Controlling ablation mechanisms in sapphire by tuning the temporal shape of femtosecond laser pulses

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We have analyzed the influence of the temporal pulse shape on femtosecond (fs) laser-induced surface ablation processes in sapphire. To this end, single transform-limited (TL), stretched, and third-order-dispersion (TOD) shaped fs pulses have been used, while the dynamics of the interaction were analyzed by fs-resolved microscopy and correlated with plasma emission intensity and crater morphology. The modification of the pulse shape enables changing the ablation mechanism from a strong, thermally mediated ablation process to a gentle ablation process mediated by Coulomb explosion (CE), with respective ablation depths of 100–200 nm and 5–10 nm. Analysis of the transient optical response allows direct comparison of the transient plasma carrier densities involved, observing comparable peak values for both processes. For strong ablation induced by TL pulses, a direct relation between plasma density and local ablation depth is found, but this does not hold for the CE-mediated process observed for TOD-shaped pulses. For TOD-shaped pulses at very high fluence, a different ablation mechanism involving explosive boiling is identified. This mechanism leads to the formation of deep craters with reduced lateral extension and steep walls. This amount of control over the ablation mechanisms by a simple selection of the pulse shape should be of interest for new surface structuring approaches.

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1. INTRODUCTION

Over the recent years, ultrafast lasers have been widely used in laser processing of dielectrics [1,2]. These laser sources show unique characteristics for this application [3]. Their extremely high peak power enables coupling the laser energy in the material via nonlinear absorption, ensuring a highly deterministic damage process [4], while their short pulse duration triggers an absorption process in which electrons remain decoupled from the lattice, leading to a reduced heat affected zone [5]. In spite of this apparently clean picture, some important questions remain open regarding the carrier excitation/relaxation mechanisms in different materials, including the relative roles of multiphoton and avalanche ionization [6,7] in the process and the influence of the pulse duration. In this context, sapphire (single crystalline Al₂O₃) is a wide bandgap material that has received considerable interest, as it was the dielectric in which gentle ablation [8,9] via Coulomb explosion (CE) [10,11] was first observed. The commonly accepted description for gentle ablation is a low fluence effect in which electron emission from the surface under ultrashort laser pulse excitation leads to the creation of an equal amount of positive charges on the target. Above a certain charge density (~10³⁵ cm⁻³), Coulomb repulsion with internal fields $E > E_m$ ($E_m = 5 \times 10^{10}$ V/m in sapphire [12]) leads to the removal of positive charges in a fast, explosive process occurring over temporal delays typically below 1 ps. Part of the residual charge can remain at the surface, though over some hundreds of picoseconds after excitation [13].

It is worth emphasizing that, unlike strong ablation, which is mediated by electron–phonon interactions [14], gentle ablation mediated by CE is nonthermal in nature, at least in the stage prior to the relaxation of the target, leading to the emission of a second population of neutrals and ions at longer delays [10]. Although initially controversial as a material removal mechanism in dielectrics, and still a subject of study [15], the importance of the CE mechanism is supported by compelling experimental evidence in sapphire [10,11], among which the emission of Al⁺ and O⁺ fast ions with the same momenta over the first picosecond after the interaction is observed. An additional feature of the gentle ablation process is the typically shallow ablation depths involved, which are characterized by smooth surfaces and enables that material removal can be accurately controlled on the nm scale using few pulses at low fluences [9,11]. Strong ablation, on the other hand, is characterized by much deeper craters, up to few hundreds of nm/pulse. In this case, the material is ejected due to a violent phase explosion, which is induced by the material overheating above the thermodynamical critical temperature [15].

Sapphire also has received attention due to the controversial interpretation of experiments aimed at correlating crater morphology and ablation mechanisms for different pulse durations [17] and experiments aimed at correlating the measured carrier dynamics with the role of the different carrier excitation mechanisms [7,18,19]. This latter problem has been analyzed in several dielectrics by different experimental approaches, mostly pump-probe experiments in configurations.
with [20] and without [18,21] spatial resolution and two-color experiments [7,22]. It also has been shown that fs-laser pulse temporal shaping [23] can be used to modify the carrier excitation dynamics [24], affecting the result of the ablation process (both using loose and tight focusing) [24–27].

