Basic Physics of Femtosecond Laser Ablation

Juergen Reif

Summary. Laser ablation being the basic process for many prominent applications of lasers in present day high technology, medicine, and other fields, its basic physics is reviewed in this chapter. In order to distinguish the fundamental, laser–material interaction from any secondary effects, we concentrate on ultrashort laser pulses (≈100 fs duration) at comparably low intensities, below the commonly indicated threshold for massive material removal. It is shown that – for these conditions – the principal light/matter coupling occurs via multiphoton excitation of electrons into the conduction band or the vacuum. The resulting perturbation of the target lattice results in the emission of positive particles, from atomic ions to larger clusters of more than ten atoms. With the increasing number of incident pulses, the light/material coupling is facilitated by the accumulation of transient crystal defects resulting from particle removal. On the other hand, the lattice destabilization, upon excitation and ablation, relaxes via self-organized formation of regular nanostructures at the irradiated area. The strong influence of laser polarization on the structural order is still not at all understood.

2.1 Introduction

Already in the early days of lasers, it had been observed that the concentrated light energy could affect the irradiated material considerably: Damage to optical components occurred because of evaporation and removal of material from the component surface. In fact, that was the first manifestation of laser ablation, i.e. the removal of material from a target upon laser impact. Rapidly, this effect became exploited in a more controlled way to process materials, e.g. in tool-free cutting and drilling, which are standard technologies in the car industry and related fields today.

Most of the early research and applications were performed using CO₂ lasers, and understood in terms of the classical thermodynamic processes, the laser being considered merely as a very concentrated heat source. About three decades ago, however, based on the observation of UV-laser ablation from organic polymers [1], it was suggested that the ablation process might
be more complicated than had been assumed until then, involving not only rapid melting and evaporation but also electronic transitions. In the following years, the ablation phenomenon began to attract increasing interest, from the point of view of its fundamental study as well as its applications[2].

Today, laser ablation is used in a wide range of high technologies other than cutting and drilling, such as, for instance, surface processing, thin film deposition by PLD, or laser cleaning, from silicon wafers to artworks. In medicine also, many applications are based on laser ablation, e.g. in ophthalmology (amongst others, laser correction of ametropia – LASIK), dermatology (tattoo removal), surgery, etc. However, undesirable effects like the destruction of laser-irradiated biological tissue or laser damage to optical components also result from laser ablation.

This chapter is devoted to the study of the fundamental aspects of laser ablation in order to gain a better understanding of the physics underlying the phenomenon. In order to distinguish the basic processes from any secondary effects, such as laser interaction with ablation products and the like, we concentrate on the interaction of ultrashort (i.e. duration of \( \approx 100 \text{ fs} \)) laser pulses with solid targets. To further reduce secondary effects, the incident fluence is so low that single pulses do not result in significant, target surface modification. Usually, only after several 10,000 pulses, significant ablation craters are observed. Our sample materials will be mainly dielectrics (\( \text{BaF}_2 \), \( \text{CaF}_2 \), \( \text{Al}_2\text{O}_3 \)), and silicon. We first review some basic features of the energy input, the laser–material coupling. Then we consider the follow-up processes, transiently modifying the material. Finally, we report on self-organized, nanostructure formation at the target surface as a consequence of material relaxation after ablation.

### 2.2 Energy Input

In principle, all decomposition or material removal from a solid target is the consequence of an energy input into the target, resulting in overcoming the solid’s binding energy. In a classical process, which is slow enough to proceed in thermodynamic equilibrium, this means that the energy input \( \Delta E \) is fully transferred into an increase of internal energy \( \Delta U \) and thus, to an increase in temperature \( \Delta T \):

\[
\Delta E = \Delta U = cm \Delta T
\]

(with heat capacity \( c \) and mass \( m \) of the heated target material).

