2(a)). The typical grating period caused by interference of the incident laser radiation with excited the SPP is $\lambda_r = \lambda_L / \eta$, where $k_r \parallel E, k_r$ is the SPP’s wave-vector and $\eta$ is the real part of dielectric permittivity of the copper-vacuum boundary for SPP.

For higher values of $F_0$ and $I_0$, respectively, and a couple of 10 or a couple of 100 shots, ripples are generated rather homogenously in a disk-shaped region (cf figure 2(b)) and with the same characteristics as those in the previous case. If $F_0$ is increased, but is still below $F_{\text{dam}}$, $D_{\text{th}}$ is increased as well. Both conditions correspond to the situation of figure 1(a).

When $F_0$ comes close to $F_{\text{dam}}$, the ripple height is increased (see later) and further increase leads to surface damage (cf figures 2(d) and 3(a)) with a break up or even an explosion (figure 3(b); see also [24–27]). In that case the centre of the laser spot is covered by a damage crater with a diameter $D_{\text{dam}}$ with a ring-shaped region around (compare figure 1(b)). This region can be well discriminated from the region where ripples are generated.

In the following we will term these regions ‘ripple region’ and ‘damage region’, respectively. In the intermediate area between both regions one can observe the formation of additional coarse and coexisting structures with orthogonal (anomalous) orientation with a period $\ll \lambda_L$ (cf SEM image in figure 3(d)). The ridges and valleys may lead to the excitation and propagation of further localized SPP (edge and channel,
increased absorption at the metal surface but the parameters differ. The scaling coefficient and the single-shot damage threshold are given by $\Gamma_d \approx -0.2 (\pm 25\%)$ and $F_{d1} = 2 \text{ J cm}^{-2} (\pm 30\%)$, respectively. The negative values of $\Gamma$ in equations (3) and (4), indicate a pulse-induced change of the material or surface property and are the result of accumulation effects. These lead, e.g., to a damage threshold reduction due to incubation as has been observed with ns pulses [2,30] and with fs-pulses [31], [32], respectively.

The single shot ablation threshold $F_{a1}$ deduced within the present work is in good agreement with the common analysis of ablation depth $d_{abl}$ (including incubation effects). In case of ablation with one shot at
modest fluence and under the assumption of linear absorption, according to Lambert-Beer’s law the ablation depth for a pulse irradiated after \( n \) proceeding ones is given by

\[
d_{abl,n} = \Lambda \cdot \ln \left( \frac{F}{F_{dam}(n)} \right) \tag{5}
\]

(this follows from, e.g. [23], [33]). Of course this requires that \( F > F_{dam}(n) \), otherwise \( d_{abl,n} = 0 \) (with \( F_{dam}(n) \) from equation (4)). \( \Lambda \) is the laser pulse penetration depth. For ablation with \( N \) multiple shots \( d_{abl,n} \) has to be summed from \( n = 0 \) to \( N - 1 \) (for single shot ablation \( N = 1 \)).

A fit of the present experimental data according to this simple model is plotted in figure 4(b). The axis intersection (i.e. \( d_{abl} = 0 \)) corresponds to the averaged reduced damage threshold due to incubation, which is consistent with \( F_{d1} = 2 \) J cm\(^{-2} \) for single shot ablation. The slope corresponds to \( \Lambda = 80 \) nm. We would like to remark that the results obtained from the present crater diameter measurements and those of the crater depth do agree very well and there is also agreement with the observation of the onset of damage in various SEM images. This note is crucial because there is doubtful work in the literature where a disagreement in the results is reported and thus additional ‘free parameters’ are introduced which however, are not an integral part of the related model (see equations (1), (4) and (5)).

The obtained threshold fluence also agrees with the result of [31], although it may be noted that the value of [31] is slightly lower. This has been expected because of the focal scan method applied by that group which leads to a value that may be identified with the seemingly lower damage threshold discussed in section 2. The threshold of the present work also agrees with the value of [32] when corrected for incubation as discussed above (\( F_{d1} = 2.4 \) J cm\(^{-2} \)).

We would also like to remark, that although equation (3) looks quite similar to equation (4), within the experimental error \( \Gamma_d \) and \( \Gamma_r \) have notably different values and \( F_{d0}(N) \) decreases less with \( N \) when compared to \( F_{dam}(N) \) (see figure 4(a)). The different scalings of \( F_{dam} \) and \( F_{d0} \), respectively, may have been expected. As material damage and ripple formation result from different physical processes, one cannot expect that the \( \Gamma \)-coefficients and the single-shot damage threshold fluences are the same.