In this work, we have analyzed the effect of fs-laser temporal pulse shaping on the ablation of sapphire by means of \textit{in situ} fs-resolved optical microscopy and post-irradiation morphological measurements. In particular, irradiations were performed using transform-limited, stretched pulses and pulses shaped by third-order dispersion. It is shown that gentle or strong ablation processes can be selected as dominant material removal mechanism by modifying the temporal shape of the pulse. A clear signature for the CE mechanism is shown for the first time in terms of \( e^+\)-plasma density and its correlation to ablated depth. A distinct ablation mechanism, different from conventional strong ablation, is also observed for third-order-dispersion (TOD) shaped pulses. This ablative process, caused by a long-delayed explosive boiling phenomenon, strongly modifies the aspect ratio of the deep ablated craters that show reduced lateral extension and more vertical walls than those produced by conventional strong ablation, an effect of clear interest for surface structuring applications.

2. EXPERIMENTS

The laser used in this work is a Ti:sapphire amplifier (Spitfire-Pro, Spectra-Physics), which produces Fourier limited pulses of 130 fs pulse duration at 800 nm and 1 mJ pulse energy. Temporal pulse shaping was carried out by using a homemade temporal shaper, specially designed to work with high-energy fs-laser pulses. The arrangement is similar to that described in [27], which is based on a zero-dispersion 4f system [28], with a liquid crystal spatial light modulator (LC-SLM-S320, Jenoptik, 320 pixels) but using 1800 lines/mm gratings and cylindrical mirrors with a focal length \( f = 1000 \) mm to enable handling pulse energies up to 1 mJ with a spectral resolution of 0.07 nm/pixel. Temporal shaping was performed by encoding phase masks in the SLM that generate different terms of the Taylor series expansion of the spectral phase [29]. The second- and third-order terms were used to produce, respectively, stretched pulses or increasing or decreasing amplitude pulse bursts. The laser pulses were characterized using a home-built Polarization-Gate Frequency Resolved Optical Gating system (PG-FROG [30]) as described in [27].

Sample irradiation and fs-resolved imaging of the irradiated zones were performed using single-transform-limited (TL), stretched (ST), and TOD-shaped irradiation pulses in a setup essentially similar to that in [18,26]. The irradiation pulses reached the sample at 54° after being focused with a lens (\( f = 80 \) mm), leading to an elliptical Gaussian spot size (1/e² diameter, 2\( \omega_0 \)) of 47.6 \( \mu \)m \( \times 24.6 \) \( \mu \)m, measured using the method proposed by Liu [21]. The angled incidence avoids direct backreflection of the strong pump pulse from the irradiated surface. Each sample location was irradiated only once. The transient reflectivity images of the surface were recorded using a fs time-resolved microscope installed at normal incidence [18,32] (objective lens 80x, NA = 0.5, tube lens, and CCD camera) using a frequency-doubled (\( \lambda = 400 \) nm) illumination probe beam obtained from a fraction of the TL pulse before the beam enters the pulse shaper. The noncollinear pump-probe configuration favors the suppression of unwanted scattered pump light reaching the CCD camera, which is further ensured by placing a narrow bandpass filter centered at 400 nm in front of the CCD camera. By blocking the illumination pulse, the same system can be used to record time-integrated images of the light emitted from the surface upon excitation in a way similar to that described in [33]. The energy values for a given lateral position have been calculated by using the Gaussian formula that describes the spatial distribution of the laser:

\[
F(x, y) = \frac{2E_0 e^{-\left(\frac{x^2}{\omega_0^2} + \frac{y^2}{\omega_y^2}\right)}}{\pi\omega_0\omega_y},
\]

where \( 2 \cdot \omega_x = 24.6 \) \( \mu \)m and \( 2 \cdot \omega_y = 47.6 \) \( \mu \)m, while the fluence is given by \( F[1/e^2] = 2 \cdot F/(\pi\omega_0\omega_y) \).

