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# Multipulse feedback in self-organized ripples formation upon femtosecond laser ablation from silicon

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**Abstract** The influence of positive feedback on self-organized nanostructure (ripples) formation is investigated for multipulse femtosecond laser ablation from silicon surface. We find an increase of the modified surface area and of complexity and feature size with accumulated dose, confirming the previously postulated feedback effect of dose accumulation. More interestingly, a variation of temporal pulse-to-pulse separation, at constant total incident irradiation dose, strongly affects the structure formation. Though the feedback becomes weaker with increasing time intervals between successive pulses, pulses do not act independently even for separations of up to one second. To account for this observation, a model of perturbation decay and outdiffusion from the excited volume is suggested and compared to the experimental results. Inspection by surface sensitive microscopy (AFM, SEM) and conventional and high-resolution transmission electron microscopy reveal complex structural modification upon the laser interaction: even well outside the irradiated area, the target surface exhibits fine ripple-like undulations, consisting of alternating crystalline and amorphous silicon. This is confirmed by photoluminescence studies on the band–band and the dislocation-related D1-line.

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## 1 Introduction

Nanostructuring of silicon surface upon ultrashort pulse laser ablation has been extensively studied in recent years [1–8]. It is widely accepted, meanwhile, that such structure formation is the result of (nonlinear) self-organization from a strong material instability, induced by ultrafast irradiation and ablation. It has been shown by numerical simulations [9–12] and time-resolved X-ray diffraction [13, 14] that on a picosecond time scale, or even faster, after the incident laser pulse, the target is driven into a nonequilibrium instability. This loss of near-order may be associated with a soft state of matter, different from a liquid after classical melting. In nonlinear dynamics, structure formation due to generation and relaxation of such instability is characteristically boosted from positive feedback during continuing excitation, resulting in increasing nonlinearity of the effect [15]. First regular, periodic structures are formed. Then, continuous feedback results, typically, in nonlinear coarsening and increasing complexity of the structures.

A peculiar feature of ultrashort-pulse-induced structure formation is that, in contrast to "classical" nonlinear dynamics, the instability is not fed continuously but by individual, well-separated energy pulses. This makes the concept of a positive feedback slightly more complicated since the system might evolve freely *between* repetitive perturbations. Nevertheless, several indications for such feedback have been observed in recent experiments: feature size and complexity generally vary across the irradiated area, from fine and regular at the edge to coarse and complex in the center [6–8, 16–18]. Taking into account the typical spatial beam profile, this implies that the feedback should be stronger at higher local intensity. Other observations indicate that the structures develop with increasing number of incident pulses [19, 20]. A combination of those observa-

tions suggests that the feedback should depend, indeed, on the irradiation dose applied.

In the present contribution we report on systematic studies intended to gain a better understanding of the role of positive pulse-to-pulse feedback in nanostructure formation on Si(100) upon ultrafast laser ablation. In a first series of experiments, we investigated the role of total accumulated irradiation dose on ripples structure and on the size of modified area. For this purpose, we kept fluence and repetition rate of the laser pulses fixed and varied the number of incident pulses. In a second series of experiments, we kept the total incident dose (fluence times number of pulses) constant and varied the time interval between successive pulses. Thus, we study the "perturbation lifetime" for which the effect of the preceding pulse is still sensible for the subsequent one, enabling some "collective" action as the origin of positive feedback. We complement these investigations by high-resolution studies of the atomic/crystalline structure in the modified volume and check for extended effects outside the irradiated area.

## 2 Experimental

In our experiments, we irradiated conventionally cleaned silicon (100) wafers in ultra-high vacuum ($10^{-9}$ mbar) by ultrashort laser pulses from an amplified Ti:Sapphire laser ($\tau_{\text{pulse}} \approx 120$ fs; $\lambda = 800$ nm; repetition rate: 1 kHz). The pulses of around 30 μJ at normal incidence were focussed to about 100-μm diameter, resulting in a maximum intensity near the ablation threshold for silicon ($I_{\text{th}} = 2 \times 10^{12}$ W/cm$^2$ [21, 22]). The intensity and the final polarization of the beam could be varied passively by polarization optics, the effective pulse cadence could be set passively by an electro-mechanical shutter.

After irradiation, the ablated/modified areas were investigated by scanning electron microscopy (SEM). Ripples features and the size of modified area were evaluated by hand from the micrographs, with an error of about ±10%. Complementary information was obtained by atomic force micrographs (AFM).