As shown in Fig. 2.1, this internal energy increase results in a classical phase transition and, occasionally, in a dissolution of the heated volume. On a microscopic scale, the temperature increase corresponds to an increase of atomic kinetic energy. In contrast to energy input by classical heating, via a global phonon bath, or by ion impact, addressing the core motion directly via a momentum transfer, energy input from laser pulses is inherently different:
Table 2.1. Process chart for laser ablation

<table>
<thead>
<tr>
<th>Time scale</th>
<th>Material response</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Femtoseconds</td>
<td>Electronic excitation</td>
<td>Electron emission</td>
</tr>
<tr>
<td>Picoseconds</td>
<td>Energy dissipation/core motion</td>
<td>Bond breaking</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoseconds</td>
<td>Surface relaxation/reorganization</td>
<td></td>
</tr>
</tbody>
</table>

the incident light “speaks” only to the electrons of the system, and all core motion is only a secondary process.¹ This allows establishing, conceptually, a history of processes starting from light absorption, leading to particle removal and, finally, to target relaxation, as is given in Table 2.1.

From these time scales, the choice of ultrashort laser pulses with duration below 150 fs for the study of fundamentals becomes justified: then, the laser light interacts only with an almost passive target. All significant target modification (e.g. transient changes in band-structure, removal of particles) occurs only after the laser pulse and, thus, should not affect the absorption properties. More important, the laser does not interact with ablated material. (For longer pulses, significant amounts of laser energy may be absorbed in the ablated plasma plume. This hot plasma might then, in turn, sputter the target surface.)

¹ Even a direct coupling to a vibration is, in fact, promoted via the electronic system, related to the cores only by electron-phonon coupling.
2.2.1 Multiphoton Excitation

In solid target, usually, the electrons will be excited across the band-gap to the conduction band. For the typical situation of ultrafast Ti:Sapphire laser pulses at a photon energy of 1.55 eV, for many materials this means that the excitation occurs via multiphoton absorption, with a number \( n \) of necessary photons given by

\[
n = \text{mod} \{ E_{\text{gap}} / 1.55 \text{ eV} \} + 1.
\]  

(2.2)

The resulting electron kinetic energy is, then, \( 0 < E_{\text{kin}} \leq 1.55 \text{ eV} \).

As the lower edge of the conduction band is close to the vacuum level, the electrons located near the target surface, at a depth less than their mean free path (cf. Fig. 2.2), can leave the target.

Indeed, the emission of electrons from the target can be observed (Fig. 2.3). As is expected for multiphoton ionization, the electron yield \( Y_{\text{electrons}} \) as a function of incident intensity follows a power law:

\[
Y_{\text{electrons}} \propto I^n.
\]  

(2.3)

![Figure 2.2](image)

Fig. 2.2. The “Universal Curve” of electron mean free path vs. electron kinetic energy [4]. The shaded area indicates the region of typical kinetic energies in the presented situation.

---

2 In a metal, the light absorption may, occasionally, just increase the electron-kinetic energy/temperature inside the conduction band.

3 Generally, in “linear optics” the absorbed energy \( E_{\text{abs}} \) is given by \( E_{\text{abs}} = \sigma F_{\text{pulse}} = \sigma I \tau_{\text{pulse}} \) \( (F: \) fluence \{areal density of incident laser energy\}, \( \sigma \) interaction cross-section, \( I \): intensity \( \tau \) pulse duration). For higher intensity, however, the quantum system becomes more and more perturbed when the electrical light field approaches the atomic binding field. Perturbation theory then makes the cross-section intensity-dependent: \( \sigma (I) = \sigma^{(n)} I^{n-1} \), hence, the absorbed energy will be \( E_{\text{abs}} = \sigma^{(n)} I^n \tau_{\text{pulse}} \). For longer pulses, additional tunneling ionization can take place [3].
Fig. 2.3. Double logarithmic plot of electron yield vs. laser intensity at 1.55 eV for three different dielectric targets: Al₂O₃ ($E_{\text{gap}} \approx 9.5$ eV), BaF₂ ($E_{\text{gap}} \approx 10.5$ eV), and CaF₂ ($E_{\text{gap}} \approx 12$ eV). The power law (2.3) results in straight lines with the slope corresponding to the number of photons $n$. The insert in the Al₂O₃ panel sketches the band-structure ($VB$: valence band; $CB$: conduction band) and indicates the energy levels of a localized $F$-centre with a 1s ground state, a 3p excited state, and the ionised $F^+$-centre energy in the conduction band.