The samples used in the study were sapphire wafers supplied by VM-TIM with a bandgap of 9.9 eV, and the surface oriented perpendicular to the \( c \) axis. They were cleaned before and after the irradiation by means of a standard process with acetone and ethanol using an ultrasonic bath. The topography of the ablated craters was analyzed with an optical interferometric microscope (OIM) (Sensofar profiler, at 460 nm, objective lens 50x, NA = 0.55). Scanning electron microscopy (SEM) was used to inspect the morphology of the irradiations.

3. RESULTS AND DISCUSSION

We have analyzed the evolution of the crater topography for single TL, ST, and TOD pulses, as shown in Fig. 1, where the temporal shape of the pulses (FROG trace and retrieved temporal profile), ablated crater topography (OIM) images, and depth cross sections are plotted. It is worth noting that the crater images in Fig. 1 can be directly related to the Gaussian intensity profile of the irradiation pulse to establish a direct correlation between ablated depth and local fluence.

![False color topography images (left column) and crater depth cross sections of laser irradiated regions with (a) single TL, (b) ST, and (c) TOD-shaped pulses. The experimentally measured temporal pulse intensity profiles are shown in the right column. The insets show the PG-FROG traces with a 30 nm spectral window (vertical axis) and 6 ps for the temporal window (horizontal axis). Irradiations were performed at different fluences: (a) 8.3 J/cm²; (b) 12.6 J/cm²; (c) 14.8 J/cm².](image-url)
Figure 1(a) shows the crater topography image corresponding to a TL pulse with a fluence of 8.3 J/cm² just above the ablation threshold [18]. Two different ablated regions can be distinguished by a subtle change of slope in the corresponding depth cross-section (see the arrows and vertical dotted lines). The crater depth at the central region is of the order of 100 nm, consistent with a strong ablation process [9,17] occurring for fluences above 7.54 J/cm². The shallow depression in the outer region of the crater reaches a depth of 10 nm and can be identified as gentle ablation for a fluence range from 5.83 J/cm² up to 7.54 J/cm². The gentle ablation fluence threshold observed is consistent with the value in [12]. Previous works on ultrafast laser structuring of sapphire show crater profiles with similar fluence-dependent strong and gentle ablation features upon irradiation with sub-200-fs pulses using both single- [17,18,34] and multiple-pulse irradiation [9,35]. A strong modification of the crater morphology is observed when the pulse duration is stretched to 560 fs. In spite of the higher local fluence at the center of the irradiated region (12.6 J/cm²), only gentle ablation is observed with a maximum crater depth of just ~15 nm. The differences between both crater morphologies can be explained by a change of the predominant ionization mechanism, depending on the peak power of the pulse, which would be multiphoton ionization (MPI) for the shortest pulse and avalanche ionization (AI) for the longest one [6]. For longer pulses, the lower peak power density should lead to the initial generation of plasma with a relatively low electron density (~10²³ cm⁻³) in which carriers can be subsequently accelerated by the field leading to impact ionization as well as electron emission, favoring the CE mechanism [10,36]. This hypothesis will be further supported when the results regarding the carrier dynamics are presented.

Finally, Fig. 1(c) shows the crater profile induced by a TOD-shaped pulse (pulse burst with decreasing intensity envelope) with a peak fluence of 14.8 J/cm². Interestingly, the crater morphology shows an appearance intermediate between that associated with the TL and a ST pulse. The outer crater region features a shallow depression with a depth of ~15 nm, which is indicative of the CE ablative process. In contrast, the shape of the inner crater might suggest a strong ablation process but showing, in this case, reduced lateral dimensions and steeper crater walls, compared with a TL pulse. The temporal shape of the TOD-shaped pulse might affect the relative roles of MPI and AI and condition the local ablation dynamics and yield, as already shown in other dielectrics irradiated with short pulse bursts [24,26,27]. However, the observed features might similarly suggest a possible distinct ablation mechanism at the largest local fluences for the TOD-shaped pulse.

