Dynamics of plasma formation, relaxation, and topography modification induced by femtosecond laser pulses in crystalline and amorphous dielectrics

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We have studied plasma formation and relaxation dynamics along with the corresponding topography modifications in fused silica and sapphire induced by single femtosecond laser pulses (800 nm and 120 fs). These materials, representative of high bandgap amorphous and crystalline dielectrics, respectively, require nonlinear mechanisms to absorb the laser light. The study employed a femtosecond time-resolved microscopy technique that allows obtaining reflectivity and transmission images of the material surface at well-defined temporal delays after the arrival of the pump pulse which excites the dielectric material. The transient evolution of the free-electron plasma formed can be followed by combining the time-resolved optical data with a Drude model to estimate transient electron densities and skin depths. The temporal evolution of the optical properties is very similar in both materials within the first few hundred picoseconds, including the formation of a high reflectivity ring at about 7 ps. In contrast, at longer delays (100 ps–20 ns) the behavior of both materials differs significantly, revealing a longer lasting ablation process in sapphire. Moreover, transient images of sapphire show a concentric ring pattern surrounding the ablation crater, which is not observed in fused silica. We attribute this phenomenon to optical diffraction at a transient elevation of the ejected molten material at the crater border. On the other hand, the final topography of the ablation crater is radically different for each material. While in fused silica a relatively smooth crater with two distinct regimes is observed, sapphire shows much steeper crater walls, surrounded by a weak depression along with cracks in the material surface. These differences are explained in terms of the most relevant thermal and mechanical properties of the material. Despite these differences the maximum crater depth is comparable in both material at the highest fluences used (16 J/cm²). The evolution of the crater depth as a function of fluence can be described taking into account the individual bandgap of each material. © 2010 Optical Society of America

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1. INTRODUCTION

With the advent of ultrashort pulse laser technology (picosecond and femtosecond), providing high peak intensities and ultrafast energy deposition, deterministic processing of dielectric materials has become possible. The resulting reduction in the collateral damage has stimulated their use in surface processing with a nanometric resolution [1–3] and for producing bulk devices [4,5]. In order to achieve optimum results, a comprehensive knowledge of absorption and excitation processes (multi-photon absorption, ionization, etc. [6]) and the subsequent dynamics of ablation process and its relation to the surface topography produced is indispensable and has thus been the focus of interest of many research groups over the last decades [1–17].

It has been shown that the topography of the femtosecond laser ablated crater strongly depends on the material. Watanabe *et al.* [7] performed a comparative study of different crystalline materials. Sapphire showed a pronounced ablation crater with steep walls, surrounded by a weak depression, with the latter being attributed to a

gentle ablation process induced by Coulomb explosion [8]. Also, the differences in the ablation features of sapphire and fused silica have been discussed in terms of the different orders of the phase transition involved upon melting in both materials and the differences in their trapping dynamics [9]. Other crystalline oxides, such as magnesium oxide or zirconium dioxide, also exhibit pronounced ablation craters, but are surrounded by small ablated particles re-deposited at the material surface. In contrast, amorphous dielectrics show a different behavior. Siegel *et al.* [10] and Puerto *et al.* [11] observed in fused silica an ablation crater with less steep walls surrounded by a pronounced depression, with the latter being attributed to material densification. In a borosilicate glass, Ben-Yakar *et al.* [12] observed material elevation (crater rim) surrounding the ablation crater, which they attributed to melt ejection (piston effect).

In order to disentangle the mechanisms responsible for differences in the surface morphology, time-resolved optical pump-probe techniques help in determining the evolution of the optical properties of the excited material. For

instance, Chowdhury *et al.* [13] studied the dynamics of the ablation process in both sapphire and fused silica. Their results showed a strong fluence dependence of the transient reflectivity and transmission, and they were able to determine the temporal evolution of those parameters at a few selected fluences. Unfortunately, these studies did not include a detailed comparison of their time-resolved results to the final (permanent) surface morphology produced, most likely because of the difficulty to relate single-point pump-probe data, measured at the center of the laser-excited region, to a complex two-dimensional (2-D) surface morphology.

A useful technique to overcome this limitation is femto-second pump-probe microscopy with a pulse-limited temporal resolution of the order of the laser pulse duration [14–19]. Based on microscopy, time-resolved optical data are acquired in the form of a series of 2-D microscopy images of the irradiated region at different time delays of the probe pulse, illuminating the excited region. The additional spatial resolution of this experimental technique (in a few micron range), compared to conventional pump-probe approaches, allows obtaining precise information of the dynamics of these processes at each position of the intensity distribution of the pump spot. This technique has already been employed for the study of femtosecond laser irradiated fused silica [10,11].

The goal of this work is to extend the previous studies to sapphire and to enable a direct comparison between the behaviors of wide bandgap amorphous and crystalline materials. This should yield information on the underlying mechanisms that lead to the pronounced differences in the surface topography. Particularly, we study the dynamics of the free-electron plasma formation-relaxation and the dynamics of the ablation process and their relationship to the final ablated crater topography.

2. EXPERIMENT

The materials used in this study are fused silica (“Lithosil” by Schott) and sapphire (VM-TIM) which have bandgaps of 7.2 and 9.9 eV, respectively. The polished material surface has been cleaned in an ultrasonic bath, is free of defects, and has not been pre-irradiated in order to avoid incubation effects [20].