In order to investigate the in-depth cross section in the region of modified surface, two TEM cross-section samples were prepared from one spot (1,000 pulses at $1 \times 10^{11}$ W/cm$^2$, 1 kHz) by cutting out two lamellae with a focused ion beam (FIB) (To protect the surface from amorphization by the high-energy FIB, the areas of interest had been covered by a 100-nm Pt layer). The lamellae were then thinned down to 100 nm [23]. The electron transparent cross-section samples were investigated by high-resolution transmission electron microscopy (HRTEM) using a JEM 4010 transmission electron microscope at an acceleration voltage of 400 kV.

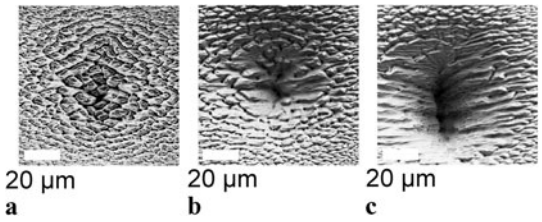


**Fig. 1** Pattern evolution in the center of ablation crater (laser intensity $2.6 \times 10^{12}$ W/cm$^2$); (**a**) 3,000 pulses, (**b**) 5,000 pulses, (**c**) 10,000 pulses; linear polarization (vertical in the *panels*)

Finally, modified areas, filled with an array of interaction spots, were mapped by photoluminescence spectroscopy at room temperature. Excited by an argon-ion laser at 514 nm, 50 mW, and a sample spot of less than 100-μm diameter, the band-band luminescence at 1127 nm and the dislocation-related D1-band luminescence at 1550 nm [24] were separated by a grating spectrometer (300 lines/mm) and detected by a liquid-nitrogen-cooled Germanium detector. For mapping the area of interest, the sample was translated in steps of 50 μm across and 100 μm along the groves written in the array.

## 3 Results and discussion

### 3.1 Irradiation dose

As has been widely shown, ripple structures become fully developed, usually, only after a sufficient number of laser pulses [17–20, 22, 25]. Even at intensities high enough to practically exclude incubation effects [26], this influence of irradiation dose accumulation on the nanostructures is observed and points to a positive pulse-to-pulse feedback on the structure formation.

To check this assumption, we recorded ablation spots for different numbers of pulses at otherwise identical conditions (pulse energy 25 μJ, spot Ø ≈ 100 μm ⇒ intensity $2.6 \times 10^{12}$ W/cm$^2$). Indeed, with increasing number of incident pulses (Fig. 1), the pattern in the central area of the ablation crater becomes bigger and more complex, involving wider but shorter ripples and distinct vertical structures.

When repeating the experiment with circular polarization, we find that not only the structure complexity but also the influence of polarization becomes more pronounced with increasing number of pulses: instead of a long central cleft in the direction of the linear polarization, a funnel of nearly radial symmetry develops at circular polarization after 10,000 pulses.

Figure 2 displays the results of a systematic variation of the number of pulses (at constant intensity and repetition rate) averaging the results from several series of identical experiments. The left panel shows the ripple density, defined as the number of elementary pattern segments per unit area.

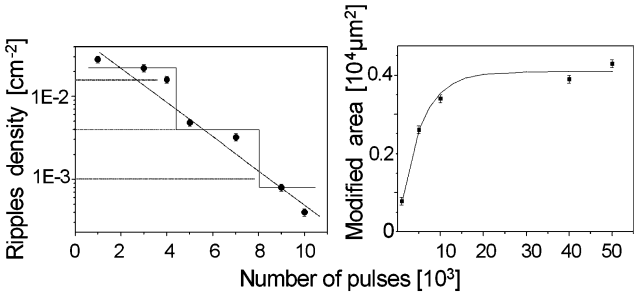


**Fig. 2** Multipulse ablation (laser intensity $2.6 \times 10^{12}$ W/cm$^2$): pulse number dependence of ripples density (*left*) and modified area (*right*). The "steps" in the *left panel* indicate dose-dependent period doubling [27]

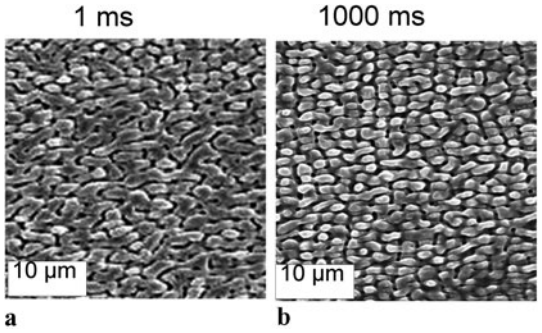


**Fig. 3** Patterns at the center of modified area for a pulse separation time of (**a**) 1 ms, (**b**) 1,000 ms. (1,000 pulses at $2.6 \times 10^{12}$ W/cm$^2$)

