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Periodic surface structures on crystalline silicon created by 532 nm picosecond Nd:YAG laser pulses

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Abstract

Creation of laser-induced morphology features, particularly laser-induced periodic surface structures (LIPSS), by a 532 nm picosecond Nd:YAG laser on crystalline silicon is reported. The LIPSS, often termed ripples, were produced at average laser irradiation fluences of 0.7, 1.6, and 7.9 J cm^{-2}. Two types of ripples were registered: micro-ripples (at micrometer scale) in the form of straight parallel lines extending over the entire irradiated spot, and nano-ripples (at nanometer scale), apparently concentric, registered only at the rim of the spot, with the periodicity dependent on laser fluence. There are indications that the parallel ripples are a consequence of the partial periodicity contained in the diffraction modulated laser beam, and the nano-ripples are very likely frozen capillary waves. The damage threshold fluence was estimated at 0.6 J cm^{-2}.

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Keywords: Surface modification; Micro-ripples; Nano-ripples; Silicon; Picosecond laser

1. Introduction

Surface modification studies of semi-conductors, especially silicon, by various types of energetic beams, including laser, are of great fundamental and technological interest. Owing to its physico-chemical and semi-conducting characteristics [1] silicon is attractive for numerous applications, e.g. in microelectronics, sensor technologies, bio-medicine, etc. It has been long known [2] that it is possible to create LIPSS as permanent wave-like structures, or ripple patterns, on target surfaces of various materials like metals, dielectrics, and semi-conductors. Recent studies showed that silicon LIPSS have potential applications in lithography, high-density data storage, etc. [3,4] Interest for studies of laser beam interaction with silicon is still extremely high. Typically, Nd:YAG [5,6], Ti:sapphire [3,4,7,8], excimer [7,9], and pulsed TEA CO_2 lasers [10] have been used.

Structuring silicon with a Nd:YAG laser beam pulsed in the picosecond domain has not been so much described in literature [11,12] as the nanosecond domain [5,6]. The present paper deals with morphological effects induced by a picosecond Nd:YAG laser emitting at 532 nm on silicon.

2. Experimental

A plate (15 mm × 10 mm × 0.5 mm) of a single crystal silicon with a (1 0 0) orientation was used in the experiment. The face side was polished, and the back was left as is. The face roughness was evaluated by AFM to less than 10 nm. Prior to laser irradiation the sample was prepared using a standard procedure that includes cleaning, rinsing, etc.

Irradiations were performed in air at 1013 mbar, with a pulse repetition rate of 2 Hz. The laser beam (near TEM_{00} mode) was focused through a quartz lens of 12.0 cm focal length, the incidence of the beam perpendicular to the sample surface. The laser was an active-passive mode-locked Nd:YAG system [12]. Pulse duration, measured by a scanning auto-correlator, of about 40 ± 2 ps was obtained by a saturable absorber dye and an acusto-optic standing wave modulator.

The samples were characterized by X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy

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(SEM), and atomic force microscopy (AFM). The SEM was coupled to an energy dispersive analyzer (EDAX) for determining surface compositions of the targets.

3. Results and discussion

Laser-induced morphology changes on silicon generally show dependence on laser beam characteristics: energy density, intensity, pulse duration, number of accumulated pulses, wavelength, etc.

The present surface morphology change is presented in Fig. 1 as a function of laser energy density, i.e. average fluence, $\Phi = 0.7$, 1.6, or 7.9 J cm^{-2} (respectively a, b, or c columns of images in Fig. 1), and as a function of the number of accumulated laser pulses, *N*, at each fluence. The average beam fluences were calculated from the ratios of the pulse energy versus damage area. Since the beam intensity profile had sharper than Gaussian drop near the edge (*vide infra*) this was a fairly justified characterization. All three fluences induced periodic micro-structures (at micrometer scale) over the entire irradiation spot at low numbers of accumulated laser pulses (e.g., 1 or 2 pulses). Increasing the fluence from 0.7 to 1.6, or 7.9 J cm^{-2} at a total *N* greater or equal to 10 resulted in modifying the periodic micro-structure, including formation of craters, especially after 50 accumulated pulses. Increasing *N* at a constant fluence tended to radically modify or destroy the periodic micro-structure. Producing periodic micro-structures in the form of straight parallel lines over the entire irradiated area is scarcely reported in

