Memory in Nonlinear Ionization of Transparent Solids

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We demonstrate a shot-to-shot reduction in the threshold laser intensity for ionization of bulk glasses illuminated by intense femtosecond pulses. For SiO_2 the threshold change serves as positive feedback reenforcing the process that produced it. This constitutes a memory in nonlinear ionization of the material. The threshold change saturates with the number of pulses incident at a given spot. Irrespective of the pulse energy, the magnitude of the saturated threshold change is constant ($\sim$20%). However, the number of shots required to reach saturation does depend on the pulse energy. Recognition of a memory in ionization is vital to understand multishot optical or electrical breakdown phenomena in dielectrics.

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Intense, nonresonant femtosecond light pulses will ionize bulk atomic [1] or molecular gases [2], transparent liquids [3] or solids [4], when focused inside them, through nonlinear interaction with the material. However, solids are unique in that the material in the focal volume remains in place between laser shots. Any nonlinear laser-induced chemical changes will accumulate and the laser-modified material constitutes a feedback mechanism, or a nonlinear memory in the system. Current models of intense light interaction with dielectrics [4–6] do not take this memory effect into account, yet it can be very important. If chemical changes lower the ionization threshold, then the feedback on the ionization process is positive and any plasma nonuniformities will be reinforced. Such a mechanism has been proposed [7] to play a pivotal role in the formation of ordered nanostructures in fused silica following femtosecond laser irradiation [8,9]. Feedback must influence the interaction and evolution of any nonlinear phenomena developing over multiple shots.

We demonstrate the existence of such a feedback by measuring the transmission of the ionizing pulse through the material. We find that the ionization threshold reduces if the material has been previously ionized. The change, which appears to be permanent, is not caused by scattering or resonant absorption since transmission in the low intensity linear regime remains unchanged. We measure that the ionization threshold for fused silica is 1.2×10^{13} W/cm^2 on the first shot and that the threshold reduces on each laser shot until it reaches a saturation value that is 20% lower. We show that the saturated threshold is independent of the peak pulse energy. However, we find that the rate at which the threshold approaches the saturated value depends on the free carrier density in the focal region and therefore on the pulse energy.

In a multiphoton context, a 20% reduction in the threshold is large. Because of the nonlinear interaction it corresponds to a large local difference in absorption. Thus our results show a new kind of nonlinearity where chemical change provides feedback that can drive a shot-to-shot nonlinear interaction. No laser-induced breakdown process in dielectrics will be free of this nonlinearity.

Our work is related to experiments that have observed incubation effects on damage thresholds for light interacting with dielectric surfaces and bulk glass [10–13]. The causes of these incubation effects are not well established due to the complexity of the damage process. As ionization is the first step in this process it is likely that nonlinear memory is important here too.

For our experiment we used 40 fs, 800 nm pulses from a Ti:sapphire laser operating at 400 Hz. The pulses are focused inside the glass samples mounted on precision X, Y stages, using a 0.25 NA microscope objective. A combination of a half-wave plate and a polarizer controls the intensity of incident light. The input beam is prechirped to compensate for material dispersion.

We use integrating spheres to monitor both the incoming light fluctuations and the transmitted light. This ensures that the transmitted beam is collected completely, even if scattered or defocused by the plasma formed by ionization. The transmission is measured on a shot-to-shot basis using a computer-controlled data acquisition system.

