High speed inscription of uniform, large-area laser-induced periodic surface structures in Cr films using a high repetition rate fs laser

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We report on the fabrication of laser-induced periodic surface structures in Cr films upon high repetition rate fs laser irradiation (up to 1 MHz, 500 fs, 1030 nm), employing beam scanning. Highly regular large-area (9 cm²) gratings with a relative diffraction efficiency of 42% can be produced within less than 6 min. The ripple period at moderate and high fluences is 0.9 μm, with a small period of 0.5 μm appearing at lower energies. The role of the irradiation parameters on the characteristics of the laser-induced periodic surface structures (LIPSS) is studied and discussed in the frame of the models presently used. We have identified the polarization vector orientation with respect to the scan direction as a key parameter for the fabrication of high-quality, large-area LIPSS, which, for perpendicular orientation, allows the coherent extension of the sub-wavelength structure over macroscopic distances. The processing strategy is robust in terms of broad parameter windows and applicable to other materials featuring LIPSS. © 2014 Optical Society of America

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The formation of laser-induced periodic surface structures (LIPSS) is a universal phenomenon [1] that can be observed in a variety of materials [2]. The beauty of the phenomenon lies in its simplicity, leading to the formation of periodic surface nanostructures, smaller than the wavelength of the laser light, without using masks or interfering laser beams. This potential has triggered intense activity within the large research community pursuing exploitation of LIPSS for nanostructuring applications.

The generally accepted view on the formation mechanism of LIPSS is that incident laser light interferes with a scattered or excited surface wave [3–5]. The interference causes a modulated intensity distribution, which is imprinted into the material. The model developed by Sipe and co-workers [4] establishes a relation between the LIPSS period and the complex refractive index of the material. While the model correctly describes many experimental findings, significant deviations were reported by several groups. As a consequence, Bonse and co-workers [5] realized the need to take into account the transient complex refractive index of the material during laser irradiation, strongly influenced by the transient formation of a dense electron-hole plasma.

LIPSS have been reported in semiconductors [1,5–6], dielectrics (inorganic [7,8] and polymers [9,10]), and metals [11–13] although the broad range of known LIPSS types [1,14] (different periods and orientations with respect to the laser polarization) renders a definitive identification, in many cases, a challenge. From an application point of view, Fauchet and Siegman demonstrated in 1982 the coherent extension of LIPSS in semiconductors along a line, by moving the laser spot along the ripple direction [3]. However, few studies report 2D grating structures with sufficient homogeneity over extended regions to be considered interesting for device fabrication. To the best of our knowledge, the most uniform grating structure reported so far for semiconductors has been obtained in silicon, using a 80 MHz Ti:Sa fs oscillator and beam scanning unit [15]. The obtained 1 cm² grating with λ/6 period, consisted of 1089 closely joined 300 μm² gratings written individually. The downside of the approach was the processing time (36 h) and the grating disruption at the joints of the individual gratings. For metals, the state-of-the-art of LIPSS gratings has been reported very recently by Öktem et al. [16]. Employing a 1 MHz fiber laser (100 fs pulses at 1060 nm) the authors achieve extremely uniform structures in titanium, processing at low speeds (2–8 μm/s) over an area of 3 mm². They attribute homogeneity to the use of a small spot size, influencing nonlocal feedback to the formation mechanism.

We report here on the fabrication of gratings in Cr with much larger sizes (9 cm²) within less than 6 min, using a high repetition rate fs laser and fast beam scanning. The grating is continuous over the entire area and written with a single scan field. We discuss the underlying reasons for the grating homogeneity, being related to the scan direction.