A. Irradiation System with Femtosecond Pump-Probe Microscopy

Femtosecond pump-probe microscopy is an optical technique, in which a laser pulse (120 fs at 800 nm) is split into two replicas: a high-energy pulse (pump) for irradiation and modification of the sample and a low-energy pulse (probe), frequency doubled to 400 nm, for stroboscopic illumination of the irradiated surface at a variable delay defined by an optical delay line. The experimental configuration is detailed in [11,14]. Briefly, the *s*-polarized pump pulse is focused at the sample surface by a lens ($f = 150$ mm) at an angle of 54° , producing an elliptical spot with an approximately Gaussian intensity distribution ($76 \mu\text{m} \times 51 \mu\text{m}$, $1/e^2$ diameter). As a consequence, the local fluence at different radial positions of the irradiated surface can be calculated in a straightforward way. However, in order to determine threshold values of mecha-

nisms with a high precision, irradiations have also been performed at different peak fluences. This eliminates the possibility of a non-perfect Gaussian intensity profile as a potential error source for absolute fluence measurements. The irradiation is performed in air with a single pulse selected from the pulse train of the regenerative amplifier running at 100 Hz, using an electronically synchronized electro-mechanical shutter. It has been ensured that neither self-focusing nor dielectric breakdown in air of the pump beam before reaching the sample occurs under the present experimental conditions. This test has been performed by removing the sample and measuring the integrated and fractional pulse energies passing through a beam clipping circular aperture after the focus as functions of the incident pulse energy. A linear behavior is observed in both cases over the whole energy range used. This is consistent with a calculation of the critical power for self-focusing in air [21,22] which in our case leads to 2.3 GW or $280 \mu\text{J}$, above the maximum energy used in our experiment ($E_{\text{max}} = 200 \mu\text{J}$).

As for the probe beam, a temporal delay can be introduced between the arrivals of the pump and probe pulses at the sample surface using motorized (up to 1 ns) and manual (up to ~ 20 ns) optical delay lines. The reflected or transmitted normal incident probe light is detected, using a standard microscopy configuration to form an image of the sample surface (illumination field of $440 \mu\text{m} \times 330 \mu\text{m}$) onto a 12 bit charge-coupled device (CCD) camera, which is synchronized with the laser system. The imaging system includes a long working distance microscope objective [$20\times$, numerical aperture (NA)=0.42] and a tube lens ($f=200$ mm), which allows one to collect the probe pulse light and acquire images of the material surface with a spatial resolution of $\sim 1 \mu\text{m}$. Furthermore, a bandpass filter (centered at 400 nm) is used to block the scattered pump light and broadband plasma emission. The estimated temporal resolutions of the system are ~ 800 fs for reflectivity and ~ 400 fs for transmission measurements [10,11].

B. Topographic and Morphological studies

After irradiation, the surface topography and morphology have been studied in detail employing three different types of microscopes: First is a white light microscope (WLM) (Carl Zeiss, Axiophot) with a high-magnification objective lens ($50\times$, NA=0.75), used in the reflection mode. The spatial resolution of this microscope is $\sim 0.5 \mu\text{m}$. Second is an optical interferometric microscope (OIM, Sensofar, PLu 2300) with a high-magnification interferometric objective lens (NA=0.55). Here, the light emitted from a light-emitting diode (460 nm wavelength) passes through a beam splitter and illuminates both the sample surface and a built-in reference mirror. The light reflected from these surfaces is recombined on a CCD camera forming a fringe interference pattern. Employing phase shift interference, the system provides a lateral resolution of $\sim 0.5 \mu\text{m}$ and a nanometric depth resolution. Third, an atomic force microscope (AFM, PSIA XE-100) in the tapping mode is used. This system provides a lateral resolution of ~ 0.15 nm and a depth resolution of ~ 0.05 nm.

3. RESULTS AND DISCUSSION

A. Dynamics of Plasma Formation and Ablation

The images in Fig. 1(a1)–1(a3) and Fig. 1(b1)–1(b3) show characteristic time-resolved images of the surface reflectivity of fused silica [Fig. 1(a)] and sapphire [Fig. 1(b)] after irradiation with single pump pulses with peak fluences of 11.9 and 13.1 J/cm², respectively. These images show a spatially extended large increase in the surface reflectivity due to the formation of a dense free-electron plasma [10,16], which reaches its maximum at $\Delta t \approx 1.5$ ps in both materials. At longer delays a central dark area is formed, reaching reflectivity values below the initial surface reflectivity of the material at $\Delta t \approx 7$ ps. This decrease is a clear sign that surface ablation has started [16]. Outside the ablating region (central dark area), a ring of high reflectivity remains at this delay. While this phenomenon has already been reported to occur in fused silica [10], Fig. 1(b2) shows that this peculiar feature is also present in sapphire under the same experimental conditions.

On the contrary, the behavior of both materials is different at delays of tens of nanoseconds. While in fused silica at 10 ns the ablation crater is already visible [Fig. 1(a3)] and similar to the surface observed several seconds after the irradiation, in sapphire the ablation process extends beyond 20 ns [Fig. 1(b3)], the maximum delay achievable in our experimental setup.

Since the laser beam has an approximately Gaussian intensity profile, different positions on the irradiated surface correspond to different local fluences [Fig. 1(a2) and 1(b2)], whose values can be determined approximately in a straightforward way [10,23]. Acquiring a series of time-resolved images at different delays we can reconstruct the temporal evolution of the surface reflectivity at different local fluences. The resulting images in Fig. 1 show an overall very similar temporal behavior for both materials during the first moments of the ablation process ($\Delta t \sim 100$ ps). This is consistent with the observations of Chowdhury *et al.* [13], which were carried out using a

pump-probe system with a focused probe pulse (no spatial resolution) in irradiation series at different fluences.

A quantitative assessment of the reflectivity evolution is plotted in Fig. 1(a4) and 1(b4). At the peak fluences for fused silica and sapphire (11.9 and 13.1 J/cm²) the reflectivity maximum occurs at $\Delta t \approx 1.5$ ps and reaches nearly the same value ($R_{\max} = 0.23$ and 0.24) in both materials. This large reflectivity increase is consistent with the formation of a dense free-electron plasma. The onset of ablation becomes evident already at $\Delta t \approx 2$ ps, when the reflectivity at the center of the excited region starts to decrease in both materials. This time delay for the ablation onset is comparable to the one provided for both materials in [13], whereas Rosenfeld *et al.* [24] found a comparable value only for fused silica ($\Delta t = 3$ ps), but a considerably higher value for sapphire ($\Delta t = 12$ ps). This difference can most likely be explained by the different experimental techniques employed. The technique used in [24] measures the scattered probe light with a photomultiplier, positioned off-axis, which detects a spatial average of the scattered light. On the contrary, our technique measures the reflected light with a CCD camera, which records a sharp image of a well-defined plane (the surface). In this way our technique is expected to be more robust against out-of-focus contributions and misalignment/defocusing of the probe beam.