Up to now, the discussion of \( F_{d0} \) has been restricted to a peak fluence (and intensity) below damage threshold (compare to figures 2(a) and (b)). In the following we will extend this to situations such as displayed in figure 2(d). Figure 5(a) shows the dependence of the radius of the ripple area \( D_{abl}/2 \) on the peak fluence of the laser pulse \( F_0 \). The experimental data are shown as the symbols where the symbol size represents the experimental error. The applied number of shots is provided in the inset. The blue solid line represents a fit according to equation (2) with \( F_{th} = 0.5 \) J cm\(^{-2} \) = const which is in good agreement with the experimental data below \( F_0 \approx 1 \) J cm\(^{-2} \). However, above this value, the radius becomes significantly larger and cannot be described by the same fit. This larger radius can be identified with \( D_{abl}/2 \) displayed in figure 1(c).

---

**Figure 5.** (a) Dependence of the radius of ripple area on the peak fluence of the laser pulse \( F_0 \). The blue solid and the blue dotted line correspond to a fit (see main text). (b) Dependence of the ripple formation threshold \( F_{d0} \) on the peak fluence of the laser pulse \( F_0 \). \( I_0 \) and \( I_0 \) are the corresponding intensities (see section 2). The straight lines are intended to guide the eye. Furthermore the inclined dashed and dotted lines correspond to a scaling with \( F_0^{-1/4} \) and \( F_0^{-1/4} \), respectively. The blue dotted line in (a) corresponds to the scaling of the blue dotted line in (b). The pink dashed curves in (a) result from damage crater measurements at \( F_0 = 1.3 \) J cm\(^{-2} \) with the damage fluence thresholds for the indicated shot numbers taken from figure 4(a). For the other values of \( F_0, D_{abl} \) is calculated from equation (1). The resulting curves are for comparison only.
The present experiments were carried out at 150 fs pulses with relative high intensity in focus.

### 4.1. General

The present experiments were carried out at 150 fs pulses with relative high intensity in focus ($I_0 > 10^{12}$ W cm$^{-2}$) when compared to usual ripple formation studies. All applied intensities were well above plasma threshold for metal targets. Consequently there was always a significant influence of the generated free electrons. Hence ripple formation was governed by plasma physics and can be described in terms of surface plasma waves (SPP).

Following the discussion in [18], which partly bases on the model of Sakabe et al as the first step [12], the process of ripple formation for the present conditions of copper targets irradiated with intense fs-pulses can be described as follows. First, via a parametric process (such as in [35,36]), a fs-laser pulse induces a plasma wave on the surface. Then during the surface plasma wave excitation and propagation, ions become enriched locally. Thus they experience a strong Coulomb repulsion until the peak of the next electron wave arrives at that position. Hence, those spatially localized ion clouds Coulomb-explode and expand to vacuum [12,37]. Consequently, third, a thin layer is ablated thus giving rise to the formation of periodic grating structures, which can be regarded as an imprint of a ‘grating’ according to the interspacing of the regions where Coulomb-explosion and thus ablation occurs [38,39]. If the laser fluence is large enough, once such structures are formed by the first pulses of a pulse train, an enhancement process might take place for the subsequent pulses within the pulse train. The rise of the heights of imprinted structures is due to the positive feedback between the laser radiation absorption and modulation depth of the resonant structures. The electric field is enhanced near the initially imprinted structures, and it leads to further ablation of the surface, which results in further deepening of

### Table 1. Ripple period $\lambda_r$ and ripple height $h$ for low and high fluence and intensity, respectively. The ‘±-values’ include the uncertainty in the analysis and take into account some small local variations. A strong change of $\lambda_r$ within the ripple region has not been observed.

| $F_0$ [J cm$^{-2}$] | $\lambda_r$ [nm] | $h$ [nm] |
|---------------------|-----------------|--------|
| $F_0 = 0.6$ | $\lambda_r \approx (640 \pm 20)$ nm | $h \approx (70 \pm 20)$ nm |
| $F_0 = 1.5$ | $\lambda_r \approx (760 \pm 20)$ nm | $h \approx (75 \pm 20)$ nm |
| $F_0 = 0.6$ | $\lambda_r \approx (650 \pm 20)$ nm | $h \approx (65 \pm 20)$ nm |
| $F_0 = 1.5$ | $\lambda_r \approx (75 \pm 20)$ nm | $h \approx (145 \pm 70)$ nm |