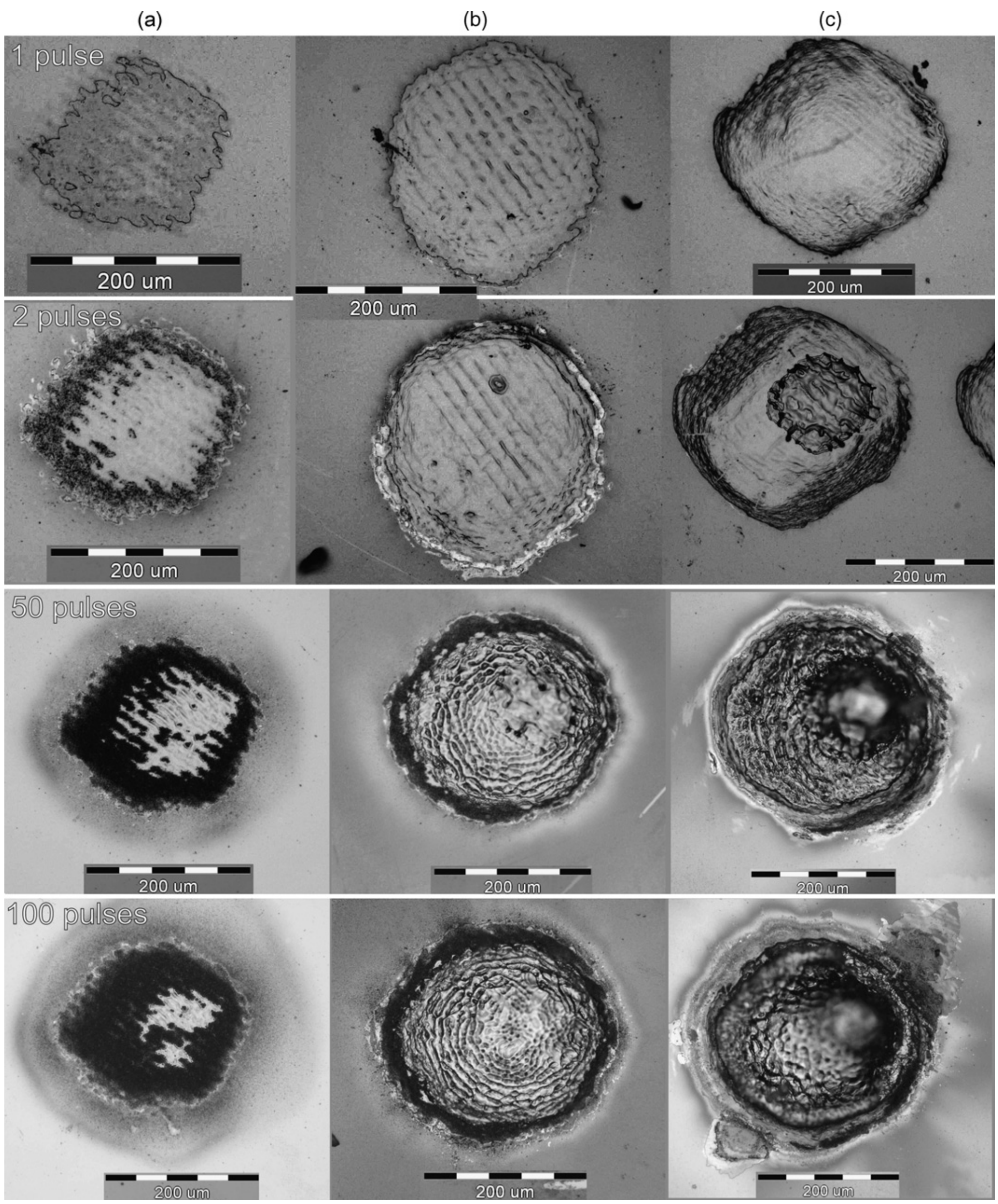

Fig. 1. Optical microscopy images of picosecond 532 nm Nd:YAG laser-induced periodic surface structures on silicon as a function of laser energy density (average fluence, Φ) and number of accumulated pulses, *N*. Images are placed in columns that represent varying fluence (a) $\Phi = 0.7$ J cm^{-2}, (b) $\Phi = 1.6$ J cm^{-2}, (c) $\Phi = 7.9$ J cm^{-2}, and rows represent varying *N*.

literature. We have registered this kind of structure on silicon surface only at the periphery (rim) of the irradiated area, with a ns/μs TEA CO_2 laser [10]. Recently, such parallel lines across the irradiated area were observed in femtosecond laser interactions with silicon [3,4,8].

