ANTENNA-LIKE EFFECT INDUCED BY SURFACE DEFECTS UPON ULTRASHORT LASER NANOSTRUCTURING OF SILICON

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Silicon is one of the most used materials in nanostructure research and in a wide range of high-technological applications spanning from the fine chemical industry to medicine and to semiconductor electronics. The processes underlying laser-induced nanostructuring of Si surfaces are still not fully understood. In particular, it is not completely clear how individual surface defects contribute to generation of ordered structures. In this contribution, we report on the influence of random defects, which are present on silicon surfaces, on the formation of periodic surface structures by laser irradiation with femto- and picosecond pulses. A thorough analysis of the results leads to the conclusion that the surface defects act as antenna-like elements directing radiation along the sample surface and determining the location, directionality and quality of structuring.

KEYWORDS

Ultrashort laser pulses, silicon, surface defects, antenna-like effect, light scattering, periodic nanostructures

1 INTRODUCTION

Short and ultrashort laser pulses are widely utilized for fabrication of micro- and nanostructures on surfaces of different kinds of materials including metals, semiconductors and dielectrics [Bonse 2012] [Gnilitskyi 2017] [Levy 2016]. The resulting laser-induced periodic surface structures (LIPSS) vary significantly in their periodicity, quality and orientation, depending on material properties and parameters of laser radiation (i.e. pulse duration, wavelength, pulse energy and repetition rate). Although LIPSS formation is a topic of large amount of studies since their first observation in 1965 [Birnbaum 1965], still some critical questions exist on the formation mechanisms, in particular on the role of surface defects (bumps, dips, scratches, etc.) in initiating the LIPSS and on the achievable quality of nanostructures [Birnbaum 2003]. The electromagnetic theory proposed in 1983 by Sipe et al. [Sipe 1983] attributes the LIPSS formation to laser light scattering on the surface roughness, which is confined in a “selvedge region” whose width is much smaller as compared to the laser wavelength. The role of individual surface defects and influence of their size and shape on the nanostructure features is still a challenging topic of research (e.g. [Birnbaum 2003] [Bhushan 2002] [Murphy 2014] [Kuchmizhak 2015]).

In this contribution, the surfaces of silicon samples have been irradiated by near-IR ultrashort laser pulses (picosecond (ps) and femtosecond (fs)) in single-shot irradiation regimes as well as for two shots with partially-overlapping irradiated spots. Our main interest, LIPSS on silicon surfaces, relates to a high demand of nanostructured surfaces in many fields including electronics, cancer diagnosis and therapy, and solar cells applications [Murphy 2014] [Degoli 2009] [Guzman-Verri 2007] [Priolo 2014] [Peng 2015]. A thorough analysis of the laser-irradiated spots have been performed with focusing on how individual surface defects influence material modification. It is concluded that the surface defects act as antenna-like elements directing radiation along the sample surface and determining the location, directionality and quality of structuring.

2 MATERIAL AND METHOD

A 0.48 mm thick monocrystalline *unpolished* Si wafers (Sigma Aldrich) with the density of 2.33 g/cm^3, were irradiated by a PHAROS laser system from Light Conversion (central wavelength 1030 nm with $M^2 \simeq 1.1$) In all experiments, pulse duration was 245 fs and 7 ps (FWHM). The average power of the laser and the repetition rate were fixed for all the experiment at 200 mW and 3 kHz respectively. The silicon wafers were preserved unpolished to explore how relatively large surface defects influence the periodic structure formation. Our intention here is to follow the process of light scattering on relatively large surface defects that can be considered as an exaggerated model of “selvage” [Sipe 1983].

The laser beam was focused on the sample surface with three different lenses of focal lengths 15, 30 and 50 cm respectively. The diameters of the irradiation spots in the focal region were evaluated using Gaussian $1/e^2$ formalism [Saleh 1991]:

$$\omega_0 = \frac{2\lambda f}{\pi D} M^2 \tag{1}$$

For the initial beam diameter D = 5 mm just after the lenses, yields 22, 43, and 73 µm focal spot diameters respectively. The determination of the geometrical focus on the sample surface was obtained qualitatively through the detection of the brightest ablation plasma along the beam propagation direction. The experimental setup is shown schematically in Fig. 1.