Studying the reflectivity evolution as a function of the local fluence [Fig. 1(a4) and 1(b4)], we find that reflectivity maximum and/or ablation onset are delayed with respect to the peak fluence in both materials, consistent with the results reported in [13]. In particular, in the low fluence regime corresponding to the characteristic ring of increased reflectivity (6.4 J/cm² for fused silica and 7.1 J/cm² for sapphire), $R_{\max}$ is reached at $\Delta t \approx 3$ ps for both materials. Moreover, in this fluence regime the reflectivity values never decrease below R_0 , the initial surface reflectivity of the material, indicating the absence of ablation.

The evolution of the transmission of the laser irradi-

Fig. 1. (Color online) The upper row shows characteristic surface reflectivity images ($\lambda_{\text{probe}} = 400$ nm) of (a1)–(a3) fused silica and (b1)–(b3) sapphire at different delay times Δt after arrival of the pump pulse ($\lambda_{\text{pump}} = 800$ nm). The dashed ellipses mark the border of the ablation crater. The image size is $58 \mu\text{m} \times 37 \mu\text{m}$ and the contrast was optimized to better visualize their most characteristic features. The graphs in the lower row [(a4) for fused silica and (b4) for sapphire] show the temporal evolution of the surface reflectivity at different local fluences corresponding to different spatial positions as indicated in (a2) and (b2). The dashed horizontal lines indicate the initial surface reflectivity R_0 before irradiation.

ated surface has also been studied and the results are shown in Fig. 2. Note that the transient transmission data have been analyzed only in the region to the left of the spot center [symbols in Fig. 2(a2) and 2(b2)] in order to avoid the complexity of a dominant influence of the electron density increase in the subsurface regions generated by the beam propagating inside the material [25]. It is observed that a strong decrease in transmission is reached very quickly (~ 400 fs) in both materials confirming the presence of a free-electron plasma, sufficiently dense as to absorb and reflect most of the probe pulse in $\Delta t < 1$ ps [26]. Interestingly, the transient transmission is reduced over the entire spot in both materials throughout the entire delay window. As opposed to reflectivity measurements, transmission measurements alone are thus not able to distinguish between the free-electron plasma formation and ablation. This can be also seen in Fig. 2(a2) and 2(b2), where no pronounced ring structure can be seen at the positions that correspond to 6.4 J/cm^2 in fused silica and 7.1 J/cm^2 in sapphire, unlike what is observed in Fig. 1(a2) and 1(b2).

A quantitative assessment of the temporal evolution of the transmission at different local fluences [Fig. 2(a4) and 2(b4)] reveals a very fast decrease in both materials, within $\Delta t \sim 400$ fs at the peak fluence. The reason for the relatively long time to reach the reflectivity maximum ($\Delta t \sim 1.5$ ps) compared to the pulse duration is caused in part by the increased group velocity dispersion contribution in the case of reflectivity measurements. However, this cannot be the sole reason for the exceptionally long time needed to reach R_{max} and we propose that impact ionization contributes even after the pulse has finished, as recently proposed by Rethfeld [27]. For lower local fluences, the minimum in transmission is temporarily delayed, in line with the behavior of the reflectivity maximum. The recovery of the transmission occurs generally faster in fused silica than in sapphire for all local fluences plotted, indicating a shorter lasting plasma relaxation and/or ablation process. This aspect will be analyzed in

detail in Subsection 3.C, once we have equipped us with an estimate of the plasma densities involved as provided in the following section.

B. Estimation of Electron Plasma Densities using the Drude Model

The electron plasma density induced in a laser-material interaction process can be estimated by comparing experimental data from optical probing to calculations made using the Drude model for a free-electron gas [28]. The optical reflectivity of an electron gas at normal incidence is given by the Fresnel equation [29],

$$R = \left| \frac{k_1 - k_2}{k_1 + k_2} \right|^2, \quad (1)$$

where the wave vectors k_1 and k_2 are given by $k_1^2 = \omega^2 \mu \epsilon = (n_1 \omega / c)^2$ and $k_2^2 = (\omega / c)^2 [n_2^2 - (\omega_p / \omega)^2 (1 + i / \omega \tau)^{-1}]$, with $\omega_p^2 = n_e e^2 / m \epsilon_0$ being the plasma frequency, ω the probe beam frequency ($\lambda = 400$ nm), n_1 the refractive index of the medium of incidence (air) and n_2 the refractive index of the dielectric at the probe beam wavelength, c the vacuum speed of light, ϵ_0 is the vacuum dielectric permittivity, and m and e are the electron mass and charge, respectively. The damping constant τ represents the scattering time that is generally assumed to be inversely proportional to the photo-generated carrier density n_e (i.e., $\tau = \tau_1 n_c / n_e$) [30]. The critical electron density is given by $n_c = \epsilon_0 m \omega^2 / e^2$, which in our case yields a value of $n_c = 7 \times 10^{21} \text{ cm}^{-3}$ [31].

Figure 3 shows the calculated reflectivity and skin depth α^{-1} (with the absorption coefficient $\alpha = \text{Im}[2k_2]$) values as functions of n_e in fused silica [Fig. 3(a)] and sapphire [Fig. 3(b)]. The calculations have been made with $\tau_1 = 2$ fs similar to the one reported by other authors [32]. This parameter mainly affects the reflectivity amplitude value and not the overall behavior of the curves. Using experimental reflectivity values we can estimate the electron plasma density attained. However, care has to be

Fig. 2. (Color online) The upper row shows transmission images ($\lambda_{\text{probe}} = 400$ nm) of (a1)–(a3) fused silica and (b1)–(b3) sapphire at different delay times Δt after arrival of the pump pulse ($\lambda_{\text{pump}} = 800$ nm). The images size is $58 \mu\text{m} \times 37 \mu\text{m}$ and the contrast was optimized to better visualize their most characteristic features. Lower row: The graphs in the lower row [(a4) for fused silica and (b4) for sapphire] show the temporal evolution of the transmission at different local fluences corresponding to different spatial positions as indicated in (a2) and (b2). The dashed horizontal lines indicate the initial sample transmission T_0 before irradiation.