Figure 1 illustrates some of the main characteristics of the nonlinear memory in SiO_2. With the laser firing at 400 Hz the transmission was measured on a shot by shot basis while the pulse energy was ramped up to 100 nJ and then back down again without moving the focal spot. The figure emphasizes four major features of the interaction. (a) The transmission drops monotonically from unity with the initiation of ionization; it defines an ionization threshold. Beyond this threshold, the transmission is reduced with an increase in pulse energy. (b) The transmission curve does not retrace when energy is decreased, indicating a memory induced in the material by the previous laser shots. Since the focus is fixed, the total number of shots incident at the spot increases continuously during the experiment. (c) The ionization threshold is indeed reduced with a previous history of ionization. (d) There is no change in transmission at low energies: the memory can

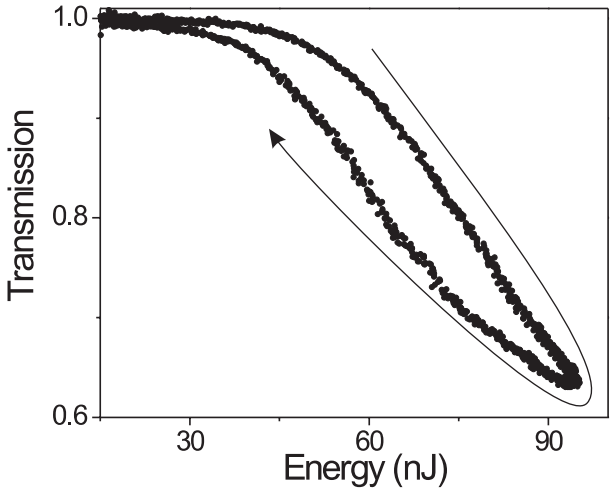

FIG. 1. Nonlinear absorption hysteresis inside fused silica. Transmission is plotted as a function of pulse energy. Keeping the laser focus at a fixed spot the energy is ramped up from shot to shot and then back down. The full cycle consists of 17 000 shots. The arrow shows the path of increasing number of shots.

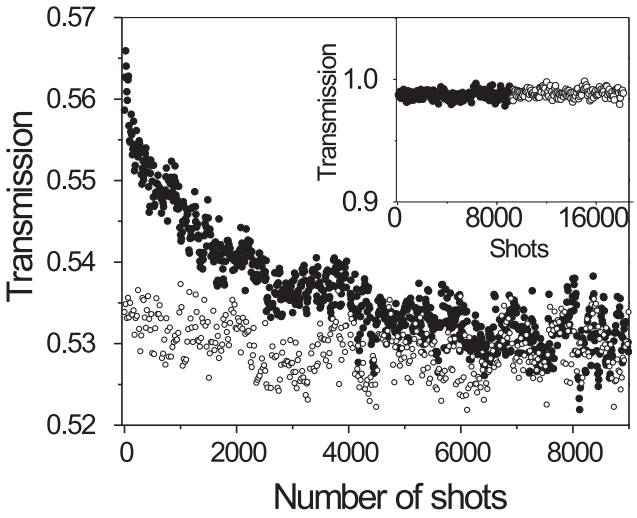

FIG. 2. Nonlinear absorption as a function of exposure at a fixed pulse energy (160 nJ). Transmission is plotted as a function of the number of laser shots. The solid circles are the result of starting in material that has not been exposed previously. The open circles show the transmission through the same spot having left the laser off for 1 h. The inset shows the transmission at low intensities before (open circles) and after (solid circles) the irradiation, demonstrating that the memory operates only in the nonlinear regime.

be observed only if the pulse energy exceeds the ionization threshold. Thus, the memory is inherent to nonlinear ionization and not caused by the cumulative damage in the material.

Figure 2 zeros in on the nonlinear memory that is uncovered by the hysteresis-like behavior when the laser intensity is increased and then decreased. It shows the transmission of an ionizing pulse as a function of number of laser shots in SiO_2. The pulse energy is 160 nJ, approximately 3 times the ionization threshold of fresh material. Following the first shot, the solid circles in the figure show that the transmission of every subsequent shot monotonically decreases and saturates after a few thousand shots. Even at these energies, there is no damage induced at the focal spot that affects transmission. This is verified by measuring the transmission of low energy pulses (10 times below the ionization threshold) through the irradiated spot and a fresh spot. Within the accuracy of our measurements there is no difference in transmission (Fig. 2 inset). Thus the memory exists in nonlinear ionization itself. The open circles in Fig. 2 show the transmission at the same spot after a delay of 1 h. There is no loss in nonlinear memory after 1 h. It is impractical to maintain alignment through the same spot for extended periods but we have qualitative evidence that the memory is permanently embedded in the material. This is further supported by the fact that the magnitude of the transmission change remains invariant of the laser repetition rate from 40 Hz to 100 kHz.