In order to analyze these alternatives, temporally integrated plasma emission (TIPE) images of the ablating surfaces were recorded. Illustrative examples are included in Fig. 2 along with the corresponding topography maps (false color scale from 0 to 75 nm). The topography image of TL-irradiated region shows, as in Fig. 1(a), a wide and deep crater (strong ablation) surrounded by a barely visible narrow and shallow depression (yellow, gentle ablation region). In comparison, the TOD-shaped pulse induces only gentle ablation below a certain threshold fluence. When the TOD-shaped pulse peak fluence is sufficiently increased, a much deeper crater is formed in the central region of the spot.

When comparing topography and TIPE images, we have to consider that light emitted by the surface is potentially related to several different phenomena: bremsstrahlung associated to the deceleration of the high kinetic energy carriers (spectrally continuous), emission from high-temperature excited ions and neutrals (discrete lines), and, to a lesser extent given the dimensions involved, thermal (blackbody) radiation (also spectrally continuous). The TIPE image for the TL pulse shows that the lateral extension of the light-emitting region is essentially similar to that of the deep (~150 nm) ablated crater. Given the depth of the ablated crater, the emission can be ascribed to both e⁻-plasma and excited species emission on a longer time scale. Interestingly, for the TOD-shaped pulse at the intermediate fluence (13.3 J/cm²), in spite of the much shallower crater depth (~10 nm), the emission reaches an intensity comparable with that observed for the TL pulse with a somewhat narrower emission spatial extension. Since the ion and neutrals emission should be much smaller than for the TL pulse (in accordance to the much smaller amount of removed material), this can be interpreted in terms of an emission dominated by bremsstrahlung. Bremsstrahlung is favored by the CE ablation mechanism since the prompt free electrons [11] have acquired a high kinetic energy by the longer lasting field excitation associated with the TOD-shaped pulse. Following the previous reasoning, the TIPE image associated with the 15.7 J/cm², TOD-shaped pulse and its corresponding cross section are puzzling. In spite of inducing a very deep crater in the central region (~100 nm), apparently caused by strong ablation, the emission intensity at the center of the spot is just a little higher than that associated with bremsstrahlung radiation for a much lower ablated depth (c.f. Fig. 2, TOD-shaped pulse at 13.3 J/cm²). This behavior is not consistent with the expected contribution of excited (ions, neutrals) species for a large ablation depth. Once again, the observed behavior suggests that the deep craters produced by TOD-shaped pulses at
the larger fluences are caused by a mechanism different from conventional strong ablation.

Further insight about the underlying ablation mechanisms can be obtained from fs-resolved microscopy images of the surface. The use of spatially resolved measurements enables a direct comparison of the most important events occurring at different time scales with the local fluence involved, and the final result in terms of ablation depth. The corresponding transient reflectivity images for different illustrative delays are shown in Fig. 3 for both a TL pulse (left column) and a TOD-shaped pulse (right column). The images at 400 fs time delay already show a significant increase of the reflectivity due to the generation of dense free-electron plasma at the center of the irradiated region. The maximum transient reflectivity, corresponding to the maximum electron density, is achieved for temporal delays of $\Delta t_{TL} = 600$ fs and $\Delta t_{TOD} = 1000$ fs, respectively, for the TL and TOD pulses, due to the different rates of laser energy coupling in the material. This behavior is consistent with the longer overall duration of the TOD pulse, depositing its energy more gradually, resulting in longer rise times. Afterward, the plasma relaxes, transferring its energy to the lattice via $e^-\text{-phonon}$ collisions, eventually causing ablation, a process that will temporarily extend to the ns range. As a consequence $[18,20]$, the reflectivity at the center of the irradiated spot starts to decrease after a few ps, reaching values below one of the unexposed surfaces ($R_{400\text{nm}} = 0.080$). For both pulse shapes, for a delay $\Delta t \sim 6-7$ ps, the ablating zone is surrounded by a bright plasma ring $[20]$, which is formed after the irradiation pulse has been absorbed at the surface. This observation is consistent with a delayed carrier generation process via impact ionization as proposed in $[6,18]$.