Figure 5(b) shows the ripple formation thresholds deduced from the data in figure 5(a) (calculated with equation (2)). It may be seen that for low peak fluences and intensities the ripple formation threshold is rather constant. $F_{th}(N)$ is nearly the same for all peak fluences up to $F_0 \approx 0.9$ J cm$^{-2}$ which is slightly larger than $F_{dam}(N)$. However, for larger values of $F_0$ there is a significantly larger radius (i.e. $D_{TH}/2$ instead of $D_{th}/2$) which can be attributed to a significant reduction of the threshold for ripple formation. The dotted blue curves in Figures 5(a) and (b) describe a scaling of $F_{th} \propto F_0^{-3/4}$, the dashed one in figure 5(b) a scaling of $F_{th} \propto F_0^{-1/4}$ (see section 4.4).

The interesting point here is that those ‘large’ fluences $F_0$ are present only in the damage region, but not in the region where the ripples are generated. As discussed above, the maximum fluence within the ripple region is always $F_{max} = F_{dam}$ which is obviously below $F_0$. But nevertheless the experimental data clearly show that an increase of the fluence in one region (namely an increase of $F_0$ in the damage region) takes influence on the threshold in another region (i.e. on $F_{th}$ in the ripple region). This situation is illustrated in figure 1: for $F_0 < 0.9$ J cm$^{-2}$ is $F_{dam}$ the same (cf figures 1(a) and (b)), but is reduced to $F_{TH} < F_{th}$ when $F_0$ clearly exceeds $F_{dam}$ (cf figure 1(c)).

One may also compare the ripple period $\lambda_r$ and the ripple height $h$ for different experimental conditions. For $F_0 < F_{dam}$ the dependence of the ripple period $\lambda_r$ on the shot number and on the fluence was investigated by several groups [12,16,18,24,26,34]. Those works have shown that $\lambda_r$ has only a very weak dependence on $N$ and $F_0$, respectively, within the range under discussion. But a repetition of details is not subject of the present work.

Instead, here we concentrate on a comparison of ripples obtained with $F_0$ below and well above $F_{dam}$. In particular, we may compare the ripple period $\lambda_r$ obtained for $F_0 = 0.6$ J cm$^{-2}$ and $F_0 = 1.5$ J cm$^{-2}$, respectively, and find a significant longer period for a fluence above the damage threshold (see Table 1). For the lower fluence $h \approx 70$ nm and $h$ does not differ significantly for $N = 80$ and $N = 120$. For $F_0$ well above $F_{dam}$ and $N = 80$, $h$ is somewhat larger and possibly even larger for $N = 120$ when compared to the low fluence case. Just for comparison we would like to note that the depth of the irregular structures in the damage region (cf figure 3(b)) is roughly 0.4 $\mu$m.

A comparison of the ripple areas $A_r$ for the low and large fluence case, respectively, yields the following: $A_r(F_0 < F_{dam}) = \pi/4(D_{th}/2)^2 \approx 600 \mu$m$^2$ and $A_r(F_0 > F_{dam}) = \pi/4(D_{TH}/2)^2 - \pi/4(D_{dam}/2)^2 \approx 2000 \mu$m$^2$ which is more than a factor 3 larger.

### 4. Discussion

#### 4.1. General

The present experiments were carried out at 150 fs pulses with relative high intensity in focus ($I_0 > 10^{12}$ W cm$^{-2}$) when compared to usual ripple formation studies. All applied intensities were well above plasma threshold for metal targets. Consequently there was always a significant influence of the generated free electrons. Hence ripple formation was governed by plasma physics and can be described in terms of surface plasma waves (SPP).

Following the discussion in [18], which partly bases on the model of Sakabe et al as the first step [12], the process of ripple formation for the present conditions of copper targets irradiated with intense fs-pulses can be described as follows. First, via a parametric process (such as in [35,36]), a fs-laser pulse induces a plasma wave on the surface. Then during the surface plasma wave excitation and propagation, ions become enriched locally. Thus they experience a strong Coulomb repulsion until the peak of the next electron wave arrives at that position. Hence, those spatially localized ion clouds Coulomb-explode and expand to vacuum [12,37]. Consequently, third, a thin layer is ablated thus giving rise to the formation of periodic grating structures, which can be regarded as an imprint of a ‘grating’ according to the interspacing of the regions where Coulomb-explosion and thus ablation occurs [38,39]. If the laser fluence is large enough, once such structures are formed by the first pulses of a pulse train, an enhancement process might take place for the subsequent pulses within the pulse train. The rise of the heights of imprinted structures is due to the positive feedback between the laser radiation absorption and modulation depth of the resonant structures. The electric field is enhanced near the initially imprinted structures, and it leads to further ablation of the surface, which results in further deepening of
the structures [11]. Nevertheless, related to this general description, a more detailed discussion of ripple formation in the ‘low’ and ‘large fluence regime’, respectively, has to be made. This is subject of the following discussion.

