Mechanism of nanograting formation on the surface of fused silica

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Abstract: Nanograting inscription with a tightly focused femtosecond beam on the surface of fused silica was studied. The width and spacing of grooves are shown to decrease with the increase of the number of overlapped shots in both stationary and scanning cases. We propose a model to explain this behavior, based on both the so-called nanoplasmonic model and the incubation effect.

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1. Introduction

Nanograting formation has been intensively studied over the last two decades. Many investigations were conducted to study their formation mechanism as a function of writing parameters such as laser wavelength, pulse energy, repetition rate, polarization, scan speed, and so on [1–7]. It has been shown that the orientation of nanograting is perpendicular to the linear electric field due to local field enhancement [5] and that well-shaped nanogratings are created when the incident laser intensity lies slightly above the threshold for nanograting formation [9]. Several models based on self-organization [2], interference [3, 4], nanoplasmonics [5] and standing wave [8] have been proposed. However, none of these models can satisfactorily explain the dependence of the width and spacing of nanoplanes/nanogrooves as a function of the number of overlapped shots [3] or pulse to pulse spacing [7]. In this paper, we present a parallel study of the formation of the nanogratings both in the stationary case (i.e. on a pulse-to-pulse evolution basis) as well as in the scanning case (i.e. as a function of the pulse to pulse spacing). The precise shape of local intensity distribution (i.e. nanoplasmonic effect [5]) together with the reduction of the ablation threshold (i.e. incubation effect [10–12]) are shown to be responsible for nanograting formation. A model is proposed accordingly.

2. Experiment

We used two Ti-sapphire lasers, Coherent RegA 9000 (beam ’A’) and Spectra-Physics Spitfire (beam ’B’) for writing nanogratings in the stationary and scanning cases, respectively. The central wavelengths of both laser systems are 800 nm. Note that the laser beam with a different pulse duration would slightly change the ablation threshold and plasma density during the interaction with transparent materials [13]. In our experiment, the laser beam was focused by an microscope objective (Melles Griot 25X, N.A. = 0.5) onto the surface of a fused silica plate (Corning 7980) mounted on a 3D motorized translation stage. A circular variable metallic ND filter was used to control the incident laser energy. The focal spot diameters ($1/e^2$ of the fluence profile) and transform limited pulse durations (FWHM) were 2.4 μm, 80 fs for beam ’A’ and 2.6 μm, 45 fs for beam ’B’, respectively. Single shot mode was used in the stationary case. A series of ablation spots was created with different number of shots per site. The delay between two successive shots was about 2 seconds. In the scanning case, nanogratings were written by translating the sample perpendicular to the laser propagation direction. After the writing, the samples were imaged under a scanning electron microscope (SEM, FEI Quanta 3D FEG).

3. Results and discussion

Figure 1 shows the shot-to-shot evolution of grooves created at 90 nJ/pulse. After the first shot, a few small craters are created apparently randomly within an interaction zone which is smaller than the beam spot size. After 4 shots, three grooves, seemingly aligned perpendicularly to the laser electric field start to emerge with a larger one in the center accompanied with a pair of smaller ones on both sides. As the pulse number increases to 6, the previous trend is confirmed as the two side grooves get elongated, and a second groove pair starts to show up (see arrows). After 9 shots, a new pair of grooves emerges from inside (see arrows). After 13 shots, a narrowing of the previously created grooves is observed whereas the newly created ones get elongated. From there on, no significant change is observed as shown by the result at 500 shots written at 10 kHz rep-rate (Fig. 1(g)). The cross-section pictures, (Fig. 1(h)) obtained after 6 shots and (Fig. 1(i)) after 14 shots, further illustrate the narrowing as well as the deepening of grooves as the number of shots is increased. We also note the enlargement of the interaction zone as the pulse number increases which can be interpreted as a reduction of the ablation threshold (i.e. incubation) presumably resulting from laser-induced defects [10–12].
Fig. 1. The shot-to-shot evolution of nanogrooves at 90 nJ/pulse. The dashed lines indicate the location for cross-section roughly.

Fig. 2. Nanograting formation as a function of \( d \) at 100 nJ/pulse. \( K \): laser propagation direction; \( S \): scan direction; \( E \): laser polarization direction.

In the scanning case, the nanogratings were written as a function of pulse to pulse spacing \( d \) for a pulse energy of 100 nJ/pulse and with laser polarization either perpendicular or parallel to the scan direction (Figs. 2(a) and 2(b)). In both cases, the width and spacing of the grooves increase significantly with \( d \). However, slight damage is observed for \( d \leq 20 \text{ nm} \) with the laser polarization parallel to the scan direction (Fig. 2(b)).