For delays in the $Dt \sim 200$ ps—ns interval, the images associated with the TL pulse show a characteristic fringe pattern surrounding what will be the final region of the strong ablation crater. The origin of these fringes is the diffraction of the probe pulse at the edge of a transient rim of molten material $[18]$, elevated by the recoil pressure of the ablating plasma over a low viscosity molten layer underneath the ablating material $[37]$. In the case of the TOD-shaped pulse, the diffractive ring pattern surrounds only the region where the final deep crater will be formed, which is much narrower than the entire ablated zone. This suggests either that, in the annular gentle ablating region around the deep crater, there is strong reduction of the recoil pressure associated with the ablative process. This behavior would perfectly be consistent with what can be expected from a CE process in the outer region of the spot irradiated with the TOD-shaped pulse. The CE process (not phonon-mediated) would lead to a relatively minor temperature increase of the lattice (extremely thin molten layer underneath the ablating material) and a very small recoil pressure.

The equal extension of the region with high plasma density (hundreds of fs delay), of the ablating region (6–7 ps delay), and of the region where strong ablation occurs (500 ps) clearly shows there is direct correlation between local plasma density and ablation diameter in the case of the TL pulse. This correlation, already pointed out for strong "thermal" ablation in several materials $[10,32]$, seems not to hold for the TOD-shaped pulse, neither in the gentle ablation annular region, the larger fluences are caused by a mechanism different from conventional strong ablation.

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nor in the deep ablation central zone, as shown by the dashed lines in Fig. 3.

More information can be extracted from the data by plotting the reflectivity evolution of the excited surface as a function of delay time and local fluence, as described in [22]. The corresponding reflectivity-delay-fluence (RDF) maps are shown in Fig. 4 for a TL and a TOD-shaped pulse of similar peak fluences, along with the final crater depth cross sections. It is worth noting that, to ease the comparison of both types of plots, the fluence scale of the RDF maps is not linear but Gaussian-like, corresponding to the intensity profile. In the RDF map, a horizontal cross section corresponds to the evolution of the reflectivity as a function of time for a given fluence, while a vertical cross section provides the evolution of the reflectivity as a function of fluence for a given delay. The maps clearly show the formation of dense electron plasma in the subpicosecond time scale with a somewhat faster buildup time for the TL pulse. The shift between the rise times is due to the different pulse lengths, which affect the progressively transferred energy of the photons onto the sample electrons (via MPI, AI, and free carrier excitation). It also can be seen that the plasma buildup time shows stronger fluence dependence for the TOD-shaped pulse (compare, for instance, the reflectivity evolution at 13 J/cm² in both maps). In spite of this, in both cases a similar reflectivity maximum is reached ($R_{\text{max}}/R_0 \approx 5.75$). After reaching maximum density, the plasma relaxes rapidly (within less than 10 ps) as a consequence of the ablation process that, depending on the pulse shape, leads to very different crater morphologies. Indeed, a first inspection of the RDF maps already makes evident the differences in the thresholds for the different ablation processes and pulse shapes: gentle (5.8 J/cm²) and strong ablation (7.6 J/cm²) for the TL pulse, gentle (8.2 J/cm²) and deep (14.0 J/cm²) ablation for the TOD-shaped pulse. Comparison of the RTF maps with the crater cross sections shows the neat correlation between the spatial position and density of the plasma and the finally ablated depth for the TL pulse.

The reflectivity values can be converted to local plasma density by using the Drude model for a free electron gas [18,38] and by assuming certain material parameters such as the electron damping constant ($\tau$) and electron effective mass in the conduction band ($m^*$). We have made such an estimation using $m^* = m_e$ and a value of $\tau = 3$ fs, following previous works [18,39]. The obtained values must be considered as approximate but can be compared to enable the correlation between ablation yield and plasma density. The corresponding values for the indicated local fluence and temporal pulse shape are given in Table 1. We can see clearly that, in spite of achieving very similar maximum carrier densities ($\sim 3\times10^{22}$ cm⁻³), there are enormous differences in the ablated depths corresponding with the TL and the TOD-shaped pulse. Indeed, in the gentle-ablation annular region for the TOD-shaped pulse, we can see reflectivity values and, thus, plasma densities clearly above those induced by the TL pulse in the region of the strong ablation crater. The lack of correlation between plasma density and ablation depth is indeed a characteristic signature of the CE process. For the deep crater zone induced by TOD-shaped pulse, the different behavior compared with the TL pulse is similarly evident, as, in this case, the maximum plasma density induced is the same, but the ablation depth is substantially smaller (about a factor of two), indicating that conventional strong ablation does not take place for the TOD-shaped pulse.

