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Plasma formation and structural modification below the visible ablation threshold in fused silica upon femtosecond laser irradiation

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We have investigated the temporal and spatial evolution of the ablation process induced in fused silica upon irradiation with single 120 fs laser pulses at 800 nm. Time-resolved microscopy images of the surface reflectivity at 400 nm reveal the existence of a transient plasma distribution with annular shape surrounding the visible ablation crater. The material in this annular zone shows an increased reflectivity after irradiation, consistent with a local refractive index increase of approximately 0.01. White light interferometry measurements indicate a shallow surface depression in this outer region, most likely due to material densification. © 2007 American Institute of Physics. [DOI: 10.1063/1.2766848]

The interaction of ultrashort laser pulses with dielectric materials involves a complex sequence of processes that eventually may lead to surface ablation, resulting in minimal collateral damage.¹ This attractive feature, widely exploited in a broad range of micromachining applications, stems from the high peak power of the pulse, able to bridge the band gap via multiphoton ionization, generating seed electrons for other electron multiplying processes such as impact ionization.² For sufficiently high carrier densities ($>10^{21}$ electrons/cm³), dielectric breakdown occurs and a dense, hot surface plasma is formed, eventually leading to the ablation of a thin surface layer. The last decade has witnessed a considerable effort to clarify the underlying mechanisms by studying the influence of the pulse duration^{1–6} and the material^{5,7–9} on the ablation threshold, as well as the dynamics of the ablation process.^{7–9} Despite this effort, the considerable differences in the reported ablation threshold values and the proposed underlying mechanisms demonstrate that many questions still remain open.^{2–5}

In this letter we provide a detailed study of ablation dynamics in the most widely studied dielectric material, fused silica. Using femtosecond time-resolved microscopy we have investigated the temporal and spatial evolution of the surface ablation process induced by single femtosecond laser pulses. This pump-probe technique allows snapshots of the surface reflectivity to be recorded at different time delays after the pump pulse has reached the sample surface, providing subpicosecond temporal and micrometer spatial resolution. The work of von der Linde and Sokolowski-Tinten *et al.*, who further improved the basic technique and added new modalities, has contributed strongly to the understanding of complex ablation phenomena in semiconductors and metals.¹⁰ However, this technique has been applied only on a few occasions to the study of dielectric materials^{7,8} and no time-resolved data have been published on fused silica so far.

The laser used for irradiation provided pulses of 120 fs duration at 800 nm (λ_{pump}). At this photon energy fused silica (“Lithosil” by Schott) requires a five-photon process to cross the band gap (7.2 eV). Irradiation was performed in air and each surface region was irradiated only once in order to avoid incubation effects.^{5,11} The *s*-polarized laser beam was focused onto the sample at an angle of incidence of 54° to a spot size of $35.7 \times 23.2 \mu\text{m}^2$ ($1/e^2$ diameter). The temporal evolution of the surface reflectivity was measured using a femtosecond time-resolved microscopy setup described in detail elsewhere.¹² Briefly, a fraction of the pump pulse was frequency doubled to 400 nm (λ_{probe}) and used as a low-intensity probe pulse to illuminate the sample at normal incidence. The sample surface was imaged onto a 12 bit charge coupled device camera using a microscope objective [20×, numerical aperture=0.42] and a tube lens, with a 10 nm bandpass filter centered at λ_{probe} placed in the imaging path. The temporal resolution of the system is ≈ 500 fs.

Figure 1 shows images of the fused silica surface at different delays, excited at a peak fluence of 12.8 J/cm². At $t=100$ fs, a weak reflectivity increase can be observed. As will be shown later, this increase is caused by the formation of a dense electron plasma at the surface and reaches its maximum value at about $t=1.5$ ps. After that, the reflectivity decreases, reaching values below the one of the unexposed surface ($t=10$ –500 ps), which indicates the occurrence of surface ablation.⁸ Interestingly, this decrease occurs only in a

FIG. 1. Surface reflectivity images ($\lambda_{\text{probe}}=400$ nm) of fused silica at different delay times t (see image labels) after exposure to the pump pulse ($\lambda_{\text{pump}}=800$ nm, 12.8 J/cm²). The intensity is encoded in a linear gray scale with an optimized contrast in each case. The frame size is $57 \times 36 \mu\text{m}^2$.

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FIG. 2. (Color online) Temporal evolution of the characteristic features of the image sequence shown in Fig. 1. Surface reflectivity at different positions (inset) and thus different local fluences (labels). The inset corresponds to an image taken at 7 ps delay.

relatively large central region, whereas a narrow outer ring shows a higher reflectivity than the unexposed surface. The image obtained at $t=10$ ns demonstrates that the ablation process has finished, featuring the same visible crater as can be seen after several seconds ($t=\infty$). A comparison between the images obtained at $t=1.5$ and 10 ps with those obtained at $t=10$ ns and ∞ reveals the existence of a transient free-electron plasma region that extends beyond the visibly ablated region.