Inspired by the idea proposed by Bhardwaj et al. [5] and based on our recent results showing the crucial role of the incubation effect on nanograting formation [12], we develop a new model to interpret the nanograting formation on the surface. In our model, a hemisphere of slightly over dense plasma (i.e. ablation zone) is assumed to be induced at the laser peak. Due to plasma formation, the dielectric constant inside the hemisphere (\( \varepsilon_i \)) is getting significantly smaller than that of the surrounding (external) material (\( \varepsilon_e \)) which leads to the local intensity distribution depicted in Fig. 3. According to that distribution, the local intensity decreases sharply at the poles (along x-axis) and is enhanced inside the ablation zone and around the equatorial direction [14]. Accordingly, any illumination dependant process such as the incubation process will be locally enhanced at the equator and suppressed at the poles. The enhancement of the incubation process along the equator actually acts as a positive feedback mechanism which contributes to the extension of the plasma zone, and in turn of the ablation zone, along y-axis. Therefore, with the increase of the number of shots leading to incubation, a small crater tends to progressively transform into a groove in the direction perpendicular to the electric field. Contrarily, along
the x-axis, we first note that a sharp decrease of the intensity is observed at the poles which is eventually followed by a pair of local maxima (Fig. 3(c)). These side-maxima whose precise location is determined by the plasma density and width of the ablation zone (see Eq. (3)) are progressively (i.e. as the number of shots increases) lowering the ablation threshold, through the incubation effect, in such a way that the ablation process is eventually locally initiated. As soon as ablation threshold is reached, a pair of peripheral nanoplasma zones is created leading to local intensity enhancement, as in the case of the central nanoplasma zone. It is this evolution of the onset of side-maxima and the corresponding “self-seeding” from incubation effect that lead to the formation of the periodic structure. Based on the previous scheme, a detailed analysis of the experimental results of Fig. 1 is now provided with the help of Fig. 4 which follows from the model detailed in the Appendix.

Starting with an ideal surface with no defect and impurity and assuming that the incident laser peak intensity is slightly above the single shot ablation threshold, a shallow crater is thus formed at the first shot (bottom of Fig. 4(a)). (Note: In the case where random surface defects and impurity exist, near-threshold ablation would be induced preferably at the defects positions thus giving rise to a random set of craters as observed in Fig. 1(a)). The corresponding local intensity distribution along electric field direction, as computed from Eq. (5), is plotted on top of Fig. 4(a). The sharp central peak is the consequence of field enhancement within the ablation zone, and its width corresponds to the diameter (width) of the ablation zone along the electric field direction (x-axis). With the increase of the number of shots, incubation takes place along the equatorial direction (y-axis) of this crater as well as at the two side-maxima. Accordingly, the ablation threshold is locally reduced over these incubation affected zones. The shallow central crater thus evolves into a groove in the y-axis whereas, as a result of incubation, a pair of new ablation zones is created at the location of the side-maxima. As a consequence of this, a pair of sharp local intensity peaks labeled 1- and 1+ arises as shown in Fig. 4(b). A new pair
of grooves is thus formed (bottom of Fig. 4(b)) in agreement with what was experimentally observed and depicted in Figs. 1(b) and 1(c). New local intensity minima are then created so that four side-maxima are now observed (Fig. 4(b)). The outer most pair of maxima with higher intensities will eventually reach ablation due to incubation and two more grooves will be created at these positions (Fig. 4(c)) as experimentally observed in Fig. 1(c) (arrows). Further irradiation will create two more grooves, but now at the position of the theoretically predicted inner pair of maxima (labeled 3- and 3+ in Fig. 4(d)) as experimentally shown in Fig. 1(d) (arrows). The very existence of these inner grooves and the way our model predict their onset is a good indication of its validity. The previous scheme was simply modeled based on the set of equations appearing in the Appendix and assuming a decrease of the ablation threshold in agreement with the experimental values reported in Ref. [12].