4.2. Low fluence regime

For the low fluence case (i.e. \( F_0 \approx 0.4 \) to \( 0.6 \) J cm\(^{-2}\), i.e. \( I_0 \approx 2 \) to \( 3 \cdot 10^{12} \) W cm\(^{-2}\); cf figure 1(a)) ripple formation starts in the vicinity of the laser peak where the gradient of the fluence and intensity, respectively, is not very large (or zero exactly at the peak; cf figure 1(a)). Due to the high intensity, plasma physics already plays a role, but the formation of an optically opaque layer due to a generated near-surface plasma does not yet occur [3]. Actually, the behaviour of \( \lambda_i \) in the range under discussion indicates the formation of structures with the participation of SPP at the metal–vacuum interface where a low concentration of electrons is emitted from the metal surface. We assume that the formation of nanostructures (i.e. ripples) in this range is the result of the combined action of thermocapillary and evaporative mechanisms in the regions where local melts occur: as surface baths of melt are produced under the non-homogeneous laser melting of the metal, and because of a temperature gradient, a surface force arises inside the temperature bath tangentially to the surface. Thus a liquid flow is generated which is proportional to the surface tension temperature gradient (see, for instance, [8,40]). The metal is squeezed from the local melt baths by surface tension force and may partially return back on timescales up to the melt crystallization.

At the same time, there is a small increase in ripple period with an increase in \( F_0 \) that can be connected with both, the radiative damping of the SPP on the structures of increasing height [5] and the dielectric permittivity behaviour [41]. In the considered range, with an increase of \( F_0 \), also a significant change of the dielectric permittivity of copper [41] and an almost linear increase in the depth of the residual surface relief up to values of \( h \approx 40 \) to 70 nm is observed (see also [16,18]). One has to remind, that the remnant relief height may be smaller than the dynamical one due to partial backflow of the metal as discussed above.

The change in the dielectric permittivity of copper is associated with an increase of the electron–ion collision frequency \( \nu_{ei} \) which depends on the electron temperature \( T_e \propto F_0^{1/2} \) (this is valid for temperatures below the Fermi temperature \( T_F \)) [11,41,42]. The growth of \( \nu_{ei} \) reduces the attenuation length \( L \) of the SPP at the end of the fluence and intensity interval under discussion (i.e. \( F_0 \approx 0.6 \) J cm\(^{-2}\); \( I_0 \approx 3 \cdot 10^{12} \) W cm\(^{-2}\)). Therefore, with an increase of \( F_0 \) and \( I_0 \), respectively, the increase in efficiency of the input via SPP to an increase in the height of the relief (see [18]) is compensated by a decrease in \( L \), which as a result does not lead to a noticeable transfer of SPP’s energy from the initial zone of structure formation. Consequently there is no unexpected change in the diameter of the ripple region \( D_{\text{ripp}} \). Because of the relatively low temperature \( T_{ei} \ll T_e \) and because of both, the growth of \( \nu_{ei} \) and that of the thermal conductivity \( \kappa_e \) is modest, the transfer of energy beyond the irradiated area at the considered time intervals is not significantly affected (from our calculations in this range \( T_e < 10 \) eV; the Fermi temperature for copper is 7 eV). We would like to note that also the gradient of the spatial laser intensity profile and that of the related \( T_e \) profile is not very large (see discussion above). Therefore, the energy density corresponding to the threshold fluence for ripple formation in the discussed fluence range remains practically constant (cf figure 2).

This conclusion is also confirmed by an estimate based on the relation \( F_{th} \propto E/A_e \) and the following scalings. The electron temperature \( T_e \) in the absorbing volume is proportional to the energy \( E \) of the laser pulse. The electron’s or heat diffusion length \( l \) scales as

\[
I = \sqrt{\frac{\tau_{ei} E}{m_e t}} = \sqrt{D_{\text{Diff}} t}
\]

where \( \tau_{ei} = \nu_{ei}^{-1} \) is the average time between the electron–ion collisions, \( m_e \) the electron mass, \( D_{\text{Diff}} \) the diffusion coefficient and \( t \) the typical time of hot electron diffusion, which usually is below 1 ps. \( A_e \propto P^2 \) and \( r_{ei} = \text{const} \) in the considered low energy density range [11]. Form these scalings it follows that \( F_{th} \propto T_e^{1/2} \) which is approximately constant with respect to \( T_e \).