The lowest average fluence to create detectable damage during the picosecond Nd:YAG laser action was presently about 0.4 J cm^{-2}. Given the intensity profile of the beam, a value of 0.6 J cm^{-2} can be taken as the real damage threshold (fluence at the maximum of the profile). A damage threshold of 0.26 J cm^{-2} on silicon has been reported with a femtosecond Ti:sapphire laser at 800 nm [8], and of 1.5 J cm^{-2} with a Nd:YAG laser at 1064 nm and the same pulse duration (40 ps) [13] as here.

Generally, when a semiconductor is irradiated, laser energy is absorbed primarily by electrons [8]. Multi-photon absorption is also possible. If the absorbed photon energy is sufficient to bridge the interband energy gap, generation of an electron/hole pair in the conduction or valence band is probable. Also, processes that include thermalization within the electron subsystem, energy transfer to the lattice, etc. typically take place upon laser irradiation.

Laser pulse duration was about 40 ps at all three fluences used here. This means that thermal effects were present, since electron thermal diffusion facilitates energy transfer to the silicon lattice, and the transition from solid to liquid occurs on a timescale between 10 ps and 100 ps [8]. The absorbed energy probably exceeded the latent heat of melting, and a melt pool was formed on the target surface. Processes in this pool can initiate irreversible features like periodic surface structures—ripples, which become ‘‘frozen’’ after cooling.

We observed that the 532 nm Nd:YAG laser pulses used here produce two types of periodic structures (ripples) on silicon, at micro- and nano-levels, Fig. 2a–c. The periodicity (spacing) of the micro-ripples was about 11 μm (Fig. 2a, b). The periodicity of the nano-ripples depended on the fluence. At the fluence of 0.7 J cm^{-2} no nano-ripples could be observed. At 1.6 J cm^{-2} it was around 100 nm (Fig. 2c), and at 7.9 cm^{-2} around 300 nm (Fig. 3). Unlike micro-ripples, the nano-ripples were registered only at the rim of the irradiated area (Figs. 2 and 3). They may be the result of processes [3,4,8,9] like: interference between the incident beam and the scattered beam parallel to the substrate; surface waves due to surface roughness and inhomogeneity; freezing of capillary waves; generation of a transient periodic heating pattern during laser irradiation, or other processes [4].

The nano-ripples obtained here appear to be concentric, following the circular shape of the spot, and occured only at higher laser fluences, i.e. $\Phi = 1.6$ and 7.9 J cm^{-2}, Figs. 2 and 3, respectively, after the first laser pulse. Their period bares no relation to the laser wavelength and depends on the laser fluence. This rules out surface optical interference as their origin. There are also no obvious conditions for generations of any periodic heating patterns. However, there is a strong indication that these nano-structures are frozen capillary waves, characteristic to molten silicon. The following is the rationale for this.

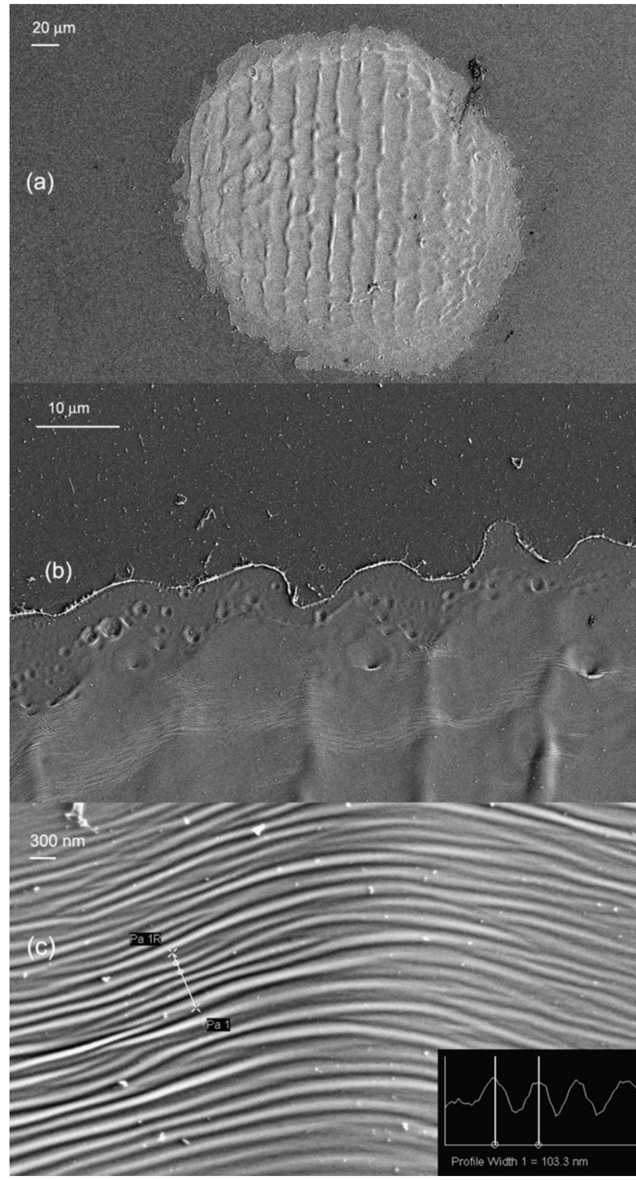

Fig. 2. Laser-induced periodic surface structures on silicon after one laser pulse, $\Phi = 1.6$ J cm^{-2}, SEM images: (a) and (b) show micro-ripples; (c) shows nano-ripples.