In analyzing the scanning case, the two situations of the electric field $E$ parallel vs perpendicular to the scanning direction $S$ must be distinguished. Let us first recall that in the $E$ perpendicular to $S$ case, the nanogrooves extend along the scan direction, as depicted in Fig. 2(a). In that situation, the previous analysis of the static case can be directly transposed by simply replacing the number of shots by the pulse to pulse spacing. In fact, the incubation process will be enhanced as the pulse to pulse spacing decreases and this will lead to the creation of a larger number of grooves, in agreement with the experiment (Fig. 2(a)). This is further illustrated by the transient case (see Fig. 1(j)) where the number of lines is shown to pass from 6 in the static case to 3 in the beam moving case. The nanogrooves thus just self-seed themselves along the scanning direction as the beam is moved. Note that, according to the model (Fig. 4), the number of grooves should always be an odd number. Even number of grooves may result from surface defects or asymmetrical intensity distribution at the focal spot. In the $E$ parallel to $S$ case, the nanogrooves are perpendicular to scan direction so that the symmetric pattern of the local intensity distribution is destroyed by the beam displacement, as illustrated in Fig. 5. The main consequence of this is that the relative amplitude of the side maxima will be changed, favoring the one along beam direction (+x axis). This will also affect the position of the side maxima with respect to the central peak and therefore the nanograting pitch through the pulse to pulse spacing. Otherwise, the previously described interplay between incubation and nanoplasmonics...
Fig. 5. Schematic drawing showing the modification of local intensity for the case of laser polarization parallel to the scan direction. The self-repetition of increase of the local intensity and decrease of the ablation threshold at the leading side-maximum in (b) is the driver for ordered grating formation.

Fig. 6. Evolution of width (a) and spacing (b) of nanogrooves at 100 nJ/pulse with laser polarization parallel to the scan direction. The red curve in (b) corresponds to the simulation performed with the following parameters: plasma density: $2.5 \times 10^{21}/cm^3$; pulse energy: 106 nJ/pulse, pulse width: 42 fs; focal spot diameter: 2.56 μm and the ablation fluence is following: $F_d = 3.06 + (3.89 - 3.06) \exp(-0.034(1.28/d - 1))$ (see Ref. [12])

is taking place leading to the progressive creation of ordered nanogrooves. This can be modeled according to the set of equations derived in the Appendix. In particular, the evolution of the groove spacing as a function of $d$, which is the typical signature of this phenomenon, is well reproduced by our model (Fig. 6(b)). In order to reproduce the experimental data, the set of equations was used along with the experimental values of the groove width as a function of $d$ (Fig. 6(a)) and the incubation induced decrease of the ablation threshold as derived in Ref. [12].

4. Conclusion

In summary, we have derived a model based on nanoplasmonics that accounts for the formation of periodic nanogrooves at the surface of glass upon exposure to ultrashort pulses. The evolution of the local intensity distribution from shot to shot, together with the reduced ablation threshold, essentially governs this nanograting formation. In particular, the local field side-maxima appearing along the laser polarization axis are shown to play a key role in triggering the nanoplane formation.
Appendix

The sphere of slightly over dense plasma induced at the laser peak modifies the electric field local distribution (see Fig. 3). From the external (e) and internal (i) electric potentials $V_e = -E_i r \cos(\theta) + \frac{\varepsilon'_1 - 1}{\varepsilon'_1 + 2} \frac{R_i^3}{r^2} E_i \cos(\theta)$ and $V_i = -\frac{3\varepsilon'_1}{\varepsilon'_1 + 2} E_i \cos(\theta)$ [14], one can derive the moduli of the external $E_e$ and internal $E_i$ fields in response to the laser field $E_l$:  

$$E_e = | -\frac{\partial V_e}{\partial r} \hat{r} - \frac{1}{r} \frac{\partial V_e}{\partial \theta} \hat{\theta} | = \sqrt{(A^2_0 + B^2_0)} E_l,$$  

$$E_i = | -\frac{\partial V_i}{\partial r} \hat{r} - \frac{1}{r} \frac{\partial V_i}{\partial \theta} \hat{\theta} | = \frac{C_0}{E_l} E_l$$

where $A_0 = (1 + 2 \varepsilon'_1 - 1 \frac{R_i^3}{r^2}) \cos(\theta)$, $B_0 = (\varepsilon'_1 - 1 \frac{R_i^3}{r^2} - 1) \sin(\theta)$, and $C_0 = \frac{3}{\varepsilon'_1 + 2}$, respectively, are field modification factors resulting from the plasma. The subscript '0' is introduced to identify this zone which will become the central groove and $\varepsilon'_1 = \varepsilon_i/\varepsilon_e$ ($\varepsilon_i = -0.1538$, $\varepsilon_e = 2.1025$). We note that the ablation zone is small so that the electric field can be considered as constant over it. We therefore assume in the following that the plasma density in the ablation zone is constant and uniformly distributed. Thus, we have fixed in our model the value of the plasma density to $2.5 \times 10^{21}/cm^3$ corresponding to a slightly over dense plasma. This value was actually found to better account for our experimental data although any value between 2 and $3 \times 10^{21}/cm^3$ lead to reasonable agreement with the experiment. The $\theta$ is the polar angle with respect to x-axis and $R_0$ is the radius of the central ablation zone as depicted on Fig. 7.