Fig. 3. (Color online) Calculations of surface reflectivity (solid line) and skin depth (dashed line) of a free-electron plasma surface layer as functions of the electron density n_e in (a) fused silica and (b) sapphire using the Drude model at the probe beam wavelength of 400 nm. The full circles mark the maximum experimental reflectivity values at high and low fluences, R_1 and R_2 , respectively, whereas the open circles mark the resulting skin depth values α_1^{-1} and α_2^{-1} .

taken at fluences where ablation is involved in the interaction process since ablation strongly reduces the surface reflectivity, directly counteracting the reflectivity increase produced by the free-electron plasma. In such situations, i.e., in the central region of the spot, the model might yield an underestimation of the free-electron density.

The transient electron densities corresponding to the maximum value of the experimental reflectivity at a high fluence in fused silica $R_{\max}(11.9 \text{ J/cm}^2)=0.23$ and sapphire $R_{\max}(13.1 \text{ J/cm}^2)=0.24$ are approximately 1.7×10^{22} and $3.0 \times 10^{22} \text{ cm}^{-3}$, respectively. The resulting values for the minimum transient optical skin depth at the 400 nm wavelength are 53 and 31 nm in fused silica and sapphire, respectively. Such small skin depths are expected to induce transient transmission values close to zero, which is consistent with the experimental values (c.f. Fig. 2) observed in fused silica $T_{\min}(11.9 \text{ J/cm}^2)=0.13$ and sapphire $T_{\min}(11.6 \text{ J/cm}^2)=0.14$. The comparable value of $T_{\min}$ for both materials and the fact that the transmission never reaches zero indicate saturation of the absorption process, which might be related to a depletion of the valence band.

While the values determined with the model at the peak fluence might be underestimating the actual transient electron density, at local fluences below the ablation threshold the model should yield a more precise estimation. Practically, this refers to the region surrounding the ablating crater, i.e., the region showing a bright ring of increased reflectivity at $\Delta t \approx 7 \text{ ps}$ [c.f. Fig. 1(a2) and 1(b2)]. The transient reflectivity maxima at these positions, corresponding to certain local fluences, can be extracted from Fig. 1(a4) and 1(b4) (star symbols) as $R_{\max}(6.4 \text{ J/cm}^2)=0.1$ for fused silica and $R_{\max}(7.1 \text{ J/cm}^2)=0.11$ for sapphire. The respective n_e -values extracted from Fig. 3 are 1.4×10^{22} and $2.2 \times 10^{22} \text{ cm}^{-3}$, and the skin depths yield values of $\alpha^{-1}=92 \text{ nm}$ for fused silica and $\alpha^{-1}=55 \text{ nm}$ for sapphire. The difference by almost a factor of 2 between both materials is consistent with the difference in the experimentally observed minimum values of the transient transmission, $T_{\min}(6.4 \text{ J/cm}^2)=0.4$ in fused silica and $T_{\min}(7.1 \text{ J/cm}^2)=0.2$ in sapphire.

C. Dynamics of Free-Electron Plasma Relaxation

A quite precise estimation of the relaxation time of the free-electron plasma can be obtained from the transient reflectivity [Fig. 1(a4) and 1(b4)] and transmission [Fig. 2(a4) and 2(b4)] measurements for fluences below the ablation threshold (6.4 J/cm^2 in fused silica and 7.1 J/cm^2 in sapphire). We define the relaxation time t_{relax} as the time needed to recover to $1/e$ of the total peak the initial reflectivity/transmission change; $t_{\text{relax},R}=t((R_{\max}-R_0)/e)-t(R_{\max})$ and $t_{\text{relax},T}=t(T_0-((T_0-T_{\min})/e))-t(T_{\min})$. The reflectivity measurements yield apparently short values for $t_{\text{relax},R} \approx 6 \text{ ps}$ and $\approx 3 \text{ ps}$, respectively, for fused silica and sapphire, which are of the order of the values reported in [13]. However, relaxation times determined from transmission measurements are markedly longer, $t_{\text{relax},T} \approx 30 \text{ ps}$ and $\approx 250 \text{ ps}$. The underlying reason for this pronounced difference can be understood already within the frame of the Drude model. The reflectivity is only sensitive to dense plasmas with $n_e > n_c$ (see Fig. 3), whereas the transmission is sensitive to much lower plasma densities because the decrease in transmission is not only caused by an increase in R but also by an increase in absorption over the skin depth (c.f. Fig. 3). As a consequence, the strong dependence of the skin depth on n_e has a strong influence on transmission, even at longer delay times. In this sense, the $t_{\text{relax},T}$ values allow for a more precise monitoring of plasma relaxation times.

The $t_{\text{relax},T}$ values we observe in sapphire ($\approx 250 \text{ ps}$) are much higher than those observed in fused silica ($\approx 30 \text{ ps}$). This difference might be related to the much stronger electron-phonon coupling in fused silica [33], which also has the particularity to quickly form self-trapped excitons (STEs) [34] and color centers. In absolute terms, our values for sapphire are comparable to the values reported in the literature ($\approx 100 \text{ ps}$) [34], whereas for fused silica they are not quite as low as those reported in the literature ($\approx 150 \text{ fs}$) [34,35]. A likely reason for this difference is the much higher laser intensity in our experiment, yielding much higher electron densities (by 1–2 orders of magnitude) compared to [34–36]. At such high intensities the relaxation times include a broad spectrum of relaxation mechanisms such as phonon emission and scattering,

Fig. 4. (Color online) Upper row: (a1),(a2) and (b1),(b2) show the time-resolved surface reflectivity images ($\lambda_{\text{probe}}=400\text{ nm}$) of (a) fused silica and (b) sapphire at 7 ps ($R_{7\text{ ps}}$) and few seconds (R_{∞}) after arrival of the pump pulse [(a) 11.9 and (b) 12.5 J/cm²], whereas (a3) and (b3) show WLM images of the same region. The images size is 58 $\mu\text{m} \times 37\text{ }\mu\text{m}$ and the contrast has been optimized. Lower row: (a4) and (b4) show horizontal topography profiles through the crater center obtained by means of an OIM. The arrows indicate a change in slope of the crater walls in fused silica (a4) and a weak surface depression surrounding the ablation crater in sapphire (b4).

electron trapping, exciton formation (fused silica), and non-radiative recombination [6,34,37]. We therefore believe that our findings of much longer relaxation times in fused silica, compared to values reported in the literature for low excitation experiments, are important for understanding that STEs and other ultrafast trapping mechanisms can be overtaken by other mechanisms at high intensities. The interpretation of differences in the ablation morphology in terms of differences in the electron trapping dynamics has thus to be carefully invoked at high excitation levels [9].