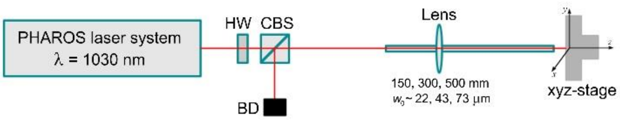

Figure 1. Scheme of the experimental setup. HW is a half wave plate, CBS is a cube beam splitter, BD is a beam damper. Silicon samples were positioned on an XYZ-stage.

Most of the experiments for silicon surface irradiation were performed with a single and with several shots on the same laser spot to inspect on how the defects within the spot influence the resulting surface morphology. In a number of experiments, the effect of overlapping laser shots was studied by manually shifting the sample positioned on a XYZ-stage (the number of shorts is specified blow for each case). The irradiated surfaces were analyzed by using an Optical Nomarski Microscope (Olympus

BX 43) that enables to evaluate the shape, periodicity, and spatial distribution of the resulting structures. Details of the experimental arrangements can be found in [Hrabovsky 2019].

3 RESULTS AND DISCUSSION

Although we have found that some LIPSS can be produced even at single shot irradiation, the structures obtained with several shots are more pronounced. Figure 2 demonstrates the LIPSS obtained on a silicon surface by three 7-ps laser shots with laser fluence of 0.8 J/cm^2. The laser beam was focused by the lens with 35-cm focal length. It is clearly seen that the presence of defects enhances the possibility to structure the material by initiating scattering. Although the target surface contained different kinds of defects such as scratches, bumps, and dips, a universal effect is clearly seen: all of them act as the antenna-like elements directing a part of the incoming laser light along the sample surface. The scattered laser wave when interfering with the incident laser wave produces the periodic surface relief on the irradiated surface in accordance with the electromagnetic theory of LIPSS formation [Sipe 1983]. The LIPSS orientation shows a clear tendency of following the boundary of a particular defect (Fig. 2). Dips and bumps direct the light along the laser polarization with LIPSS "waves" slightly curved to mimic the defect shapes. Interestingly, scratch, which is not perpendicular to the laser light polarization, creates well-regular structures which are parallel to the scratch but not following the polarization. The antenna-like effect is also underlined by the distance to which the LIPSS are imprinted from a "parent" defect: the scratch imprints the LIPSS up to several dozens of micrometers while the structures originated from the circular defects are rapidly degrading with the distance.

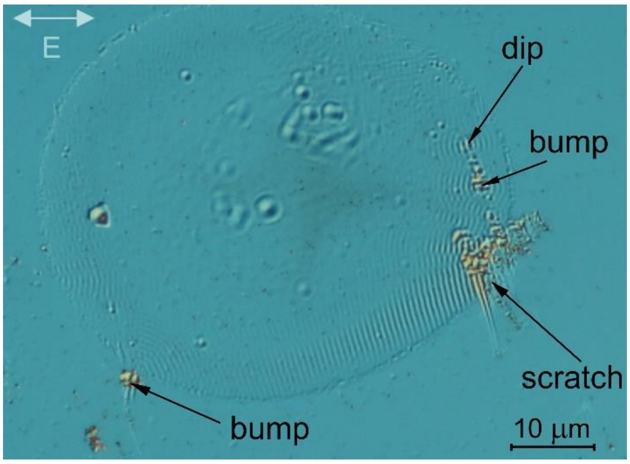

Figure 2. Periodic structures obtained on silicon at three 7-ps laser shots coupling to the same irradiation area. Laser fluence was 0.8 J/cm^2; the laser beam was focused by the lens of 35-cm focal length. The structures demonstrate a tendency to follow the shapes of defects, which act like antennas when scattering polarized laser light. One can see "circular antennas" (bumps and dips) and a "linear antenna" (scratch).