The laser system used was a fiber-based fs-laser amplifier (Tangerine, Amplitude Systems) operating at a wavelength $\lambda = 1030$ nm, a pulse duration $\tau \approx 500$ fs, a maximum pulse energy $E_{\text{max}} = 10$ μJ, and a maximum repetition rate $\nu_{\text{rep,max}} = 2$ MHz. The linearly polarized output beam has a Gaussian intensity distribution with an initial diameter of $d_0 = 3.6$ mm ($1/e^2$ intensity), is slightly divergent, and passes a Faraday isolator to prevent back-reflections into the laser, a lambda-half ($\lambda/2$) wave plate/thin film polarizer system for energy control and a second $\lambda/2$ wave plate for polarization control. The
beam was then sent through a galvanometer beam scanning unit, combined with an F-Theta lens \((f = 100 \text{ mm})\) for scanning the focused beam over the static sample. The measured spot diameter at the sample surface was \(2w_0 = 80 \mu \text{m} (1/e^2\text{ intensity})\). The F-Theta lens ensured flat-field focusing and a displacement linear with the deflected beam angle. The maximum scan speed of the laser focus at the sample surface was \(v_{\text{max}} = 2.5 \text{ m/s}\) and line scanning was performed using a triangle wave \((\text{right}–\text{left}–\text{right}–…\text{...})\) rather than a saw-tooth wave \((\text{right}–\text{left}–\text{blank}–\text{right}–\text{left}–…\text{...})\) to increase processing speed. The step size between lines was varied from \(d = 2–80 \mu \text{m}\). The samples used were \(1 \mu \text{m}\) thick Cr films, evaporated onto a composite substrate, consisting of a top Ni layer \((20 \mu \text{m}\text{ thick})\), an intermediate adhesion layer made of Cu \((1 \mu \text{m}\text{ thick})\), and a \(1 \text{mm}\) thick polymer slab. The lateral sample dimensions were \(8 \text{ cm} \times 15 \text{ cm}\).

Figure 1(a) shows a color photograph of a \(9 \text{ cm}^2\) surface grating written in Cr in less than \(6 \text{ min}\), featuring a range of colors due to diffraction of the illuminating non-polarized white light. We used a repetition rate of \(f_{\text{rep}} = 250 \text{ kHz}\), vertical polarization, a pulse energy of \(1.95 \mu \text{J}\), a scan speed of \(v = 1.5 \text{ m/s}\), a step size between lines of \(d = 2 \mu \text{m}\) and horizontal line scanning. The highly regular grating structure formed by LIPSS can be seen under an optical microscope \((\text{NA} = 0.9, \lambda_{\text{illumination}} = 460 \text{ nm})\), lateral resolution \(r = 260 \text{ nm}\) [Fig. 1(b)], featuring grooves perpendicular to the laser polarization. We have performed a fast Fourier transform \((\text{FFT})\) of the micrograph to determine the grating period. The result is displayed as an in inset in Fig. 1(b) and features two very sharp peaks, whose positions yield a grating period \(\Lambda = 0.91 \mu \text{m} = 0.88 \lambda\). This value is slightly smaller than the laser wavelength, which is consistent with other studies of LIPSS in metals for normal incidence [12,13,17].

We have also quantified the diffraction efficiency of the LIPSS grating. For that purpose, a He–Ne laser beam was expanded to a diameter of \(5 \text{ mm}\) to probe a representative large grating area, and sent at normal incidence onto the grating, with its polarization axis \((\text{E-vector})\) being aligned perpendicular to the ripples. The power diffracted into the +1 order was measured and divided by the power reflected from the unprocessed sample. We obtained a relative diffraction efficiency of \(\eta = 42\%\), which is, to the best of our knowledge, the highest efficiency reported for gratings fabricated by LIPSS in any material.

The above result was obtained under optimized processing conditions. We have also investigated the influence of the scan direction with respect to the laser polarization and found it to be a crucial parameter. We wrote a set of square gratings with horizontal scanning for different orientations of the E-vector, controlled by the \(\lambda/2\) wave plate. As expected, the grating orientation rotated correspondingly with the laser polarization, staying always perpendicular to it. Yet, we noticed that, for specific wave plate orientations \((\text{separated by} 90\%)\), the grating quality improved, whereas for other ones it strongly degraded. To rule out the possibility of an undesired contribution of elliptic polarization due to a wavelength-dependent phase-shift of the wave plate [17], we removed the wave plate to keep the polarization direction constant, but changed instead the beam scan direction.