D. Study of the Crater Topography and Material Modifications

Figure 4 shows transient reflectivity images of fused silica [Fig. 4(a)] and sapphire [Fig. 4(b)] at $\Delta t=7\text{ ps}$ ($R_{7\text{ ps}}$) and at $\Delta t=\text{a few seconds}$ (R_{∞}) after irradiation with a high pump pulse fluence. Comparing these images [Fig. 4(a1) and 4(a2), and Fig. 4(b1) and 4(b2)] one notices that the high reflectivity ring in $R_{7\text{ ps}}$ lies outside the border of the visible ablation crater border seen in R_{∞} , for both materials. This fact ultimately confirms what had already been deduced from the evolution of the reflectivity with the delay time in Fig. 1(a4) and 1(b4) (star symbols): The presence of a free-electron plasma outside the ablating region. Yet, WLM images (R_{WLM}) of the same region [Fig. 4(a3) and 4(b3)] do reveal some sort of surface modification outside the ablation crater, spatially coincident with the bright ring of the 7 ps reflectivity image [Fig. 4(a1) and 4(b1)]. In particular, fused silica shows a featureless crater surrounded by a weak ring of higher reflectivity [Fig. 4(a3)] [10], while sapphire shows a crater full of fissures surrounded by a gray annulus [Fig. 4(b3)].

We have measured the crater topography using an OIM and Fig. 4 includes the obtained horizontal cross-sections through the crater centers in fused silica [Fig. 4(a4)] and sapphire [Fig. 4(b4)]. The topographic profile in fused silica is smooth with a depth of $\approx 150\text{ nm}$, which is gradually reduced toward the crater edge. Besides, a change in the slope of the crater wall [Fig. 4(a4), blue arrows] can be appreciated at that radial distance, where the WLM image [Fig. 4(a3), R_{WLM}] features a ring of enhanced reflectivity. On the other hand, the topography profile in sap-

phire [Fig. 4(b4)] shows a crater with a maximum depth of 150 nm whose inner surface is rougher than that in fused silica, surrounded by a weak depression at the same radial distance as the gray annulus in Fig. 4(b3).

An interesting point is that the crater depths in both materials are similar, despite their different bandgap values ($E_g=7.2\text{ eV}$ in fused silica and $E_g=9.9\text{ eV}$ in sapphire). The negligibly higher fluence in sapphire (12.5 J/cm², compared to 11.9 J/cm² in fused silica) cannot possibly make up for the fact that seven photons are needed to bridge the gap, compared to five in fused silica. In order to investigate the underlying reasons for this apparent inconsistency we have performed in both materials a series of single pulse irradiations at increasing peak fluences F_0 . The series of ablation craters has been measured with an OIM, determining the individual maximum crater depth d_{max} . Figure 5 shows the experimental data obtained for both materials. The curves for fused silica [Fig. 5(a)] and for sapphire [Fig. 5(b)] both show a characteristic saturating behavior at $\sim 180\text{ nm}$ crater depth for the highest fluences. In order to analyze the absorption process in detail, we have used a simple physical model of pure multi-photon absorption of the order m , neglecting free-carrier absorption, absorption saturation, carrier diffusion, recombination, and other energy relaxation processes during the laser pulses [38,39]. In that

Fig. 5. (Color online) Crater depth in (a) fused silica and (b) sapphire as a function of the incident peak laser fluence. The solid lines represent least-squares-fits according to Eq. (2) for (a) pure five-photon absorption in fused silica and (b) pure seven-photon absorption in sapphire. The dashed lines are fits according to the Lambert-Beer Law [12] for linear absorption in both materials, illustrating the pronounced deviation of the data from this case.

model (which for simplicity assumes a temporal square pulse), the change in the local fluence (F) within the absorbing material along the beam direction (z) can be described by the differential equation $dF/dz = -\alpha_m F^m$, with the m -photon absorption coefficient α_m . Solving this equation for $m \geq 2$ along with the boundary condition that threshold fluence F_{th} is reached at the ablation crater bottom directly leads to the following polynomial expression for the ablation crater depth d_{max} as a function of the peak fluence ($F_0 \geq F_{th}$):

$$d_{max} = B_m - \frac{A_m}{F_0^{m-1}}. \quad (2)$$

The constants $B_m = [(m-1)\alpha_m F_{th}^{m-1}]^{-1}$ and $A_m = [(m-1)\alpha_m]^{-1}$ can be used as fit parameters to determine F_{th} and α_m from a least-squares-fit to the experimental data shown in Fig. 5 (solid line). Figure 5 also shows the fits according to the Lambert–Beer law [12] (dashed lines) for linear absorption in both materials in order to illustrate the pronounced deviation of the data from this case.

Assuming that the simultaneous absorption of five photons ($m=5$) dominates the energy deposition in fused silica leads to an excellent agreement between the experimental data and the least-squares-fit over the entire fluence range [see the solid line in Fig. 5(a)], with $F_{th, \text{FuSi}} = 5.4 \text{ J/cm}^2$ and $\alpha_{5, \text{FuSi}} = 16 \text{ cm}^7/\text{J}^4$. Although this agreement does not imply the full validity of the model, which is too simple, it does suggest that multi-photon ionization plays a key role in energy deposition. In this sense, a similar behavior of the ablation process in fused silica is observed by Jia *et al.* [40], which includes in the model not only multi-photon ionization but also avalanche ionization with a reasonable fit. The experimentally determined threshold value in Fig. 5(a) yields consistently $F_{th} = 5.5 \text{ J/cm}^2$, using as a criterion the mean fluence value between zero and the minimum crater depth. Even when considering that for crater depths of $d_{max} \leq 25 \text{ nm}$ no ablation occurs but electron plasma-induced densification and surface depression, as shown in [10], only a slightly higher value of $F_{th} = 5.6 \text{ J/cm}^2$ is obtained, still consistent with the simple model.