It has been found that the periodicity of LIPSS is slightly changing with the distance from the parent defect. Close to the defects, the LIPSS period is only slightly smaller than the laser wavelength while with distance the period decreases down to 700 nm (evaluated from Fig. 2 by the ImageJ software).

The antenna-like effect is independent on the focal length of the lens: for large and small focal lengths, the periodic structures are definitely originated from the light scattering from the local defects. However, the final picture of the structured surface depends on the distribution of the random defects and their shapes. A demonstrative example is given in Fig. 3 where the same experimental conditions were applied except the lens whose focal length was 50 cm (laser fluence was ensured to be also 0.8 J/cm^2). A striking difference from Fig. 2 in the distribution of the periodic features is conditioned by a larger amount of surface defects, which are located denser within the larger irradiation spot. Interestingly, stronger light scattering on the densely located defects results in more pronounced modification of the surface with the same number of shots at the same average laser fluence (compare Figs. 2 and 3). However, the periodicity is independent on the focusing lens and, according to ImageJ analysis, it is ~1 µm nearby the scattering features and is reducing with the distance from a defect with saturating at ~700 nm.

Figure 3 demonstrates the interaction between the periodic structures, which are originated from closely located defects, in the form of a constructive interference (outlined by the dashed square). It is clearly seen that the periodic structures resulted from the surface defects are merging with a tendency to create a regular periodic structure on an extended surface area. One may speculate that this picture provides evidence of how the LIPSS are formed on smoother surfaces: small closely-located features of surface roughness (selvage [Sipe 1983]) scatter incident laser light which constructively interferes, thus creating a periodic absorption profile. On the other hand, if roughness features are distant, the periodic absorption profiles are distorted upon interference that may lead to a higher dispersion in the LIPSS orientation angle (DLOA) [Gnilitskyi 2017] and the possible appearance of bifurcations (outlined by the dashed hexagon in Fig. 3).

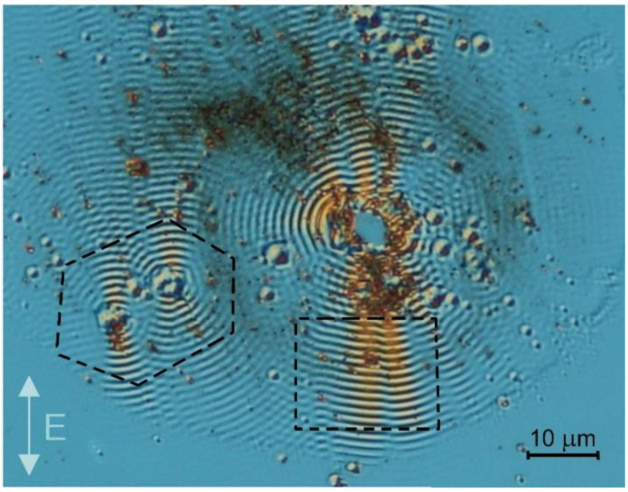

Figure 3. Periodic structures obtained on silicon at the same experimental conditions as for Fig. 2 with the lens of 50-cm focal length. The distribution of the surface defects was much denser than in the case of Fig. 2. Constructive interference of the periodic structures created by the different defects is clearly seen. The most demonstrative examples are highlighted by the dashed-lined boxes for closely and distantly located surface defects (square and hexagon respectively).

From Fig. 3, it can also be noticed that larger defects are dominating so that the structures, which are originating from a smaller defect, are either erased or redirected by structures created by larger roughness features. To explore how the periodic structures interact upon laser beam scanning, experiments with shifting the irradiation spot from shot to short were performed. A striking example is shown in Fig. 4.