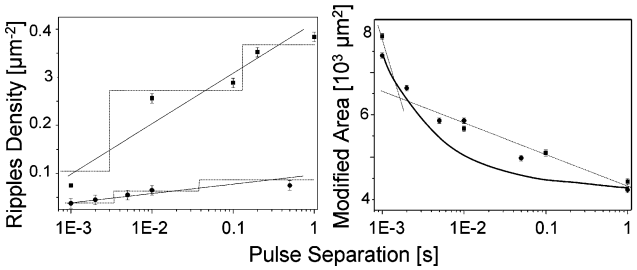


**Fig. 4** Ripples density (*left*) and modified area (*right*) as a function of pulse separation (1,000 pulses at 25 µJ [*squares*] resp. 32 µJ [*circles*]). The *straight lines* in the *left panel* indicate the dose-dependent period doubling, the *bold line* in the *right panel* indicates a fit to the model presented below

Though, at first sight, an exponential decrease of ripples density appears reasonable (straight line), the result also is compatible with the assumption of period doubling (the reciprocal of ripples density) with increasing dose [27] which is typical for nonlinear dynamic structure formation.

The regular increase of modified area (right panel in Fig. 2) can be considered as reflecting a reduction of threshold intensity with increasing feedback, similar to the effect of incubation [26]: if the Gaussian spatial beam profile at the first pulses only exceeds the modification threshold at the very center, an exponential reduction of modification threshold with increasing dose involves larger and larger parts of the beam cross-section, as is indicated in (1):

$$\begin{aligned} A &= A_{\max}\left(1 - \exp\{-k \cdot d\}\right) \\ &= A_{\max}\left(1 - \exp\left\{-k' \cdot N_{\text{pulses}}\right\}\right) \end{aligned} \tag{1}$$

where $A$ is the modified area, $A_{\max}$ the maximum beam cross section, $d$ is the total dose, $N_{\text{pulses}}$ is the number of incident pulses, and $k, k'$ are coupling constants.

From these results it appears reasonable to assume that the incident pulses do not act individually and independently, but add to the effect of the previous pulses. Following our previously developed ideas of structure formation dynamics [19], indicating that the incident laser pulse and the induced desorption of particles create a state of nonequilibrium, the subsequent pulses hit the residues of this "soft" state and thus act, in a way, collectively.

### 3.2 Pulse separation

To check this supposition, we investigated the influence of the time elapsed between successive pulses. We changed the pulse repetition rate, keeping the total incident dose $NE_{\text{pulse}}$ fixed. When changing the pulse repetition rate from 1 kHz to 1 Hz, i.e., the pulse separation time from 1 ms to 1000 ms, the observed patterns change in a way suggesting that at longer separation the accumulated dose is less than at short separation (Fig. 3): The ripples density is higher at 1000 ms, the complexity is more developed at 1 ms: less regular, but longer and wider "merged" and meandering structures appear only in panel (a).

A more quantitative study reveals that, indeed, the increase of pulse separation appears to lower the effective dose. For both ripples density and modified area, the feedback is reduced but still present, even at times as long as 1 second as is shown in Fig. 4.

### 3.3 Feedback model

Taking into account that the surface modification and structure formation is a result of an instability perturbation, induced by the energy input and particle emission, the following scenario for the feedback is suggested:

The key parameter for structure formation is the total coupled energy dose $d$,

$$d = N_{\text{pulses}} \alpha F, \tag{2}$$

given by the number of pulses $N$, the fluence $F$ per pulse, and the coupling coefficient $\alpha$. This dose creates a perturbation density $\rho_{\text{pert}}$ in the active volume. Then, feedback means that the coupling efficiency depends on that perturbation:

$$\alpha = \alpha_0 + \alpha' \rho_{\text{pert}}. \tag{3}$$

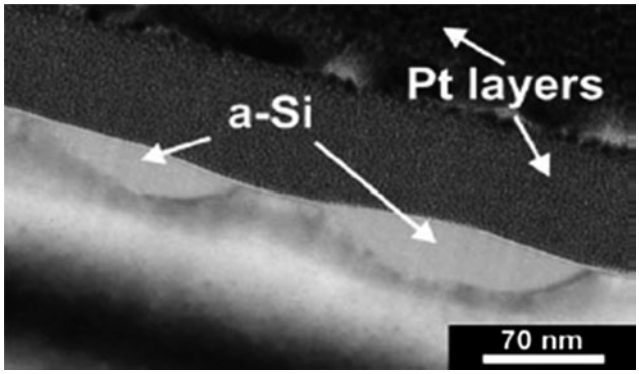


**Fig. 5** HRTEM image of pseudo ripples outside the apparently modified area, showing the alternation of crystalline and amorphous zones