A similar analysis for the case of sapphire ($m=7$) also shows a reasonable agreement with the experimental data for fluences larger than $\sim 8 \text{ J/cm}^2$ [see the solid line in Fig. 5(b)], with $F_{th, \text{sapphire}} = 7.0 \text{ J/cm}^2$ and $\alpha_{7, \text{sapphire}} = 8.7 \text{ cm}^{11}/\text{J}^6$. Interestingly, the experimental data points scatter considerably more than for fused silica, which may be related to the material being crystalline and more vulnerable to the presence of trapping sites, lattice-impurities, or defects [41]. Furthermore, the fit does not reproduce with a satisfactory precision the data evolution in the low fluence range. In particular deviations are found in the extremely sharp ablation threshold and the sudden increase in the crater depth, also observed by Guizard *et al.* [42]. The sharpness of the threshold in the representation of the experimental data shown in Fig. 5(b) facilitates its determination using as a criterion the mean fluence value between zero and the minimum crater depth, yielding a value of $F_{th} = 7.5 \text{ J/cm}^2$, higher than the value deduced from the fit. Still, compared to fused silica,

the ablation threshold in sapphire is much higher, consistent with the higher bandgap.

In this context another relevant material property is the latent heat of melting ΔH_m , which has to be provided before the temperature of the melt can be increased beyond the melting temperature T_m . ΔH_m is much higher for sapphire (111.1 kJ/mol) than for fused silica (8.51 kJ/mol) [43], in line with the observation of a higher threshold value. This large difference is related to the different phase transitions in both materials. While in sapphire melting is a first-order phase transition, in fused silica a second-order phase transition, liquefaction, occurs. The “late start” in sapphire (higher value of F_{th}), is compensated for increasing fluences by a dramatic rise in crater depth, a behavior whose driving force (high plasma pressure on the molten material) is investigated in detail in Subsection 3.E. It leads to a situation in which at high fluences both materials show the same crater depth.

In short four main observations can be made comparing both materials: (i) The ablation threshold in sapphire is higher, (ii) it is more sensitive to fluence values very close to this threshold, (iii) similar maximum crater depths are reached, and finally (iv) both materials generally show a behavior as predicted by Eq. (2) for their corresponding orders of multi-photon absorption. All these observations clearly indicate that multi-photon absorption of different orders is essential in the ablation process of both dielectrics under investigation, although it only forms the initial seed for other processes to start.

An investigation of the outer region of the crater in both materials brings up clear differences. The barely visible gray ring surrounding the crater in sapphire [Fig. 4(b3)] is in clear contrast to the bright ring in fused silica [Fig. 4(a3)], which points to a different origin of the observed surface depression in sapphire. In a previous work we have shown that this reflectivity increase in fused silica, consistent with a positive change in the refractive index, is in turn consistent with a laser-induced densification process [10] in this region, as opposed to an ablation process. However, since in sapphire its density ($\rho_{\text{sapphire}} = 3.98 \text{ g/cm}^3$) is already high, almost twice that of fused silica ($\rho_{\text{FuSi}} = 2.20 \text{ g/cm}^3$) and the material is single-crystalline, it is difficult to achieve densification in this case. Watanabe *et al.* [7] observed a similar behavior in sapphire, namely, an ablation crater with much steeper walls, surrounded by a subtle surface depression. The authors proposed Coulomb explosion as the possible origin of the depression in the outer region, in which binding electrons are being torn off and the resulting charged ions separate by Coulomb repulsion. The initial condition for this process to happen, tearing off of binding electrons, is readily met if we recall the presence of the free-electron plasma observed in this spatial region [Fig. 4(b1)], whose density ($n_e = 2.2 \times 10^{22} \text{ cm}^{-3}$) is even larger than in the case of fused silica ($n_e = 1.4 \times 10^{22} \text{ cm}^{-3}$). This picture is consistent with that given in other works [8,44], where Coulomb explosion is held responsible for a gentle ablation process, upon which only a thin layer of a few nanometers is removed, whereas strong ablation is defined as a process upon which drastically more material is removed. It is worth emphasizing though that generally studies on Coulomb explosion refer to experimental results obtained

Fig. 6. (Color online) Images: (a1)–(a4) and (b1)–(b4) show surface regions after irradiation with a single femtosecond laser pulse at (a) 5.8 J/cm^2 in fused silica and (b) 7.6 J/cm^2 in sapphire. The images have been recorded with the femtosecond-microscope at a delay of 7.5 ps [(a2),(b2)] a few seconds after the arrival of the pump pulse [(a1),(b1)], with (a3),(b3) an AFM and (a4),(b4) the WLM. The image size is in all cases $35 \mu\text{m} \times 23 \mu\text{m}$ and the contrast has been optimized. The ellipses are included to aid the eye to distinguish different regions, as detailed in the text. Plots: (a5) and (b5) show horizontal cross-sections through the center (dashed line) and radial averaging (solid line) of the AFM images. The arrows indicate the radial positions of the ellipses in the above images.

upon multiple pulse irradiation (e.g., [8,44].), where incubation plays a major role. In contrast, our work and that of [7] focuses on single pulse results.

The modifications surrounding the ablation crater, i.e., at reduced local fluences, are more clearly seen in irradiation results obtained at lower peak fluences, only slightly above F_{th} . Figure 6 compares results obtained from single pulse irradiations at 5.8 J/cm^2 in fused silica and 7.6 J/cm^2 in sapphire, using femtosecond time-resolved microscopy, AFM, and WLM. The different characteristics of spatial regions are marked by ellipses in the images and by arrows in the plots. In fused silica, essentially two regimes can be seen: Regime I (circumvented by dotted lines): A central region with weak signs of the onset of ablation, in particular a slightly more granular appearance in [Fig. 6(a1)] and a lowered reflectivity in [Fig. 6(a4)], and Regime II (circumvented by dashed lines): A surrounding annular region with increased reflectivity [Fig. 6(a4)]. Despite the small but noticeable differences between the two regimes, the cross-sectional AFM depth profile [Fig. 6(a5)] does only reveal the transition from the annular region to the non-affected material, but not the transition to the central disk. This is an indication that the fluence chosen is indeed very close to the ablation threshold, which is confirmed by the depth measured of $d_{max} \approx 28 \text{ nm}$.