A closer inspection of typical results as shown in Fig. 2.3 [5,6] reveals, however, that the nonlinearity may be, occasionally, less than expected from the band-gap. A probable reason is indicated as an insert in the Al₂O₃ panel: localized energy states within the band-gap, e.g. due to an $F$-centre (i.e. an anion vacancy) may act as intermediate resonances and thus reduce the order of nonlinearity. Indeed, we could observe blue radiation of the 3p–1s transition of such $F$-centres [7]. A similar influence of localized or transient defect states [8] should also be responsible for the reduced nonlinearity at low intensities on the fluorides shown in Fig. 2.3.

Later (Sect. 2.4), we will come back to such defects, in particular those generated by the laser interaction itself.

When the incident fluence becomes so high that the density of conduction band electrons inside the target bulk overcomes a critical density, additional coupling mechanisms like hot carrier absorption occurs [9] (via electron–photon–electron – three-body collisions), resulting in a significant increase of ablation efficiency.

2.3 Ion Emission: Ablation

2.3.1 Experimental Observation

The actual ablation, i.e. the emission of heavier target constituents, can be monitored by Time-of-Flight (ToF) mass spectrometry [5,6]. In fact, under
Fig. 2.4. ToF-spectra of positive ions emitted from BaF$_2$ [7] and single crystalline, p-doped Si(100) [11] at laser intensities around $10^{12}$ W cm$^{-2}$ and a photon energy of 1.55 eV ($\lambda = 800$ nm), below the threshold for a massive ablation/damage for the respective material [12]. Not only positive ions of all surface constituents are observed, but also larger clusters of up to more than ten atoms (in panel (a): index $m = 0, 1, 2, \ldots$)

the conditions we are dealing with, an abundant emission of positive ions is observed (Fig. 2.4). In particular, from ionic crystals not only the usual cations are emitted but also positive ions of the “anionic” species are detected. In fact, almost all ablated particles, under the considered low-laser intensities, appear to be positive ions, with neutrals and negatives occurring only at a substantially higher excitation [10].

Not only individual atomic ions are desorbed, but also large cluster ions of up to more than ten atoms. This is a general effect, not depending on the target material, as can be seen in Fig. 2.4.

The positive ions exhibit an unexpectedly high kinetic energy. From experiments using a retarding voltage (Fig. 2.5) [13], as well as from experiments using the ToF-spectrometer in “drift mode,” i.e. with a field-free region (without collecting field) between target and spectrometer [5,6], ion kinetic energies between $\approx 10$ eV and over 100 eV are measured, depending on the target material and irradiation conditions.

By “desorption” we denote an ablation rate at the individual particle level.
2 Basic Physics of Femtosecond Laser Ablation

Fig. 2.5. Kinetic energy of positive ions desorbed from Al$_2$O$_3$ after irradiation with 1.55 eV laser pulses at $\approx 10^{12}$ W cm$^{-2}$ [6,13]. The left panel shows the Al$^+$-ion yield at the detector vs. the retardation energy, fitted by a sigmoid function. The central panel shows the ion velocity distribution, derived from the sigmoid of the left panel (solid line). For comparison, a Maxwell–Boltzmann distribution (dotted line) and a shifted Maxwellian (cf. (2.1)) (dashed line) are shown, both with the same center velocity. On the right panel, the kinetic energies of the different desorbed ion species are compared by plotting the squared velocity vs. the reciprocal mass. (From $E_{\text{kin}} = \frac{1}{2}mv^2$ the plot shows $v^2 = 2E_{\text{kin}}$ m$^{-1}$ and the straight slope indicates a constant kinetic energy)

The ion velocity distribution (solid line in the central panel of Fig. 2.5), derived from the sigmoidal fit to the retardation energies in the left panel, is, obviously, not compatible with the assumption of a thermodynamic Maxwell–Boltzmann distribution (dotted line). Instead, it resembles very well a much “colder” distribution, centered on a high drift velocity, a situation which is typical for “seeded beams,” and can be described by a so-called “shifted” Maxwellian for the distribution function $f(v)$:

$$f(v) = cv^2 \exp\left(-\frac{m(v-u)^2}{2kT}\right), \quad (2.4)$$

where $v$ is the total velocity, $u$ the center of mass or drift velocity, $k$ Boltzmann’s constant, $m$ the particle mass, and $T$ the temperature.