Capillary wave spacing d in this case can be described by Eq. (1) [11]:

$$d = \left[\frac{\sigma h}{\rho}\right]^{1/4} (2\pi\tau_L)^{1/2} \quad (1)$$

where σ is the surface tension coefficient of molten silicon (850 mN m^{-1}), ρ the liquid mass density (2.5 g cm^{-3}), τ_L the life time of the molten state, and h is the height of the molten layer estimated by Eq. (2) [11]:

$$h = \frac{\phi_0(1-R)}{c_v T_m + L_m} \quad (2)$$

where ϕ_0 is the laser fluence, R the reflectivity (0.37 at 532 nm), c_v the specific heat capacity (2 J cm^{-3} K^{-1}), T_m the melting temperature (1685 K), and L_m is the specific heat of melting

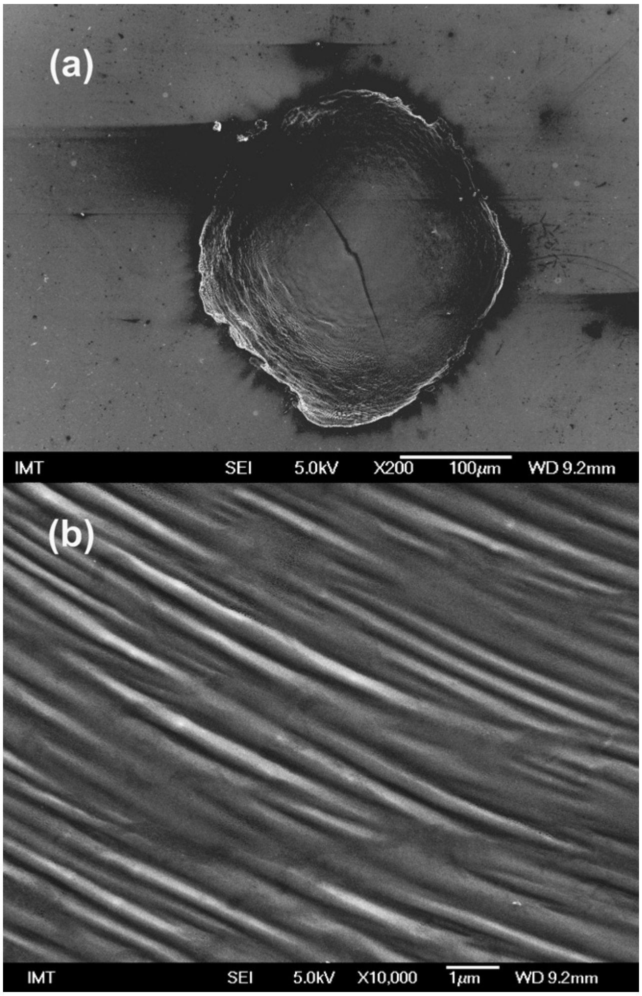

Fig. 3. Laser-induced periodic surface structures on silicon after one laser pulse, $\Phi = 7.9$ J cm^{-2}, SEM images: (a) shows the whole spot and (b) just the nano-structures around the rim.

(4130 J cm^{-3}). The ripples in the present case appear at the periphery of the damage spot, which means that they are close to the point of threshold fluence. Theoretically, at threshold fluence, the melt has nearly the same duration as the pulse itself, which would be 40 ps in the present case. Thus, with $\phi_0 = 0.6$ J cm^{-2} (threshold) and $\tau_L = 40$ ps the estimated capillary wave spacing calculated from (1) and (2) would be $d = 57$ nm in the threshold region exactly. However, the time of the molten state here is certainly longer than the pulse duration, because of the vicinity of the completely molten center, whose duration runs into hundreds of picoseconds [11]. Therefore, if the molten state duration at the location of the ripples is estimated at anything between 40 ps and 600 ps, ripple spacings of $d = 57$–221 nm are obtained from (1) and (2). This certainly covers the value of around 100 nm obtained with pulses of 1.6 J cm^{-2} average fluence. Eqs. (1) and (2) predict longer wavelengths for longer molten state durations, obtainable with higher fluences. This agrees with the observation of the period of about 300 nm at the higher average fluence of 7.9 J cm^{-2}.