Due to both statistical decay and outdiffusion from the excited volume (distribution over a larger volume), the perturbation density depends on the time elapsed since the excitation:

$$\rho_{\text{pert}}(t) = \rho_0 \exp\{-t/T\} \cdot (Dt)^{1/2}, \tag{4}$$

with decay time constant $T$ and diffusion constant $D$. The bold line in Fig. 4 is a fit to such behavior.

In a simulation, based on Anisimov's two-temperature model [28], we evaluated the temporal evolution of free carrier density and of electron and lattice temperature. Well after laser pulse, the surface temperature appears to be above the melting temperature for up to a few nanoseconds. Then, the surface cools down, mainly due to diffusion. When applying additional pulses during that cooling phase, the temperature can increase, showing a $(1 - \exp\{-kN\})$-behavior. The carrier density exhibits a similar tendency, however with a sharp drop after about 1 ms due to recombination. Though the simulation indicates, indeed, a feedback behavior, the time scale is still by far shorter than the experimental observation.

### 3.4 TEM investigations

In order to learn more about the structural changes underneath the rippled surface, we cut out two vertical slices from the modified region of one spot for TEM analysis, one slice at the center and one slice at the edge, extending to an apparently unmodified region.

In the spot center, we find that the ripples still consist of—though heavily distorted-crystalline material. Only in the hollows between the ripples, very little amorphous silicon can be found. This confirms the assumption that the ripples are *not* formed from an equilibrium melt but, more likely, from a heavily perturbed material.

More interesting is, however, the result shown in Fig. 5: far outside the apparently modified area, still a structural modification can be detected. Continuing the crest/valley sequence, we find here a similar sequence of amorphous and crystalline regions. This confirms the idea of an outdiffusion of the perturbation from the irradiated area.

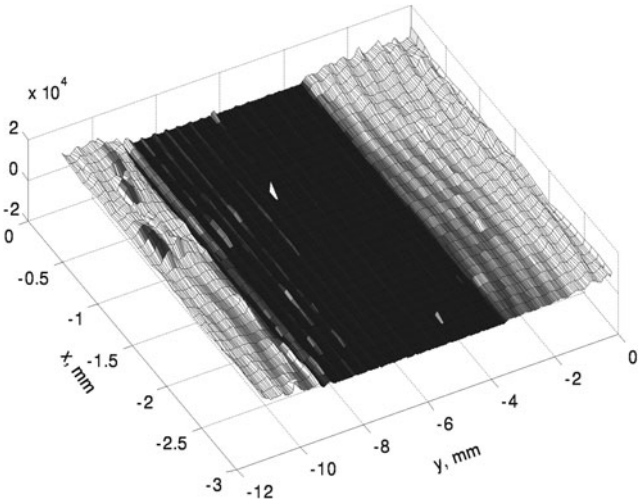


**Fig. 6** Modulated free carrier lifetime in silicon outside the irradiated area, detected by band–band photoluminescence (the *dark area* is the modified area, filled by *lines* of *irradiated spots*)

The finding is further corroborated by photoluminescence mapping (Fig. 6) in and *around* a modified area produced by superimposing several lines of irradiated spots. Obviously, the band–band luminescence (reflecting the free carrier lifetime) from the modified area is strongly reduced and, in addition, modulated, clearly reflecting the structural modulation (traces), scribed in the modified area. Moreover, however, this modulation of carrier lifetime is coherently continued outside the irradiated area, where no morphological change could be detected. Further, comparing the ratio of band–band and defect-related D1-luminescence, we find evidence of extended defect formation at the ablation area but no signature of melting, similar to the single-spot TEM analysis.

## 4 Conclusion

We have shown that there is a considerable pulse-to-pulse feedback in self-organized structure formation at the silicon surface upon multipulse laser ablation. This is attributed to a long-lived perturbation, only slowly decaying by diffusion of the excitation out of the irradiated volume. Indeed, even well outside the irradiated domain, surface modification is detectable.

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