4.3. Increased fluence regime

For increased energy density, i.e. \( F_0 \approx 0.6 \) to \( 0.9 \) J cm\(^{-2}\), and \( I_0 \approx 3 \) to \( 4.5 \cdot 10^{12} \) W cm\(^{-2}\) (cf figure 1(b)), respectively, the electron density \( n_e \) becomes close to the critical one which results in a change in the mechanism of structure formation and an increase of \( \lambda_i \) with an increase in \( F_0 \) (cf table 1). This is in contrast to the observations for the low fluence case where it was found that \( d \lambda_i / d F_0 \) is approximately constant (established for copper for the low power density regime, see [12]). But for the present intermediate fluence regime this is in agreement with the positive sign of \( d \lambda_i / d F_0 \) reported in [12] and verifications for other metals, including tungsten, titanium, platinum etc [13]. In this regime where a plasma layer becomes to be present, the plasma optical properties impose that \( \lambda_i \) begins to change with \( F_0 \).
4.4. Large fluence regime

For even larger fluence and intensity as discussed before, namely for \( F_0 > 0.9 \) J cm\(^{-2} \) (i.e. \( I_0 > 4.5 \times 10^{12} \) W cm\(^{-2} \); cf figure 1(c)), due to the further increased absorbed amount of laser pulse energy a significant opaque plasma layer is formed. In this regime \( T_e \propto F_0^{1/2} \) and \( T_s \propto 20 \) eV \([43,44]\). Moreover, the gradients of the fluence, and of the intensity and of \( T_e \) are much larger than before. The appearance of the opaque plasma layer signifies the mechanism of the structures formation change. This change is confirmed by following.

First, the transition is characterized by a definite threshold energy density which has been estimated \([11]\) with a value of approximately \( 1 \) J cm\(^{-2} \). Second, there is a large decrease of the experimental value of the real part of the dielectric permittivity \( \eta \) which (partially) reflects the dispersion relation of the considered systems (in our simple case the period of grating is given by relation \( \lambda_0 = \lambda_I / \eta \) see section 3). The values of \( \eta \) can be deduced from table 1. For the low energy density regime discussed in section 4.2, \( \eta \approx 1.25 \) and this roughly reflects the dispersion relation of a copper-vacuum boundary for SPP’s. For the present higher energy density regime \( \eta \approx 1.05 \). This value cannot be related to the copper-vacuum boundary because it cannot be explained well by a change of the optical parameters of copper. Instead, the onset of a plasma layer, namely a plasma layer—vacuum boundary is indicated. This layer is characterised by an electron-ion collision frequency \( \nu_{ei} \propto T_e^{-3/2} \) \([11]\) which according to the scaling of \( T_e \) on \( F_0 \) decreases with fluence at the plasma-vacuum interface (compare also \([45]\)).

Consequently \( \eta \) is decreased and thus there is a clear tendency that \( \lambda_0 \) approaches \( \lambda_I / \eta \) (the decrease of the dielectric permittivity follows directly from Drude’s model with \( \nu_{ei} / \omega_L \) as the damping factor; \( \omega_L \) is the angular frequency of the laser radiation) This is in agreement with theoretical predictions \([46]\) for the regime \( T_e \gg T_s \) (for the present work this corresponds to \( 20 \) eV \( \gg 7 \) eV) and experimental observations for a number of metals in the high \( F_0 \) regime \([12–14]\). Also the positive sign of \( d \lambda_0 / d F_0 \) is typical for this case. In addition, thirdly, the transition to new an optical system, i.e. a vacuum—plasma layer—metal, results in a drop of \( F_{th} \) with \( F_0 \) as observed in the experiment (figure 5(b)).