Even if these estimates are coarse, they support the indication that the nano-structures obtained are actually ‘‘frozen’’ capillary waves of molten silicon.

The relatively large periodicity/spacing of the parallel micro-ripples obtained, 11 μm (Figs. 1 and 2), is somewhat unexpected. It is well known [3,8] that this periodicity, except in some cases [4,9,12], is typically in correlation with the laser wavelength used, whereas in the present case there is no correlation whatsoever, even for the nano-ripples. An attempt has been made at explaining such ripple spacing obtained earlier [9], 1.6–15 μm, which was high compared to the laser wavelength used. The authors [9] empirically verified that the ripple periodicity was a function of the thickness of the Si-oxide layer deposited on the silicon surface, and proposed that surface waves generated by the laser pulses can be responsible for the phenomenon. Qualitative EDAX chemical analysis of our silicon sample confirmed existence of Si-oxide on the surface prior to irradiation. This is a normal consequence of silicon exposure to air [14]. It can be assumed that similar effects as in Ref. [9] may have been responsible for the periodicity obtained in the present case.

However, the most probable cause of the parallel ripples in the present case may have been the cross-section of the laser beam, which had some periodical intensity modulation, due to optical components used in the system. The intensity profile of the spot is presented in Fig. 4, obtained without focusing. With focusing, the image of the profile is basically maintained. It can be observed that the left-hand side of the laser beam profile along the x-axis in Fig. 4 has rather pronounced periodicity, due to internal optical components of the laser. Although the right-hand side has no clear periodicity, we believe that the periodicity of the left side is sufficient to induce surface waves in the melted pond of silicon, in the same way that, e.g. a single wooden stick would make on free water surface. This is supported by the fact that the size of the waves relative to the effective beam diameter (Fig. 4) matches well the relative size of the waves obtained on silicon surface (Figs. 1 and 2). This also implies that ripples on silicon can be created in a controlled way, even by controlling only part of the source diffraction image.

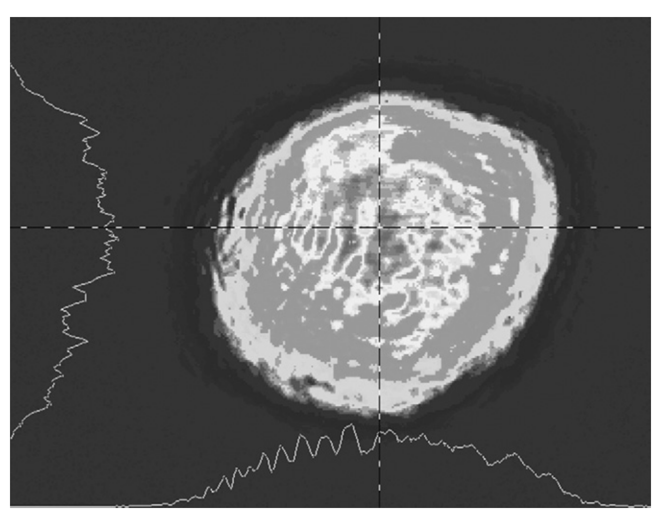

Fig. 4. Cross-sectional intensity profile of the laser beam with two perpendicular sections along the y and x axes, left and bottom, respectively. Total diameter of the spot image is around 1.6 mm.

4. Conclusion

It can be concluded that, although existing reports on laser-induced periodic structures are mostly associated with femtosecond lasers, a picosecond Nd:YAG is also capable of producing them on single-crystalline silicon in the form of straight parallel lines over the entire irradiated area. Lower laser fluence (around 0.7–1.6 J cm^{-2}) is apparently favorable in this respect. Higher fluences lead to destruction of the structures created and generation of crater-like features. The lowest fluence found to produce detectable damage was about 0.6 J cm^{-2}. Both micrometer and nanometer scale ripples were formed on the surface. The former had a form of parallel lines across the entire surface of the spot, and the latter were concentric. The main cause of ripple formation was obviously melting, combined with subsequent processes. A match between the cross-sectional intensity profile of the laser beam and the parallel ripples obtained on the surface is an indication that such ripples can be obtained in a controlled way even if only part of the beam profile is structured. The periodicity of the concentric nano-ripples depend on laser fluence and they seem to be frozen capillary waves of the transiently molten silicon.

Acknowledgements

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