The internal dielectric constant $\varepsilon_i = n^2 - \frac{e^2 N_{pl}}{m_e \omega_0 (\omega_0^2 + (1/\varepsilon_e)^2)}$ was calculated according to the Drude model [15] where $n = 1.45$ is the refractive index of the sample, $e$ is the electron charge, $N_{pl}$ is the plasma density, $m_e = 0.635m$ is the effective electron mass, $m$ is the electron mass, $\varepsilon_0$ is the vacuum permittivity, $\omega_0$ is the laser frequency, and $\tau_e = 23.3$ fs is the electron collision time. The initial value of $R_0$ can be simply calculated by $R_0 = \sqrt{\frac{w_0^2 \ln(I_l/I_{th})}{2}}$, where $I_{th}$ is the single shot ablation threshold and $I_l$ is the laser intensity distribution. To simplify the analysis we restrict ourselves in the following to the evolution of the local intensity distribution along the x-axis. By setting $\theta = 0$, we obtain:

$$I_{e,0} = A^2_0 I_l, \quad I_{i,0} = C_0^2 I_l$$

$$I_{local,0} = I_{e,0} + I_{i,0}$$

We note that the local intensity distribution $I_{local,0}$ has two side-maxima. With the increase of the number of shots, a pair of new ablation zones (with half width $R_1$) will be created at distance $s_1$ from the central groove once the reduced ablation threshold is exceeded (see Fig. 7). The presence of this new pair of ablation zones will in turn affect the local intensity distribution according to a new set of local field modification factors. Iteratively, new pairs of ablation zones will be created with modification factors taking the general form:

$$A_{n+} = [1 + 2 \frac{\varepsilon'_1 - 1}{\varepsilon'_1 + 2} \frac{R_n^3}{(s_n-s_0)^3}], \quad |x-s_n| > R_n,$$

$$A_{n-} = [1 + 2 \frac{\varepsilon'_1 - 1}{\varepsilon'_1 + 2} \frac{R_n^3}{(s_n+s_0)^3}], \quad |x+s_n| > R_n,$$

$$C_{n+} = C_{n-} = C_0 = \frac{3}{\varepsilon'_1 + 2}, \quad |x \pm s_n| \leq R_n, \quad n \geq 1$$

where $R_n$ and $s_n$ are generalized from $R_1$ and $s_1$ defined in Fig. 7. The integer ‘$n$’ thus stands for the $n^{th}$ pair of grooves whereas ‘+/-’ refers to the groove on the right/left hand side of the
central groove (as labeled in Fig. 4). Thus, the local intensity distributions in the presence of multiple grooves become:

\[
\begin{align*}
I_{e,n} &= (A^2_n + A^2_{n-1})I_{\text{local},n-1} \\
I_{i,n} &= (C^2_n + C^2_{n-1})I_{\text{local},n-1} \\
I_{\text{local},n} &= I_{e,n} + I_{i,n}, \quad n \geq 1
\end{align*}
\]  

(5)

By applying the standard recursive method for the local intensity distribution, \(s_n, R_n\) and \(I_{\text{local},n}\) are iteratively determined. In the scanning case (with electric field parallel to scan direction), we assume it is the laser that is moved instead of the sample. The moving laser is defined as:

\[I_l = I_0 \exp \left[-2(x - (N - 1)d)^2/w_0^2\right],\]

where \(N\) is the pulse number. The new groove is created only by the leading side-maximum whose distribution is mainly governed by its adjacent groove:

\[I_{e,n} = A_n^2 I_l, \quad |x - s_n| > R_n, \quad n \geq 0\]

(6)

where: \(A_n = [1 + 2e^{r-1} - \frac{R_1^2}{|x-s_n|^2}]\). The initial position of the first groove \(s_0\) is set to 0. During the scanning, the amplitude of leading side-maximum is boosted which leads, through incubation, to a reduction of ablation threshold in the corresponding area. Ablation followed by groove formation occur once this side-maximum exceeds the reduced ablation threshold \((s_1 \text{ and } R_1 \text{ are thus determined}). A new leading side-maximum then arises which eventually lead to the onset of a new groove in such a way that the process repeats itself until the beam scanning stops. Because of our limited knowledge of shot-to-shot ablation threshold, the width of grooves is difficult to calculate. In the simulation, the width of grooves was set in agreement with the experimental results (Fig. 1 and Fig. 6(a)) and the previously reported average reduced ablation threshold [12] was also used.

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