The evolution of the surface reflectivity as a function of the delay time, $R(t)$, is plotted in Fig. 2. The spatial profile of the laser pulse at the sample plane was determined to be Gaussian,⁷ which allows extracting $R(t)$ at different local fluences, corresponding to different positions of the spot, from the same image sequence. At the peak fluence (12.8 J/cm^2), the reflectivity increases from $R_0=0.036$, for the unexposed region, up to $R_{\text{max}}=0.234$ at $t=1.5$ ps, which corresponds to a relative increase of 550%. This large value confirms the origin of the reflectivity increase to be free-electron plasma. The considerable delay between the end of the pump pulse and the occurrence of R_{max} is consistent with other reports.^{9,13} The reflectivity decay following R_{max} is initiated by a decrease of the electron density due to the expansion of the free-electron plasma during ablation. The reflectivity reaches values below R_0 already at a 7 ps delay, maintaining a constant level ($R=0.01$) between 10 and 500 ps, before recovering to values close to R_0 on a time scale of a few nanoseconds. The low reflectivity values are attributed to ablation.⁸ Due to further expansion of the ablating material, this becomes transparent to the probe beam light for delay times in the nanosecond range (fluence dependent). As a consequence, the setup is now again sensitive to the processes occurring at the surface.

We have performed calculations of the reflectivity evolution based on the Drude model for a free electron gas.¹⁴ The damping term is given by the electron-electron scattering time τ , which is related to the electron density n_e as $\tau = \tau_1 \times n_c/n_e$.¹⁵ It is worth pointing out that it is λ_{pump} that defines the critical electron density n_c ($1.7 \times 10^{21} \text{ cm}^{-3}$), whereas λ_{probe} is used to calculate the reflectivity evolution for comparison with the measured reflectivity data. This simple model yields $\tau_1=3.7$ fs to match our experimental value of $R_{\text{max}}=0.23$. We have also applied this model with the same value for τ_1 to the data reported in Ref. 8, obtaining

FIG. 3. (Color online) Upper row: Transient reflectivity image at $t=10$ ps ($R_{10 \text{ ps}}$), static white light reflection image (R_{WLM}) and surface topography from white light interferometry (D_{WLI}) of the irradiated area. Bottom: Horizontal cross sections through these images, normalized to its maximum value for $R_{10 \text{ ps}}$ and to the unexposed region for R_{WLM} .

excellent agreement. This fact may indicate that the electron-electron scattering time depends very little on the glass composition. However, as already pointed out by Sun *et al.*¹⁶ the τ_1 values reported in literature do vary considerably, from less than 1 fs up to tens of femtosecond, even for the same material. The reflectivity evolution at intermediate local fluences (10.5 and 8.5 J/cm^2) in Fig. 2(a) is similar to the one observed at the peak fluence, differing mainly in the lower R_{max} value obtained as a result of the lower local electron plasma density. Using a similar setup (pump 800 nm, probe 800 nm), although probing only at a single point in the center of the pump spot, Chowdhury *et al.* have observed a similar behavior for high and intermediate fluences.⁹

A markedly different behavior, however, can be observed for the curve at the lowest local fluence plotted (6.4 J/cm^2). Here, R_{max} occurs later ($t=3$ ps) and its amplitude is much lower. Moreover, the subsequent decrease is much slower and no appreciable decrease below R_0 can be observed for any delay, indicating the absence of surface ablation. The apparent decay time of the electron plasma is ≈ 17 ps, which is consistent with the value reported in Ref. 13, but much longer than commonly reported values (≈ 150 fs).^{16,17} These very short decay times are attributed to the formation of self-trapped excitons and have been determined in the bulk at much lower electron densities (two to three orders of magnitude) than those present here. We thus conclude that the 17 ps value determined in our case corresponds to the overall decay time of the dense electron plasma, including energy relaxation by phonon emission and scattering as well as electron trapping, at that particular local fluence. If the material in this region liquefies cannot be determined by our setup due to the low reflectivity contrast between liquid and solid glasses.