As thermal effects are important, this is significant. In this high energy density range the dependence of \( \tau_e \) on \( T_e \) changes. As has been mentioned above, \( \tau_e \propto T_e^{3/2} \) \([11]\) and thus from equation (6) one can see that the diffusion coefficient scales as \( D_{diff} \propto T_e^{3/2} \) and the diffusion length as \( l \propto T_e^{3/4} \). Hence, e.g., for \( F_0 \approx 1.5 \) J cm\(^{-2} \), the thermal conductivity \( \kappa_e = C_e(T_e) \eta_e D_{diff} \) increases significantly (\( C_e \) is the heat capacity). In this case the threshold energy density scales as follows: \( F_{th} \propto E A_e \propto T_e / T_e^{3/2} = T_e^{-3/2} \). Then according to \( T_e \propto F_0^{1/2} \), one may expect a scaling of \( F_{th} \propto F_0^{3/4} \) which means that the ripple formation threshold decreases with \( F_0 \). For \( F_0 \approx 1.5 \) J cm\(^{-2} \), with equation (6) one obtains \( l \approx 5 \) \( \mu \)m which well agrees with the increase of the ripple radius by \( (D_{TH}/2 - D_{th}/2) \approx 5 \) \( \mu \)m (see figure 5(a)).

On the other hand there might be an energy transfer by propagating electromagnetic surface excitations, namely SPP’s, which transfer their energy mainly in the vacuum. For normal incidence of laser radiation the SPP’s are excited and propagated in two opposite directions governed by the electric field with the directions discussed in section 3. In the area of the first ring of ripples (area in between \( D_{diss} \) and \( D_{th} \), see figure 1(c)) an amplification and dissipation of SPP’s occurs at rather large intensity and a rather large intensity gradient with a propagation outward from the first ring boundary. If this would be dominant, \( F_{th} \) would be proportional to \( E L^2 \propto T_e / \tau_e \) which in the end would lead to a propagation of the excited SPP with a longer propagation path at the interface \( L \approx 1.2 - \lambda_I / F_0 = 1.5 \) J cm\(^{-2} \) and to a scaling \( D_{th} \propto F_0^{1/4} \). The energy dissipation would occur on a spatial scale length of 2 to 3 times \( L \).

However, although this process may contribute to a reduction of \( F_{th} \) in the range under discussion, it cannot be the dominant one. First, the scaling of \( F_{th} \) on \( F_0 \) is different when compared to the experimental data (see figure 5(b)) and second the increase from \( D_{th}/2 \) to \( D_{TH}/2 \) (approximately \( 5 \) \( \mu \)m difference) is significantly larger than 2 to 3 times \( L \) (less than \( 3 \) \( \mu \)m). Moreover, third, this would be in contradiction to the experimental observations where an asymmetric increase of the ripple ring has not been observed (note that SPP have a directionality as discussed above and in section 3).

Hence, in the large fluence regime the declining dependence \( F_{th}(F_0) \) results mostly from the heat transfer by nonlinear thermal diffusion of hot electrons. This effect, as the dominant one, increases with \( F_0 \). It might be supplemented by an energy transfer out the ripple area by SPP’s propagating along the vacuum-plasma layer boundary. However this is limited by the finite length of their propagation length which even at large \( F_0 \) is below the observed increase of the ripple ring region.

Thus one may conclude that in the frame of the considered model the dependence \( F_{th}(F_0) \) and, in particular, the decrease of the threshold with fluence, is mainly due to the nonlinearity of \( D_{diff} \) and \( l \) as functions of \( T_e \). The supplied energy \( E \) increases linearly with irradiated fluence and the ripple area \( A \) increases super-linear. Thus for
the discussed fluence range of approximately 1 to 1.5 J cm\(^{-2}\), the reduction of \(F_{th}\) with \(F_0^{3/4}\) correlates qualitatively with the experimental observation (see dotted blue line in figure 5(b)). This confirms the important role of enhanced lateral heat transport by (hot) electron diffusion from the central region of the laser spot (located within \(D_{\text{dam}}\) and/or \(D_{\text{th}}\) respectively) to the neighboured region (\(>D_{\text{th}}\)). This present result confirms also the conclusion of [20] where a tendency of an increased (fast) electron diffusion coefficient related to increased electron energies with increasing \(F_0\) has been discussed. However, we have to note that in [20] \(F_0 \leq 1.5\) mJ cm\(^{-2}\) which is 3 orders of magnitude less than the typical metal surface damage threshold by pump radiation (\(\leq 1.5\) J cm\(^{-2}\)) and much less than the applied fluence within the present work which is close to \(F_{\text{dam}}\).

Furthermore the maximum electron energies in [20] were rather low, namely \(\leq 0.14\) eV.

5. Summary

In summary, within the present work nanostructure generation with ultrashort laser pulses has been investigated in the regime of rather high laser intensity. At these conditions with the intensity (and fluence) close to the damage threshold, the intensity is sufficiently large to generate a laser induced plasma, in particular, an opaque surface plasma layer. Consequently plasma physics plays a major role for the whole interaction process.