Interestingly, all desorbed species have about the same kinetic energy (right panel of Fig. 2.5). This indicates, at first, that all species originate from the target and are not formed by reactions in the ablation “plume,” as they all travel with different velocities and thus, do not “meet” during their flight. Second, it leads to a possible understanding of the desorption mechanism, which will be described in the following subsection.

2.3.2 Desorption Mechanism – Coulomb Explosion

We have already shown in Sect. 2.2.1 that laser impact results in the emission of a considerable amount of electrons from the target. This is assumed to occur instantaneously during the laser pulse, leaving behind positive holes in the surface-near region. In dielectrics, and even in semiconductors [14,15], the time for bulk electrons to fill these holes is at the order of about a picosecond
or even longer. Thus, the surface-near region will be positively charged for a considerable time. This charged region may become electrostatically instable, so that, at a sufficiently high hole density, the surface will break apart by emitting positive particles, which will be accelerated in the residual field. This electrostatic repulsion is known by the name of Coulomb explosion [16–18].\(^5\)

At a still higher excitation, when hot carrier absorption becomes important, a hot electron bath is generated [3], rapidly coupling to the lattice via electron–phonon collisions in a large volume, and bulk super-heating starts to set in. Then, additional, efficient desorption mechanisms like phase explosion [19] become effective.

### 2.4 Transient, Local Target Modification

Obviously, with interaction pulse the remanent target surface will change. Already the electron excitation and ionization may influence the absorption properties. This change can be transient, i.e. after relaxation the electronic system returns to its previous state. Additionally, however, desorption will change the local surface composition. As was indicated in Fig. 2.3, (surface) vacancies will perturb the normal band structure and produce localized states within the band-gap.

Depending on diffusion probabilities, this local disorder can last for a considerable time [20] and thus modify the absorption probabilities for subsequent pulses. As indicated in Fig. 2.3, the order of the absorption nonlinearity may be reduced, and, thus, the cross-section is increased.

#### 2.4.1 Incubation

For multiple-pulse irradiation (“\(N\)-on-1”), this effect of (transiently) increased ablation efficiency – and thus, decreased threshold intensity – can accumulate from pulse to pulse, if the defect lifetime is sufficiently long. This “incubation” has been known for more than two decades [21,22].

As a consequence of this incubation, the desorption yield at a fixed intensity, typically, increases continuously from pulse to pulse, and finally saturates [6] when the surface defect density reaches a steady state between the generation of new and the annihilation of previous defects.

In the first attempt to understand this incubation a merely statistical model was introduced [21], assuming the ablation threshold \(I_t\) to decrease inversely proportional to a power \(\alpha\) of the number of pulses \(N\): \(I_t (N) \propto 1/N^\alpha\). A more “physical” model, assuming an exponential increase in the number

\(^5\) In contrast to Coulomb explosion in molecular physics, it is not evident whether here momentum conservation – via recoil [17] – or energy conservation – via the same repulsive field [18] – is a good parameter; obviously, the experimental data are compatible with both models within experimental error.
of defects (responsible for the threshold reduction), was presented in [22], postulating \( I_t (N) \propto e^{-\alpha N} \). In fact, as is shown in Fig. 2.6, recent experimental results favor this exponential model [23].

Indeed, the lifetime of such structural defects, responsible for incubation, has been observed to extend to several 10 ms, as could be shown by interrupting the irradiation pulse series for controlled periods [24]. Also, the luminescence of bulk defects has been observed for more than 50 ms after excitation, thus persisting over several pulses at a repetition rate of, typically, 1 kHz. This is demonstrated in Fig. 2.7 [23].

2.4.2 Transient Dynamics

As already indicated, not only relatively long-lived defects are produced, due to the local particle removal during desorption, but also electronic excitation and ionization have an influence on the absorption properties. The lifetime of such modifications is expected, however, to be much shorter and closer related to the exciting pulse. Information at the relevant time scale can be obtained by appropriately designed pump-probe experiments, as displayed in Fig. 2.8.

The target is “prepared” by a pump pulse and then, after a defined delay time, “interrogated” by a second pulse, the probe. As shown in Fig. 2.8, both pulses may be derived from one parent pulse in a Michelson interferometer; the interdelay can be adjusted by a variation of one-arm length. The combined action of both pulses can be monitored by detecting the emitted particles.