The pattern shown in Fig. 4 was obtained by the following way. Irradiation was performed at laser fluence of 0.8 J/cm^2 using the lens with the focusing length of 50 cm. First, four laser shots were coupling on the same irradiation spot (right-side spot in Fig. 4). For the subsequent three shots, the target was shifted to the right so that the following irradiation spots were overlapping only slightly (three spots to the left from the first, more pronounced spot). The effect of mimicking of the LIPSS to the new irradiation areas is clearly seen. The pattern in the spot 2 looks like a collection of stripes covered by the LIPSS translated to a new area by the defects present in the first spot. Moreover, the next two spots reproduce the patterns from the previous spots, however gradually decaying.

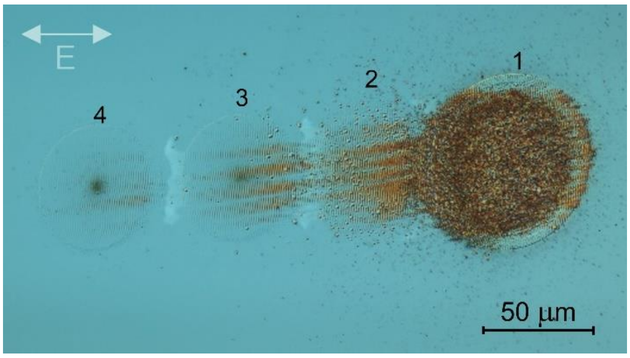

Figure 4. An example demonstrating how a periodic pattern formed within an irradiation spot reproduces itself to new irradiation areas. The spot on the right (1) was obtained by irradiation of the same area by four subsequent pulses. Spots 2-4 were created by single pulses by shifting the sample manually by 60 µm in respect to the previous pulse. The laser pulse parameters are as in Fig. 3; the focal length of the focusing lens was 50 mm.

Surprising is that the "LIPSS" antennas send the signal to a large distance, up to several dozens of micrometers. Furthermore, in the area where 3rd and 4th spots are slightly overlapping, the periodic pattern is almost invisible. However, it appears toward the center of the 4th spot where the local fluence of the Gaussian beam is higher, again reproducing the LIPSS stripes from the 3rd spot. We can state that even a relatively small perturbation in the form of the surface scattered wave is amplified by interference with the incoming laser beam.

It is important to notice that the nanoantenna effects illustrated in Figs. 2-3 are definitely related to the cases of overlapping irradiation spots. Although the spots 3 and 4 in Fig. 4 do not have abundant defects, structures from the previous spots are translated to the new irradiation areas. Thus, if a periodic structure has been created in the first laser spot, it is transmitted to a new irradiation area irrespectively to the presence or absence of relatively-large surface defects on this area. Surprising is quite distant transmission of the structures as well as their amplification toward the center of the new laser spot. It can be speculated that the incident laser light, being scattered along the surface, reaches the structures formed in the previous spot and is "reradiated back", thus mimicking the previously obtained structure to new area.

This observation has to be related to the propagation distance of the surface scattered waves [Gnilitskyi 2017]. It is expected that the observed effect can be more pronounced for low-loss materials that, however, calls for further studies. Interestingly, the structures obtained with 245-fs pulses at the same laser fluence are essentially similar to those demonstrated in Figs. 2-4 for ps laser pulses, indicating that the scattered laser energy density during the pulse but not intensity is important for the manifestation of the antenna-like effect. Although fs laser pulses are preferentially used for LIPSS formation, the LIPSS are efficiently formed by ps laser pulses on metal surfaces even at low laser fluences (lower intensities) [Gedvilas 2015] and also on large areas of silicon at the conditions similar to those used in the present studies [Sarbada 2016]. Thus, our study contributes to understanding of the mechanisms of LIPSS formation and its results can be useful for optimization of surface structuring. We can conclude that the antenna-like effect plays an essential (if not determining) role in reproducing the LIPSS to new surface areas upon laser scanning.