In contrast three regimes can be seen in sapphire: Regime I (circumvented by solid lines): A central region with strong signs of ablation, in particular a crater rim in Fig. 6(b1) and a deep crater in Fig. 6(b3) that can be quantified to a depth of $d_{max} \approx 70 \text{ nm}$ [Fig. 6(b5)] with much steeper walls; Regime II (circumvented by dotted lines): A surrounding annular region, showing strong signs of surface cracks [Fig. 6(b1), 6(b3), and 6(b4)]; and Regime III (circumvented by dashed lines): A larger surrounding an-

nular region, displaying no cracks but a reduced reflectivity [Fig. 6(b4)] and a weak surface depression [Fig. 6(b5)] of $d \approx 5 \text{ nm}$. It is this third region, which shows signs of a Coulomb explosion process to take place, producing a gentle ablation [7,8].

The cracked rough surface of sapphire in Regime II in combination with the much steeper slope of the crater wall even at fluences close to the ablation threshold indicates a fundamentally different ablation process compared to fused silica. The appearance of cracks in sapphire is possibly related to its much higher stiffness, which causes the material to fracture more easily instead of deforming it upon external pressure. For comparison, the value of Young's modulus E is 340 GPa for sapphire compared to 72 GPa for fused silica. This interpretation of the origin of the surface cracks is supported by their orientation, which is not well defined but on average approximately parallel to the laser polarization and their spacing, which is of a few microns. For electric-field-induced fracture reported in the literature [45], the orientation should be perpendicular to the laser polarization and the spacing shorter than the laser wavelength.

The existence of different and complex surface modifications around the visible ablation crater in both materials suggests that it might be useful to define a minimum threshold for any surface modifications to take place ($F_{surf} < F_{th}$). A possible common criterion is the maximum spatial extension of the free-electron plasma, which seems to extend to the outermost permanent surface modification in both materials [outermost dashed ellipses in Figs. 6(a) and 6(b)]. Conceptually, this criterion was already introduced by Varel *et al.* [20]; our method provides additional spatial and temporal resolutions, thus increasing considerably the precision. For this we have measured the spatial extension of the electron plasma at $\Delta t = 7 \text{ ps}$

delay at increasing fluences and plotted the squared diameter of the spatial extension versus the logarithm of the peak laser fluence (data not shown here). By extracting the intersection with the fluence axis [46], it is possible to determine the threshold fluence for the free-electron plasma formation $F_{e\text{-plasma}}$. We obtain values of 3.9 J/cm^2 for fused silica and 5.8 J/cm^2 for sapphire. The different bandgaps of both materials are most likely the main reason for the different threshold values since for a lower bandgap the order of absorption is reduced and consequently less laser pulse energy is required to generate a critical density of electrons.

E. Temporal Evolution of the Crater Formation: Ejection Dynamics of Molten Material

Besides the ability to temporally and spatially resolve the formation and decay of free-electron plasmas as shown in Figs. 1 and 2, our technique also allows observing transient optical effects produced during the formation of the ablation crater. Figure 7 shows representative transient reflectivity images of fused silica [Fig. 7(a)] and sapphire [Fig. 7(b)] covering a delay range from hundreds of picoseconds to a few nanoseconds after the arrival of the pump pulse. In this temporal window, hardly ever investigated by ultrafast pump-probe studies, a striking difference between both materials is observed: the existence of a transient optical fringe pattern surrounding the ablation crater in sapphire. This fringe pattern appears approximately at $\Delta t \approx 200 \text{ ps}$ [Fig. 7(b1)], reaches its maximum modulation depth at $\Delta t \approx 400 \text{ ps}$ [Fig. 7(b2)], and begins to fade at $\Delta t \approx 2 \text{ ns}$ [Fig. 7(b3)], although still being present at $\Delta t \approx 20 \text{ ns}$ [c.f. Fig. 1(b3)]. However, in the final image recorded several seconds after irradiation, the pattern has disappeared [Fig. 7(b4)]. The fringe pattern has an approximately constant periodicity with the delay time and only shows changes in the modulation depth of the reflectivity, as mentioned above.

As we will show in the following, the appearance of the fringe pattern can be attributed to scattering of the probe beam at a transient crater rim, composed of an ejected molten material. The scattered probe light interferes at a given position outside the rim with a directly incident probe light, producing a periodic fringe pattern due to constructive/destructive interference. The change in the modulation depth of the pattern is thus a direct measure of the formation/disappearance of the transient rim of the

molten material, reaching its maximum visibility at $\Delta t \approx 410 \text{ ps}$, indicated by the peak in the modulation depth.

In order to rule out other possible origins for the ring pattern such as surface acoustic wave propagation or other phenomena caused by lattice vibration, we have recorded images using two different probe beam wavelengths of 800 nm [Fig. 8(a1)] and 400 nm [Fig. 8(b1)]. The apparently strong signal observed in the center of the spot at 800 nm in Fig. 8(a1) is an artifact caused by the scatter of the pump pulse. Yet, despite the problem of scatter artifacts in the spot center, the region surrounding the crater is not affected and the fringe pattern can be observed clearly. A visual comparison of the transient images at 400 and 800 nm probe wavelength [Fig. 8(a1) and 8(b1)] already shows that the period of the fringe pattern scales approximately with the probe wavelength. The vertical intensity cross-sectional profiles (normalized to the reflectivity of the non-excited surface) through the spot center of these images [Fig. 8(a2) and 8(b2)] allow a quantitative determination of the spatial period, yielding values of $\approx 2.5 \mu\text{m}$ at 800 nm and $\approx 1.3 \mu\text{m}$ at 400 nm. This confirms a linear scaling of the fringe period with the probe wavelength and further supports our interpretation of diffraction of the probe light at a transient rim of the excited/molten material to be the origin of the fringe pattern.

A similar transient fringe pattern has already been observed by Stojanovic *et al.* [47], although the authors did not discuss it. Using femtosecond pump-probe microscopy with a 532 nm 10 ps probe pulse they image the ablation dynamics in silicon induced by an extreme ultraviolet (33 nm wavelength) 25 fs free-electron-laser pulse. As in our case, a transient fringe pattern is observed that appears within the same time scale than ours, and which also shows a constant periodicity and changing modulation depth. In contrast to ours, their fringe pattern does not disappear in the final structure produced, which is consistent with their observation of a permanent crater rim after irradiation, featuring signs of a splashed molten material that has resolidified, forming a permanent rim.