To investigate the transient target behavior alone, care must be taken to exclude longer lived modifications like those considered in Sect. 2.4.1. In
Fig. 2.7. Bulk and plasma fluorescence from CaF$_2$ irradiated with a single 1.55 eV pulse at a fluence of $\approx 10^{15}$ W cm$^{-2}$ (well above the single-shot ablation threshold). The pulse duration was either 50 fs (upper panels) or 120 fs (lower panels). The fluorescence was observed – without spectral resolution – at two different delays after the excitation: 1 $\mu$s (left panels) and 50 ms (right panels). In all panels, the target surface is indicated by the vertical white line, with the bulk at the left and vacuum at the right. While at 1 $\mu$s strong plasma emission is visible (more intense for the shorter pulse), at 50 ms delay strong bulk defect luminescence survives, much more pronounced for the longer pulse.

Fig. 2.8. Typical pump-probe setup to investigate the transient desorption dynamics. The laser beam is split into two partial beams of equal properties in a Michelson configuration. By varying the length of one interferometer arm, a temporal separation between both beams at the target can be adjusted. The combined effect of both pulses is monitored – in our case – by a ToF-spectrometer, capable to measure positively- and negatively charged particles (target and detection are placed in UHV at $\approx 10^{-10}$ hPa)

particular, the combined intensity from both pulses at zero delay, i.e. at full temporal overlap, must be sufficiently low [25]. If both pulses are of equal intensity, this “soft” interaction can be verified by a result which is symmetrical with respect to negative$^6$ and positive$^7$ delays.

$^6$ Pulse A is pump, pulse B is probe.
$^7$ Pulse B is pump, pulse A is probe.
Fig. 2.9. Pump-probe experiment on particle emission from BaF$_2$ using pairs of 1.55 eV pulses at $0.5 \times 10^{12}$ W cm$^{-2}$. The single-pulse signal is negligibly small (cf. delay of $\pm 3$ ps). Around zero delay the observed signal is influenced by interference effects from the Michelson setup.

A typical result of such pump-probe experiments [26] is shown in Fig. 2.9 for BaF$_2$, monitoring positive ions (Ba$^+$), electrons, and negative ions (as secondary products [9]). Both pulses were of the same intensity, yielding each only a very weak signal of any type of particles, as can be seen at delays of $\pm 3$ ps, where the pulses are obviously separated far enough to act independently. At zero delay, i.e. at optimal pulse overlap, both pulses act coherently and the combined intensity\(^8\) results in a strong excitation. Consequently, strong electron emission and, in turn, strong positive ion emission occurs, as expected. With increasing pulse separation, the emission yield decreases and reaches almost the level of an independent pulse action.

After a certain delay, however, i.e. from a certain pulse separation on, the signal increases again, reaches a maximum (for BaF$_2$ at a pulse separation of $\approx 700$ fs) and then slowly diminishes again toward the individual pulse result for pulses separations larger than $\approx 2.5$ ps. This behavior, generalized

\(^8\) In the Michelson interferometer, this corresponds to four times the single arm intensity.
in Fig. 2.10, indicates that the energy deposition from the pump pulse evolves in the target in such a way that the absorption probability increases to reach a maximum after \(\approx 700\) fs. Subsequently, this transient state of enhanced absorptivity dies out again. Even secondary particles, such as negative ions [9], follow this dynamics. Interestingly, the behavior is a very general one, observed for very many types of targets, even metals [27], though the explicit nature of the transient, high-absorption state may be different.

Associating the general behavior with possible relaxation processes, it appears appropriate to compare it with the excitation decay in magnetic resonance [26]. Then, the “coherence peak” should correspond to the phase relaxation with (“transverse”) time \(T_2\), and the occurrence of the transient modification should be due to energy dissipation into the target, characterized by (“longitudinal”) time \(T_1\), as indicated in Fig. 2.10.

2.5 Transient Instability and Self-Organized Structure Formation

2.5.1 Periodic “Ripples” Structures

When inspecting the bottom of an ablated area after very many pulses, the target surface morphology appears considerably changed (Fig. 2.11): a regular pattern of almost parallel modulation lines has developed, with typical feature size below the incident wavelength.