Experiments were performed with a train of linearly polarized 150 fs pulses which were focused on flat solid copper samples at normal incidence. The experimental results with an increase of the intensity from \(I_0 = 2\) to \(8 \times 10^{12}\) W cm\(^{-2}\) with the corresponding peak fluences \(F_0 \approx 0.5\) to 1.5 J cm\(^{-2}\) have been explained by a change of the transient interaction regime from laser pulse absorption by a metal solid state plasma to one by an opaque near surface plasma layer. The absorption process is then followed by the resonant nanostructure formation via the Coulomb mechanism with surface plasmon-polariton excitation and propagation. Here the particular influence of the laser pulse on the optical properties of the surface region play an important role as they take influence on the SPP’s dispersion relation and its attenuation length. In the present work, we have considered this influence for a low and a high intensity/fluence interaction regime, where the regimes are discriminated by the damage threshold.

In particular, we have discovered experimentally that for the high intensity regime the process of plasma formation is followed by a considerable lateral energy transfer. According to theoretical estimations, the energy transfer is mainly due to nonlinear hot electron diffusion which may be supplemented by an energy transfer by non-equilibrium surface plasmon-polaritons excited at and propagating along the plasma-vacuum boundary. This conclusion extends the results of previous works on low-energy electron transport, now to the much higher hot electron energy. This takes influence on the ripple formation.

Another important novel aspect is the observed reduction of the ripple formation threshold at high intensity or peak fluence, respectively. This is associated with a noticeable super-linear increase of the ripple area. As the intensity in the ripple region always has an upper limit which may be well below that at the central peak of the laser spot, the experimental observation of the laser-induced ripple threshold lowering is caused mainly by rapid electronic lateral diffusion from the spot centre. The scaling of this process, i.e. \(F_{\text{th}} \propto F_0^{3/4}\), is in good agreement with the experimental data.

A further issue associated with the electronic transport is the smooth increase of the nanostructure period with laser fluence. In the plasma formation regime this is due to the decrease of the hot electron’s collision frequency and the increase of the plasma density which is typical for most metals.

All together the present experimental work with its theoretical estimates provides an important contribution for nanostructure generation with femtosecond laser pulses at rather high laser intensity, where the term ‘high’ has to be regarded with respect to experiments related to ripple formation. In that sense it may also stimulate further theoretical work.

Acknowledgments

The authors would like to thank V Braun for supplementary microscope measurements. A A and U T are grateful to the Deutscher Akademischer Austauschdienst (DAAD) for support by the DAAD Gastdozentenprogramm, grant no. 57371110.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
References