We thus interpret the appearance of the rim at $\Delta t \approx 200 \text{ ps}$ in Fig. 7 as the formation of a transient elevation of the molten material, produced by the piston effect of the expanding plasma, which exerts strong forces onto the molten layer underneath. The molten layer is compressed and the melt pushed toward regions of lower pressure,

Fig. 7. Time-resolved reflectivity images of (a) fused silica and (b) sapphire at long delay times (see labels) after the irradiation with pump pulse lasers of 11.9 and 13.1 J/cm^2 , respectively. The frame size is in all cases $58 \mu\text{m} \times 37 \mu\text{m}$.

Fig. 8. Time-resolved images of a sapphire surface upon irradiation with a 800 nm femtosecond laser pulse at (a1) 11.9 and (b1) 13.1 J/cm², illuminated with a femtosecond probe pulse at two different probe wavelengths λ_{probe} : (a1) $\lambda_{\text{probe}}=800$ nm at $t=600$ ps; (b1) $\lambda_{\text{probe}}=400$ nm at $t=410$ ps. The bright granular appearance of the central region in (a1) is an artifact, caused by scatter of the 800 nm pump beam, which is suppressed in (b2) by spectral filtering. In both cases, only the surrounding region showing the fringe pattern is analyzed. The image size is $81\text{ }\mu\text{m} \times 58\text{ }\mu\text{m}$ and the contrast has been optimized. (a2) and (b2) show the normalized vertical intensity profiles of (a1) and (b1), respectively.

i.e., radially outside building up a transient wave front of considerable amplitude. A similar process is proposed by Ben-Yakar *et al.* [12] to explain the formation of a permanent elevation surrounding ablation craters in a borosilicate glass after solidification. In contrast, the pronounced elevation in sapphire is only of transient nature as can be seen by the absence of a pronounced rim in the depth profile [Fig. 4(b4)]. We attribute this very different behavior of sapphire to another property of the molten phase, the viscosity η . Table 1 includes viscosity values for molten fused silica and sapphire at low, moderate, and high temperatures [48,49]. For all temperatures the material viscosity order is $\eta_{\text{(fused silica)}} \gg \eta_{\text{(sapphire)}}$. The scenario we picture is the following: The high viscosity of the molten fused silica slows down the movement of the molten material underneath the ablating material to the border of the ablation crater. As a result fused silica does not show a transient fringe pattern in the picosecond–nanosecond

delay range [Fig. 7(a)]. The high viscosity may also be the underlying reason for fused silica to show such a smooth crater topography [Fig. 4(a4) and Fig. 6(a5)]. Molten sapphire, with its very low viscosity, easily responds to the recoil pressure distribution provided by the ablating material, allowing for the formation, growth, and movement of transient rims of the molten material [Fig. 7(b1)–7(b3)]. However, it is also the very low viscosity of molten sapphire that prevents the formation of a significant permanent elevation upon solidification.

Despite the very different crater topography and transient ablation behavior as shown in Fig. 7, neither sapphire nor fused silica shows a significant permanent elevation in the final crater border topography. This is in strong contrast to studies of the borosilicate glass [12] showing a pronounced elevation and clear signs of splashing of the ejected molten material, resolidified around the crater. We attribute this difference mainly to the excessively high fluence used in [12], $F_0^{\text{peak}} \approx 25\text{--}68\text{ J/cm}^2$, and the viscosity values lying in between those of fused silica and sapphire ($\eta_{\text{(borosilicate glass)}} \approx 1\text{--}10\text{ Pa s}$ at $T > 2500\text{ K}$).

4. CONCLUSION

We have performed a detailed study of the spatial and temporal evolutions of the dynamics of the plasma formation and ablation process of fused silica and sapphire upon irradiation with single femtosecond laser pulses. An analysis of the dynamical aspects has allowed us to determine the relaxation times of the free-electron plasma near the ablation threshold ($\Delta t \approx 30$ ps in fused silica and $\Delta t \approx 250$ ps in sapphire). The different values could be a main reason for our observation of a longer lasting ablation process in sapphire. As for the surface topography of the irradiated regions, above the ablation threshold the crater is surrounded by a weak surface depression in both materials, although of different origins and characteristics. While in fused silica material densification originated by the electron plasma seems to be the main cause, in sapphire Coulomb explosion appears to be the driving force at low fluences. Moreover, sapphire features an intermediate regime covered with surface cracks, whose origin is consistent with being caused by the high recoil pressure of the expanding plasma. The evolution of the crater depth with laser fluences can be described with a basic model taking into account the different bandgaps of

Table 1. Material, Thermal, and Optical Properties of Fused Silica and Sapphire, along with the Threshold Values Determined in this Paper [48,49]

	Fused Silica	Sapphire
Melting/softening temperature T_m (K)	1873	2300
Density ρ (g/cm ³)	2.2	3.98
Heat capacity C_p [J/(kg K)]	1450 (at 1873 K)	1430 (at 2300 K)
Latent heat of melting (kJ/mol)	8.51	111.1
Ablation threshold F_{th} (J/cm ²)	5.6	7.5
Free-electron plasma threshold $F_{e\text{-plasma}}$ (J/cm ²)	3.9	5.8
Viscosity at high T (Pa s)	≈ 340 ($T=2755\text{ K}$)	≈ 0.01 ($T=3000\text{ K}$)
Viscosity at moderate T (Pa s)	$\approx 2.3 \times 10^3$ ($T=2541\text{ K}$)	≈ 0.027 ($T=2500\text{ K}$)
Viscosity at low T (Pa s)	$\approx 796 \times 10^3$ ($T=2049\text{ K}$)	≈ 0.037 ($T=2409\text{ K}$)

the materials. A transient elevation of the molten material is observed in sapphire within a time-window of hundreds of picoseconds, not present in fused silica. The extremely low viscosity value of the molten sapphire is identified as the probable reason for this phenomenon.

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