Already about 40 years ago, similar structures were observed [28, 29] after irradiation with nanosecond pulses, termed “ripples.” Until the mid-1980s, a model was developed attributing the phenomenon to a modulated energy
Fig. 2.11. Ripples pattern at the bottom of an ablated area on BaF$_2$ after 10,000 1.55 eV-pulses at $\approx 10^{12}$ W cm$^{-2}$. The white double arrows indicate the laser wavelength for comparison with the ripples features input, which was ascribed to an interference of the incident wave with surface-scattered electromagnetic waves [30].

The structures observed after femtosecond illumination, however, display features which are not really compatible with that interference model. In Fig. 2.11, structures that are much finer than the wavelength, i.e. the diffraction limit, can be seen. Further, two superimposed patterns of different periodicity are observed. Finally, characteristic deviations from the regular structure, namely splitting of one line into two (bifurcations) occur.

Another, very peculiar feature is shown in Fig. 2.12. Across the ablation spot, produced by a beam of Gaussian spatial intensity distribution, the ripples periodicity changes *abruptly* between a very fine structure in the edge region of lower intensity and a coarser structure, of about double spacing, in the high-intensity central region. Again, bifurcations as well as truncations are observed which are not at all compatible with simple interference structures. Instead, the structures are very similar to those observed, typically, in the structure formation attributed to self-organization from instability, such as, for instance, large sandy areas subjected to windy erosion (Fig. 2.13). In particular, the structures are almost identical to those observed upon sputtering by an ion beam impact [6,31,32].

A very successful way of modeling such self-organized structure formation [33,34] in ion sputtering and sand ripples involves the principles of nonlinear dynamics, and there have been first approaches to apply these models to the present phenomena [6,32].
Fig. 2.12. Ripples structures in one ablation spot, irradiated by a beam of Gaussian spatial profile. The magnification in the left panel shows an abrupt transition from fine, sub-wavelength structures at the low-irradiation edge and coarser structures of about double spacing at the high-irradiation center.

Fig. 2.13. Ripples formation in a sandy area subjected to windy erosion and diffusion (photo: courtesy of Gediminas Raciukaitis). Note the coexistence of coarse and fine ripples and the presence of bifurcations.

2.5.2 Instability and Self-Organization

The general idea for such modeling is the assumption that the excitation and ablation create a state of extreme instability for the target:

Since – at least in dielectrics and semiconductors – the excitation involves conduction band electrons in a considerable fraction, it results in a corresponding perturbation of the target crystalline order, coordinated by the electron configuration. Moreover, the surface equilibrium order is destroyed by the emission of (individual) surface constituents. Consequently, the crystalline order is perturbed even though the target is not molten (i.e. the target is not in a state of thermodynamic equilibrium). Theoretical modeling indicates, in
fact, a destabilization of the crystalline lattice on a several hundred to thousand femtoseconds [35,36]. Such transiently disordered or “soft” material has been, actually, observed by femtosecond, time-resolved, X-ray diffraction [37], where the short-range crystalline order disappeared shortly after excitation. The long-range order, however, persisted, excluding an equilibrium liquid state.

The corresponding instability must relax in an extremely short time, due to a steep gradient in crystalline order to the surrounding target material. This excludes “thermal” processes like crystallization or glassification. To model the relaxation [32], based on the ion-sputtering analogue [34], the surface may be assumed to be a corrugated, thin “liquid” film. In such configuration, the instability consists of a competition between corrugation increase (surface roughening due to desorption) and surface smoothing, due to diffusion. Surface corrugation and “film” thickness $h$ can be analyzed using an approach based on the Cahn–Hilliard/Kuramoto–Sivashinsky differential equation [38], involving removed-particle speed $v$, sputter coefficient $\gamma$, and surface-diffusion constant $D$:

$$\frac{\partial h}{\partial t} = -v_0 + \gamma \nabla h + v \Delta h - D \Delta^2 h. \tag{2.5}$$

Transient solutions of this equation predict the formation of periodic structures like stripes, squares etc., increasing linearly. At a certain level of perturbation, the transient solution saturates and a nonlinear regime of structure formation sets in, showing, typically, coarsening and merging into larger, more complex structures.