We have characterized the sample after irradiation in reflection using white light microscopy (WLM) and white light interferometry (WLI). In Fig. 3, the so-obtained reflectivity image (R_{WLM}) and topography map (D_{WLI}) are compared against the transient reflectivity image at $t=10$ ps ($R_{10 \text{ ps}}$). Interestingly, the R_{WLM} image shows a weak ring of increased reflectivity within the same region as the transient annular plasma ring in $R_{10 \text{ ps}}$. This fact can be appreciated more clearly in the horizontal cross-sections through the center of these images (Fig. 3, bottom). The normalized increase

in R_{WLM} reflectivity is $\Delta R/R \approx 3\%$, which is consistent with a refractive index increase of $\Delta n/n \approx 0.01$, as reported to occur upon fs laser irradiation inside bulk fused silica for the production of optical waveguides.¹⁸ In surface irradiation experiments by other groups this subtle effect seems to have gone unnoticed. The location of the annular ΔR -region coincides with the region between the maximum reflectivity of $R_{10 \text{ ps}}$ and its maximum spatial extension (dotted vertical lines). It demonstrates that the annular ΔR -region is produced just outside the visibly ablated region, since the dark region in $R_{10 \text{ ps}}$ corresponds to the visibly ablated region at $t = \infty$ (c.f. Fig. 1). This interpretation is consistent with the surface topography after irradiation (D_{WLI} , Fig. 3). The cross section reveals two distinct regimes; a deep ablation crater in the center ($\Delta d \approx -150 \text{ nm}$) and a more subtle surface depression at radii $> 19 \mu\text{m}$ ($0 \text{ nm} > \Delta d > -30 \text{ nm}$). The latter is spatially coincident with the region of increased reflectivity in R_{WLM} and $R_{10 \text{ ps}}$ and can have several origins, including material densification and Coulomb explosion. Densification would be consistent with our observation of a positive ΔR corresponding to a Δn -increase. Based on the assumption of a linear relation between refractive index n , material density ρ and thickness d of the transformed volume in fused silica we can estimate $\Delta n/n \approx 0.01 \approx \Delta \rho/\rho \approx -\Delta d/d$. For a measured maximum shrinking of $\Delta d < -30 \text{ nm}$ (Fig. 3 for radii $> 19 \mu\text{m}$) this relation indicates $d \approx 3 \mu\text{m}$. Such a value is of the same order as the one ($d \approx 1 \mu\text{m}$) reported by Ben-Yakar *et al.* upon irradiation of borosilicate glass.¹⁹ The second possible origin, gentle material removal via Coulomb explosion as recently reported in sapphire²⁰ would also be consistent with surface depression but cannot explain the positive ΔR after irradiation. Using the Drude model, we have calculated the electron density associated with the experimentally observed R_{max} values in the outer region, yielding values of $n_e \approx 1.6 \times 10^{22} \text{ cm}^{-3}$. Such high n_e values support the hypothesis of a direct photoinduced structural transformation, as opposed to a densification caused by a radially expanding shock wave.²¹ Similarly, lateral carrier diffusion cannot account for the dense electron plasma outside the crater since the typical diffusion length is $\approx 100 \text{ nm}$,⁶ much shorter than the spatial extension of the transformed region.

Finally, our results demonstrate the difficulty to assign a sharply defined threshold for surface ablation of fused silica. The visible extension of the crater (Fig. 1, $t = \infty$) is considerably smaller than the extension of the annular transient plasma emission region (Fig. 1, $t = 10 \text{ ps}$), the region of positive ΔR (Fig. 3, R_{WLM}) and the region of shallow surface depression (Fig. 3, D_{WLI}); all the latter being approximately of the same size. As discussed in detail by Tien *et al.*,² care has to be taken in comparing results from different groups because the experimental parameters (pulse number, duration, wavelength, angle of incidence, polarization, and focusing conditions) or the method for threshold determination (light microscopy and detection of plasma emission) may vary. Our threshold fluence value for the formation of a free-electron plasma (consistent with the appearance of a permanent positive ΔR and shallow surface depression) is found to be $F_{\text{e-plasma}} = 4.7 \text{ J/cm}^2$, and thus in between the single-pulse thresholds reported by Varel *et al.*⁵ (5.8 J/cm^2 using Nomarski microscopy and 5.3 J/cm^2 using plasma emission)

and the one reported by Tien *et al.*² (3.7 J/cm^2 using Nomarski microscopy).

In summary, our experiments provide quantitative information about the temporal and spatial evolutions of the ablation process in fused silica upon irradiation with single femtosecond laser pulses. We report a regime of structural modification below the visible ablation threshold, caused by a transient photoinduced electron plasma. This structural modification becomes manifest in a local increase of the reflectivity. The shallow surface depression observed in this regime is consistent with a material densification that leads to a refractive index increase. A contribution from gentle material removal via Coulomb explosion cannot be ruled out. This regime could play a major role in multiple pulse irradiation studies and help explaining the difference in ablation thresholds compared to single pulse studies.

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