[1] Akhmanov S A, Emel’yanov V I, Koroteev N I and Seminogov V N 1985 Sov. Phys. Usp. 28 1084–124
[2] Bonch-Bruevich A M, Liberson M N, Makin V S and Trubave V V 1992 Opt. Eng. 31 718–30
[3] Agranat M B, Ashitkov S I, Fortov V E, Anisimov S I, Dykhn A M and Kondratenko P S 1999 J. Experimental and Theoretical Physics 88 376–6
[4] Bonse J, Hohm S, Kirner S V, Rosenfeld A and Krüger J 2017 IEEE J. Sel. Top. Quantum Electron. 23 9000615
[5] Huang M, Zhao F, Cheng Y, Xu N and Xu Z 2010 ACS Nano 4 4962
[6] Makin V S, Makin R S, Vorobyev A Y and Guo C 2008 Tech. Phys. Lett. 34 387–90
[7] Bonse J and Graf S 2020 Laser Photonics Rev. 14 2000215
[8] Kirchenko N A, Barmina E V and Shafeev G A 2018 Physics of Wave Phenomena 26 264–73
[9] Fragelakis F, Tsibidis G D and Startakis E 2021 Phys. Rev. B 103 054105
[10] Rudenko A, Abu-Saleh A, Pigeon F, Musclair C, Garrelie F, Stoian R and Colombier J-P 2020 20 Acta Mater. 194 93–105
[11] Gamaly E G and Rode A V 2013 Prog. Quantum Electron. 37 215–323
[12] Sakabe S, Hashida M, Tokita S, Namba S and Okamuro K 2009 Phys. Rev. B 79 033409
[13] Okamura K, Hashida M, Miyazaka Y, Ikuta Y, Tokita S and Sakabe S 2010 Phys. Rev. B 82 165417
[14] Cheng J, Liu J, Cao K, Chen L, Zhang Y, Han R, Deng D, Liu J, Zhang S, Sun Z and Jia T 2018 Phys. Rev. B 98 184106
[15] Cheng K, Cao K, Zhang Y, Han R, Deng D, Liu J, Zhang S, Sun Z and Jia T 2020 J. Phys. D: Applied Phys. 53 85102
[16] Zuhlke C A, Tsibidis G D, Anderson T, Startakis E, Gogos G and Alexander D R 2018 AIP Adv. 8 015212
[17] Yang X, Yang J, Xue I and Guo Y 2010 Appl. Phys. Lett. 97 141101–5
[18] Andreev A, Imgrunt J, Braun V, Dittmar I and Teubner U 2021 Appl. Phys. A 127 564
[19] Graf S 2020 Adv. opt. technol ed K Sugioka and Y Cheng
[20] Block A, Liebel M, Yu R, Spector M, Sivan Y, Garcia-Abajo F J and van Hulst N F 2019 Science Advances. 5 eaav8965
[21] Andreev A, Platonov K, Braenzel J, Lübeck A, Das S, Messoudi H, Grunwald R, Gray C, McGlynn E and Schnirer M 2016 Plasma Phys. Control. Fusion 58 014038
[22] Andreev A, Kumar N, Platonov K Yu and Pukhov A 2011 Phys. Plasmas 18 103103
[23] Imgrunt J, Chakanga K, von Maydell K and Teubner U 2017 Appl. Phys. A 123 776
[24] Trang T, Huynh D and Seminar N 2014 Appl. Phys. A 116 1429–35
[25] Vorobyev A and Guo C 2012 Laser Phot. Reviews 7 385–407
[26] Zuhlke C, A, Tsibidis G D, Anderson T, Startakis E, Gogos G and Alexander D B 2018 AIP Adv. 8 015212
[27] Makin V S, Pestov Y I and Makin R S 2020 Opt. Spectrosc. 128 264–8
[28] Nathala C S R, Ajumi A, Husinsky W, Farooq B, Kusdryashov S I, Daskalova A, Bliznakova I and Asson A 2016 Appl. Phys. A 122 107
[29] Hashida M, Miyazaka Y, Ikuta Y, Tokita S and Sakabe S 2011 Phys. Rev. B 83 235413
[30] Jee Y, Becker M F and Walser R M 1988 J. Opt. Soc. Am. B 5 648–59
[31] Bytskov–Nielsen J, Savolainen J–M, Christensen M S and Balling P 2010 Appl. Phys. A 101 97
[32] Cheng C W 2017 Int. J. Adv. Manuf. Technol. 92 151–6
[33] Nolle S, Momma C, Jacobs H, Tünnermann A, Chichkov B N, Welgehausen B and Welling H 1997 J. Opt. Soc. Am. B 14 2716
[34] Tsibidis G D, Barberoglou M, Loukakos P A, Startakis E and Fotakis C 2012 Phys. Rev. B 86 115316
[35] Tsidakis G D and Startakis E 2017 J. Appl. Physics. 121 163106
[36] Kumar N and Tripathi V K 2007 Phys. Plasmas 14 103108
[37] Macchi A 2018 Phys. Plasmas 25 033106
[38] Chimerio B, Tikhonchuk V T and Hallo L 2007 Phys. Rev. B 75 195124
[39] Bulgakova N M, Stoian R, Rosenfeld A, Hertel I V, Marine W and Campbell E E B 2005 Appl. Phys. A 81 345
[40] Jonin A A, Kudryashov S I, Makarov S V, Selenev I V and Smitsyn D V 2014 Appl. Phys. A 117 1757
[41] Bennett T D, Krajnovich D J, Grigopoulos C P, Baumgart P and Tam A C 1997 J. Heat Transfer 119 589–96
[42] Winter J, Rapp S, Schmidt M and Huber H P 2017 Appl. Surf. Sci. 417 2–15
[43] Zel’ dovich Y B and Raizer Y P 1966 Physics of Shock Waves and High Temperature Hydrodynamic Phenomena (New York: Academic) 652–74
[44] Teubner U, Theobald W, Wulkker C and Förster E 1995 Phys. Plasmas 3 2679–85
[45] Teubner U, Gibbon P, Förster E, Fally E, Audebert P, Geindre J P and Gauthier J C 1996 Phys. Plasmas 3 2679–85
[46] Dragla R and Gamaly E G 1991 Phys. Rev. A 44 6828
[47] Makin V S, Silantjeva I A and Makin R S 2011 Proc. SPIE 7996 799601–8