Figure 2 shows a comparison of two grating structures written under the same conditions as in Fig. 1, but with different scan directions. It is evident that the quality of the grating written with horizontal lines is superior to the one written with vertical lines. The underlying reason is most likely that the grating can be coherently extended [2] while it is being formed for a horizontal line scan. In other words, the self-forming groove structure is laterally extended along the scan direction. This is not possible in the other configuration, in which the laser spot scans across the forming grooves. Similar results have been observed in high-spatial frequency LIPSS in fused silica and correspondingly interpreted [2].

We have also studied the ripple topography as well as how it is influenced by the pulse energy. Figure 3(a) shows atomic force microscopy \((\text{AFM})\) measurements obtained from a region processed at \(E = 1.95 \mu \text{J}\), which led to the fabrication of an optimum grating, equivalent to the one shown in Fig. 1. The corresponding topography profile, shown in Fig. 3(c), features a sinusoidal-like shape composed of ridges and trenches, with a period \(\Lambda_{1.95 \mu \text{J}} = 0.93 \mu \text{m}\) and a large modulation amplitude of up to \(h = 350 \text{ nm}\). In contrast, a grating written at lower

![Fig. 1. (a) Color photograph of a LIPSS-based diffraction grating written in a Cr film. (b) Optical micrograph of a zoomed region. The double-headed arrow indicates the laser polarization (E-vector) direction and the scan principle and direction (“S”) are indicated below. The inset in (b) shows the 2D FFT image of the micrograph.](image-url)

![Fig. 2. Optical micrographs of LIPSS gratings written with the scan direction S (a) parallel and (b) perpendicular to the ripples.](image-url)
As for the modulation amplitude of the ripples, it has been observed that, within the studied range of critical parameters that need careful adjustment. For this study, we have performed a systematic study at two repetition rates (250 kHz and 1 MHz), three energies (1.3, 1.95, and 2.6 μJ), three scan speeds (750 nm/s, 1.5 m/s, and 2.5 m/s) and different spot sizes (2, 4, 20, 55 μm). We have calculated the number of pulses incident on an area equal to the spot size as follows. For \( v = 750 \text{ nm/s} \) and \( \nu_{\text{rep}} = 250 \text{ kHz} \) the step size in the scanning direction is \( d_{\text{scan}} = 3 \mu m \). Considering a spot size of \( 2\nu_{\text{opt}} = 80 \mu m \), this gives, along the scan direction, \( \#_{\text{scan}} = 27 \) pulses and between lines (for a step size \( d = 4 \mu m \)) \( \#_{\text{step}} = 20 \) pulses. This yields a pulse dose \( \pi \cdot \#_{\text{scan}} \cdot \#_{\text{step}} / 4 = 424 \) for this specific case. The ripple period has been measured by optical microscopy to benefit from the larger field of view and, thus, a more representative value was obtained. The shorter period with \( \Lambda_{\text{fine}}(1.3 \mu J) \) around 0.5 μm was close to the resolution limit of the microscope and was, therefore, evaluated indirectly as \( \Lambda_{\text{fine}}(1.3 \mu J) = \Lambda_{\text{coarse}}(1.3 \mu J) / 2 \) (c.f. Fig. 3).

Figure 4 is a representation of the measured ripple period versus the pulse energy and peak fluence. It can be immediately seen that, within the studied range of repetition rate, scan speed and step size, the ripple period features only two regimes that depend on the pulse energy. At low energy (1.3 μJ) a short period \( \Lambda_{\text{fine}} \approx 0.5 \) is observed, whereas at moderate and high energies (1.95 and 2.6 μJ) the expected period \( \Lambda \approx 0.9 \) is observed. It is worth emphasizing that even the pulse dose does not influence the ripple period. These results demonstrate the robustness of the structuring technique, featuring a broad window of suitable processing parameters.

Energy \( E = 1.3 \mu J \), c.f. Fig. 3(b), has an entirely different appearance. Each ridge is split into two, separated by a small trench, which can also be appreciated in the topography profile shown in Fig. 3(c). The corresponding amplitude of the overall modulation is much lower, \( h = 200 \) nm, compared with the grating written at higher energy. The periodicity of the double ridge structure can be separated into a coarse modulation, with \( \Lambda_{\text{coarse}}(1.3 \mu J) = 1.0 \mu m \), and a fine modulation, with \( \Lambda_{\text{fine}}(1.3 \mu J) = 0.5 \mu m \).