4 CONCLUSIONS

In this study, we have detected that random surface defects (scratches, bumps, dips) play a role of nanoantennas for the formation of periodic nanopattern on material surfaces. Although the surface roughness (selvedge) is the main requirement of the LIPSS formation in accordance with Sipe's theory, the role of individual defects and their interactive action during laser irradiation is not completely understood. Here we show that the defects determine the shape and regularity of periodic structures. Furthermore, the defects play a substantial role in transferring the structures to new irradiation areas upon laser scanning. In doing so, they can transmit surface-scattered electromagnetic wave to a long distance. The transmitted waves can serve as a perturbation for the incoming laser pulse, thus leading to periodic modulation of the beam intensity [Levy 2016]. It must be underlined that the LIPSS created in a certain surface area can be considered as the surface periodic defects which are copying themselves to new areas upon laser scanning.

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REFERENCES

[Bhushan 2002] Bhushan B., Agrawal G.B., Stress analysis of nanostructures using a finite element method. Nanotechnology, June 2002, 13, 515-523.

[Birnbaum 1965] Birnbaum M., Semiconductor surface damage produced by ruby lasers. J. Appl. Phys., July 1965, 36, 3688-3689.

[Birnbaum 2003] Bhushan B., Agrawal G.B., Finite element analysis of nanostructures with roughness and scratches, Ultramicroscopy, Oct-Nov 2003, 97(1-4), 495-507.

[Bonse 2012] Bonse J., et al. Femtosecond laser-induced periodic surface structures, J. Laser Appl., July 2012, 24(4), 042006.

[Degoli 2009] Degoli E., Ossicini S., Engineering quantum confined silicon nanostructures: ab-initio study of the structural, electronic and optical properties, Advances in Quantum Chemistry, December 2009, 58, 203-279.

[Gedvilas 2015] Gedvilas M., et al. Flexible periodical micro- and nano-structuring of a stainless steel surface using dual-wavelength double-pulse picosecond laser irradiation, RSC Adv., August 2015, 5, 75075.

[Gnilitskyi 2017] Gnilitskyi I., et al. High-speed, highly regular femtosecond laser printing of laser-induced periodic surface structures on metals: physical origin of the regularity, Sci. Report., August 2017, 7(1):8485.

[Guzman-Verri 2007] Guzman-Verri G.G., Lew Yan Voon L.C., Electronic structure of silicon-based nanostructures, Physical Review B, August 2007, 76, 075131.
[Hrabovsky 2019] Hrabovsky J., et al. Surface structuring of Kapton polyimide with femtosecond and picosecond IR laser pulses, Interf. Phenom. Heat Transf., Sept 2019, 7, 113-121.
[Kuchmizhak 2015] Kuchmizhak A. A., et al. Flash-imprinting of intense femtosecond surface plasmons for advanced nanoantenna fabrication, Opt. Lett. April 2015, 40, 1687-1690.
[Levy 2016] Levy Y., et al. Relaxation dynamics of femtosecond-laser-induced temperature modulation on the surfaces of metals and semiconductors, Appl. Surf. Sci., July 2016, 374, 157–164.
[Murphy 2014] Murphy R.D., et al. Polarization dependent formation of femtosecond laser-induced periodic surface structures near stepped features, Appl. Phys. Lett., June 2014, 104, 231117.
[Peng 2015] Fei Peng, et al. Silicon nanostructures for cancer diagnosis and therapy, Nanomedicine, 2015, 10, 2109-2123.
[Priolo 2014] Priolo F., et al. Silicon Nanostructures for photonics and photovoltaic, Nature Nanotechnology, Jan 2014, 9, 19-32.
[Saleh 1991] Saleh, B.E.A., Teich, M.C., Fundamentals of Photonics, New York: John Wiley & Sons, Inc., pp.80-107, 1991.
[Sarbada 2016] Sarbada S., et al. Low-reflectance laser-induced surface nanostructures created with a picosecond laser, Appl. Phys. A, January 2016, 122, 453.
[Sipe 1983] Sipe J. E., et al. Laser-induced periodic surface structure. I. Theory. Phys. Rev. B, January 1983, 27, 1141–1154.

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