This conclusion is further supported by SEM measurements of the irradiated spots. Figure 5(a) shows an overview of a crater of an irradiation generated using a single TL pulse featuring a relatively smooth surface. In contrast, the right crater, produced using the TOD-shaped pulse [Fig. 5(b)], features a rough morphology, which is particularly visible at the walls of the central crater and outer edge of the irradiated spot. A higher-resolution overview is shown in Figs. 5(a1)–5(b1), blue rectangles. While the ablation crater for the TL pulse shows a

![Fig. 5. SEM images of craters produced using a TL pulse (14.4 J/cm² peak fluence, left column) and a TOD-shaped pulse (14.8 J/cm² peak fluence, right column). (a) and (b) General view of the irradiated zone. (a1) and (b1) High-resolution images of the crater (blue rectangles). (a2) and (b2) zoom of the central crater region (black rectangles). (a3) and (b3) zoom of the external edge (orange rectangles). In some cases, the zoomed images are rotated. This is indicated by the position of a colored dot in the rectangular regions in the first row of images.](image-url)
smooth central region, along with a narrow and well-defined sharp edge, the one produced using the TOD-shaped pulse shows three differentiated regions of interest. We have marked them as I and II, the strong and gentle ablation regions, respectively, and as III, the external crater rim, where high roughness can be observed. Figures 5(a2)–5(b2) show detail of the central region for each irradiation (black rectangles). While the center of the TL-pulse-generated crater shows smooth topography, the inner crater (I) produced by the TOD-shaped pulse shows an irregular edge, small protuberances, small bubbles, and melting features. These features are consistent with the occurrence of an explosive boiling process at the center of the irradiated region, as suggested to occur for pulse durations in the picosecond range [8, 9]. Figures 5(a3) and 5(b3) show zoomed areas of the crater edge for both pulse shapes, confirming that the modification produced by a TL pulse is much smoother, while the edge of the crater of the TOD-shaped pulse (III) shows pore-like cavities at the material surface. Such porosity, especially at the crater edge, where the ablation process is at its threshold, is consistent with an ablation process not being completely deterministic but being influenced by material defects. This nondeterministic ablation behavior is expected for longer pulses, which is the case of the TOD pulse extending up to 2 ps as opposed to the TL pulse with a width of 130 fs.

4. CONCLUSIONS

The above-discussed results demonstrate the feasibility of controlling the ablation mechanism of sapphire by using temporally shaped fs-laser pulses. Strong (thermal) ablation, gentle (nonthermal) CE-mediated ablation, or explosive boiling dominated processes can be induced by proper control of the temporal shape and fluence. These mechanisms lead to distinct ablation morphologies, with maximum ablation depths ranging from a few to hundreds of nm and give rise to very different depth/diameter aspect ratios that can be of interest in surface structuring applications.

From the point of view of the process dynamics, the signatures of the dominant mechanisms involved in each case have been identified, with direct correlation between maximum local plasma density induced and local ablation depth in the case of strong ablation. This relation does not hold for the CE-mediated gentle ablation process, with maximum plasma densities above \(10^{22} \text{ cm}^{-3}\) leading to ablation depths of just a few nm. The ultimate reason for these pulse-shape-dependent effects is the different rate of laser energy coupling to the material and how this influences the rate of surface charging and energy transfer to the lattice in a material (sapphire), in which surface charging can lead to a direct nonthermal ablation process. We anticipate that the insight and control over the mechanisms gained in our study, using relatively large spot sizes, also will lead to better submicrometer structuring results in conditions where tight focusing is employed.

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