Indeed, such effects are observed in experiments. This is shown, exemplary, in Fig. 2.14, which represents, similar to Fig. 2.12, one single ablation spot on silicon, irradiated by a Gaussian intensity distribution, increasing from left to right (the white separation lines are only inserted to guide the eye). At low-perturbation (left) linear, periodic ripples are observed with a period length of $\Lambda \approx 660$ nm. At higher perturbation (central part of Fig. 2.14), the ripples appear merged to larger units with about double spacing, $\Lambda \approx 1,300$ nm. In addition, the structures become more complex, like meandering. At a still higher perturbation (right), the structure is still more complex, with another period doubling to $\Lambda \approx 2,500$ nm.

The microphysical details of these new surface structures are not yet clear. Some features, however, are remarkable:

- The ripples orientation is not at all correlated to the target crystal structure (cf. Sect. 2.5.3)
- Micro-Raman spectroscopy on silicon reveals that there can be a crystallographic reordering, as has been known from high-pressure modifications [6]
- The nanostructured surface exhibits peculiar electrical features [39], as shown in Fig. 2.15

Obviously, the electrical properties reflect the morphology well. The EFM phase contrast, measuring the force on the tip, at a bias of $-1V$ follows
Fig. 2.14. Period doubling during self-organization of ripples-structures: one spot on silicon surface with three different structure sizes $\Lambda$ from fine (spot edge, left) to coarse (spot center, right). The white lines are drawn to guide the eye. Note also the structure change from “simple” straight lines to more complicated, two-dimensional ordering.

Fig. 2.15. Electrical properties of self-organized nanostructures (on p-Si surface irradiated by a circular polarized light (cf. Sect. 2.5.3), measured by electrostatic force microscopy (EFM) [39]. (b) line-scans as indicated in the corresponding panels of (a)

the morphology derivative, i.e. it is strongest at the edge of the nanospheres (cf. Sect. 2.5.3). More surprising is the high nanostructure electric charge relative to the unaffected surface, showing up in the contact potential varying between $-120$ mV at the top of the spheres and $+50$ mV in the valleys. A possible origin could be dopant segregation during the “soft” nonequilibrium state,
but a local modification of crystalline structure (e.g. high pressure phases [6])
cannot be ruled out. More information should be gained by TEM analysis of
the atomic details which is, presently, under way.

2.5.3 Polarization Dependence

Although a general picture of self-organized, ripples formation seems to be
already fairly coherent, one characteristic feature of the effect is by far not yet
understood. In all experiments, a dominant influence of the laser polarization
on the shape and orientation of the nanostructures has been observed.

For linear polarization, typically, the predominant ripples are aligned per-
pendicular to the light electric field. Additionally, secondary structures (most
often of larger spacing) can occur, aligned perpendicular to the prominent
ones (i.e. parallel to the laser field). This is shown in Fig. 2.11, where the laser
was polarized vertically. When rotating the polarization and keeping the tar-
get fixed, the ripples orientation follows the polarization, independent of the
target crystalline structure [5,32]. When the polarization is rotated during a
long, continuing series of pulses, the ripples orientation is determined by the
latest polarization direction.

An even more startling phenomenon is observed when, during repetitive
irradiation, the target is moved to “write” ablation lines or areas: if the spots
are slightly overlapping, the ripples structure is continued coherently over the
whole line [40] resp. area [41].

To shed more light on this polarization influence, experiments were per-
formed using circular and elliptical polarization under normal incidence.

In fact, new structures appear. As can be seen from Fig.2.16 for irradi-
ation with nearly circular polarization, arrays of spherical nanoparticles are
generated, with a diameter of 100 nm or even less. Only a very weak linear
alignment, bead-string like, is observed, due to a very slightly, non-optimal
adjustment of the quarter-wave plate used for generating circular polarization.

Fig. 2.16. AFM picture of self-organized nanostructures upon ablation with
(almost) circular polarization: arrays of nanospheres with a diameter of ≈100 nm
(right panel showing a scan along the line indicated in the full area picture, left).
The apparent “alignment” of the “bead strings” is due to a very slight maladjust-
ment of the λ/4-plate, used for generating the circular polarization, resulting in
weak ellipticity (cf. Fig. 2.17)
This loss of linear order correlates with the fact that, for circular polarization, the strong directional influence of the laser electric field on the structure formation is missing. To substantiate this observation, the directed electric field is reintroduced by polarizing the beam elliptically. Indeed, more and more oriented and ripples-like structures develop (Fig. 2.17) upon increasing the polarization eccentricity $\epsilon$, resulting from the imbalance of major axis, $a$, and minor axis, $b$:

$$
\epsilon = \sqrt{a^2 - b^2/a^2}
$$

Intriguingly, the structure's long-range order, measured by the average distance between two bifurcations, depends on the third power of eccentricity $\epsilon$ (Fig. 2.17).