Several groups have reported an energy dependence of the ripple period in metals, which they attribute to differences in the transient plasma densities [13,18]. Hou et al. [18] observe two discrete ripples periods in steel, with the fine ripples being half as wide as the coarse ones. The authors perform numerical simulations of the electric field distribution at the surface and conclude that, at lower fluence (lower plasma density), a field localization develops also at the protuberance between two grooves, inducing the split of the ripples. Our results are in excellent agreement with this work.

As for the modulation amplitude of the ripples, it has been related in metals to the electron–phonon coupling strength \( \gamma \) of the specific metal [19]. Colombier et al. [12] have demonstrated this relation in Ru, W, Ni, and Cu, with Ru showing the highest amplitude (\( \Lambda_{Ru} \approx 270 \) nm) and strongest coupling (\( \gamma_{Ru} = 18.5 \cdot 10^{17} \text{ W/(m}^2\cdot \text{K}) \)). The underlying physical picture the authors propose is that, upon fs laser irradiation, hot electrons diffuse into a depth \( L_e \), which is related to the depth of a thin molten metal surface layer. The smaller the value \( L_e \), the higher the temperature gradient in depth, which is the driving force for material expansion perpendicular to the surface, thus generating ripples. The electron diffusion length is given by [20]
When generating LIPSS not in bulk material, but thin films or coatings, as in our case of a 1 μm thick Cr film, it is vital to choose processing parameters with a minimal ablation rate. We have performed white light interference microscopy (WLIM) measurements to measure the depth of the processed region. WLIM combines a wide field-of-view (630 μm × 470 μm) and high depth resolution (~1 nm) at the expense of moderate lateral resolution (~0.6 μm). Figure 5(a) shows a WLIM micrograph of the edge of the large grating, processed with optimum conditions (c.f. Fig. 1). A sharp transition from the unexposed to the exposed region can be seen, featuring a homogeneous and constant ablation depth, except at the very transition region, where the scan direction was inverted, leading for a short time to a slower scan speed, and thus higher dose. The average ablation depth in the homogeneous region is \( h_{\text{abl}} = 600 \) nm. The modulation height \( h = 350 \) nm has to be added to this value, since WLIM does not resolve the trenches. This yields a maximum ablation depth at the bottom of the trenches of 950 nm, which is approximately equal to the film thickness. We have calculated the corresponding ablation rate, estimating that, for the modulated layer thickness of \( h = 350 \) nm, the ablated material is at best 40% [c.f. the plateau-like structure with narrow trenches shown in Fig. 3(c)], which leads to an effective ablation depth of 740 nm. This yields an ablation rate of approximately 2 nm/pulse.

In conclusion, we have demonstrated that large-area homogeneous gratings, based on LIPSS, can be written within minutes in Cr films using high-repetition rate lasers and beam scanning. The processing approach is found to be robust, featuring a broad window of suitable parameters in terms of laser repetition rate, scan speed, and line separation. The fundamental parameter for grating quality is the scan direction with respect to the laser polarization. For perpendicular orientation, the forming LIPSS can be coherently extended, thus greatly enhancing alignment and order. The depth modulation is up to 350 nm, which is very high for LIPSS in metals in general, and higher than expected for Cr, based on its electron–phonon coupling constant. The scanning strategy chosen is likely to contribute to this high depth modulation, which translates to the high diffraction efficiency (42%) of the grating. In addition to the expected LIPSS period \( \Lambda \approx 0.9 - \lambda \), we have identified an energy range in which ripples with a much smaller period \( \Lambda \approx 0.5 - \lambda \) are produced, which is likely related to the dependence of the wavelength of the scattered plasma wave on the laser-produced electron density. The achieved ripple homogeneity over large areas is not only relevant for applications, but greatly enhances the precision of detailed scientific studies of LIPSS phenomena in other materials. Specific studies are already underway.

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