The important role of the laser electric field direction is further corroborated by the result shown in Fig. 2.18, where an artificial eccentricity was introduced by changing the angle of incidence for circular (Fig. 2.18a) resp. elliptical (Fig. 2.18b) polarization. By the beam inclination, the surface spot is expanded in the plane of incidence (p-polarized fraction) though it is unchanged along the axis of beam rotation, i.e. perpendicular to the plane of incidence (s-polarized fraction). Correspondingly, the $s$-component of the electric field remains unchanged and the $p$-component is reduced by the projection. Thus, for circular polarization (at beam cross-section $E_s = E_p$), $s$ becomes the major axis $a$ of an artificial ellipse, with eccentricity increasing with the increasing angle of incidence. Conversely, for elliptical polarization (with minor axis $b$ corresponding to the $s$-direction) the eccentricity is reduced, becoming more and more circular.

Similar to observations with linear polarization, the major axis of stronger electric field $a$ controls the alignment of the long-range order. This is not only
Fig. 2.18. Artificial eccentricity, introduced by oblique incidence of circularly (a) resp. elliptically (b) polarized beam. The angle of incidence, indicated in the panels, is obtained by a rotation about the horizontal, corresponding to s-polarization (all panels are $3 \times 3 \mu m^2$ AFM pictures)

○ Circular control parameter ○ Linear control parameter

Fig. 2.19. Theoretical simulation [6,32] of the influence of the control-parameter directionality. The simulation assumes ion beam sputtering, the control parameter being normal (left panel) or oblique incidence (right panel)

observed in Fig. 2.18, but also shows up, when the whole polarization ellipse is rotated [42] and the ripples alignment follows. Finally, the role of the electric field direction as a control parameter for ripples arrangement is confirmed by the result of first model simulations [6,32], as shown in Fig. 2.19.
Fig. 2.20. Timing diagram of observed phenomena/processes: only after the termination of the laser pulse, desorption/ablation sets in, at the same time scale as structural perturbation takes place [26,27,35–37] (cf. also Sect. 2.4.2). Defect lifetime (cf. fluorescence in Fig. 2.7) may even extend longer than the pulse separation.

2.6 Discussion

So far, empirically, the scenario for the formation of regular nanostructures upon femtosecond laser ablation appears rather rational: the short, powerful energy input first perturbs the target’s electronic system, causing an instability which results in ablation/desorption. This emission further increases the instability by roughening the surface. Concomitantly, the surface diffusion tends to smooth the surface again, still further increasing the instability. All this occurring on a very fast time scale, with a tremendous order-gradient to the surrounding target material, requires a very fast relaxation, far away from equilibrium pathways. Therefore, it results in self-organized nanostructure formation. The arrangement of these ripples is controlled by the direction of the ablating laser electric field.

Closer consideration, however, reveals some severe inconsistency (as is shown in Fig. 2.20): the time scales of ongoing processes put the role of laser polarization on structure formation severely into question: when the processes of structure formation, i.e. the motion and immobilization of atoms at the surface, occur the laser pulse has terminated already for a considerably long time. So, when a structure formation takes place there is no more, electric laser field.

Consequently, the question of “polarization memory” remains still open, so far. A possible explanation may involve the excitation of surface plasmons, with a sufficient lifetime (cf. Fig. 2.7), arranging according to the incident field, and then encouraging directional diffusion during the self-organized relaxation. This picture is, however, only very speculative, so far.

Acknowledgements

The author greatly appreciates the fruitful and congenial collaboration with Florenta Costache, Olga Varlamova, Markus Ratzke, and Michael Bestehorn. Profitable discussion and interaction within the Cottbus JointLab is greatly
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2010, XVI, 358 p. 200 illus., 23 illus. in color., Hardcover
ISBN: 978-3-642-03306-3