Having shown the existence of the nonlinear memory and how it evolves as a function of the number of shots, we now quantify the change by modeling the transmission. Our approach is based on the self-limiting absorption model for bulk dielectrics that recognizes that nonlinear absorption depletes the beam as it propagates towards the focus [5,14]. It is a unique feature of multiphoton ionization in condensed media that an ultrashort laser pulse will be depleted of photons long before the medium is depleted of unionized atoms. For example, the density per unit area of atoms over the focus is given by $n_a z$ where n_a is the atomic density and z is the confocal parameter of the laser beam. The comparable fluence is $I\tau/kh\nu$ where I is the light intensity, τ the pulse duration, $h\nu$ the photon energy, and k the number of photons absorbed. If $z = 10\ \mu$m, $n_a = 2 \times 10^{22}\ \mathrm{cm}^{-3}$, $\tau = 40$ fs, $h\nu = 2.5 \times 10^{-19}$ J, and $I = 10^{13}\ \mathrm{W/cm}^2$, all typical numbers, then there are 100 times more atoms available than can be ionized by the pulse.

Figure 3 compares the transmission curves of fresh glass (obtained by moving the sample between shots) and glass that has previously been exposed to 10 000 shots at 160 nJ/pulse, sufficient to saturate the memory effect. The solid line fits are obtained by solving the self-limiting model numerically and include avalanche ionization, with the carrier generation rate given by

$$\frac{dn}{dt} = \alpha I n + W(I), \tag{1}$$

where α is the avalanche coefficient and $W(I)$ is the nonlinear ionization rate. Here we have chosen to approximate the absorption rate as $W(I) = \sigma_k I^k$, where k is the multiphoton order and σ_k is the kth order cross section. The fits take into account the fact that the profile of the laser beam at the focus of our 0.25 NA objective was found to be

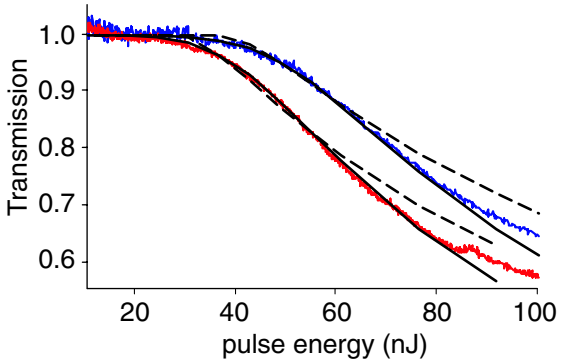

FIG. 3 (color online). modeling nonlinear absorption to characterize the memory. Transmission is plotted as a function of laser pulse energy. The experimental curve showing the higher threshold (blue in the online version) is obtained by moving the sample so that fresh material is irradiated on each shot. This curve forms a baseline for assessing the memory effect. The lower threshold curve (red online) is obtained at a single spot after exposure to 10 000 shots at 160 nJ. This is sufficient to saturate the memory effect. The solid lines through the data are fits from numerical modeling that includes nonlinear absorption due to multiphoton and avalanche ionization and considers pulse propagation as described in the text. The dashed lines show fits of a simple sudden onset analytical model, that neglects avalanche, to the early portions of the transmission curves. This fit can be used to obtain threshold intensities as also described in the text.

approximated by a super-Gaussian rather than a Gaussian. Both fits were obtained with α set at 4 J^{-1} cm^2, the same as the value obtained by Lenzner *et al.* from measurements of damage thresholds on fused silica surfaces [10].

Given the 9 eV band gap of fused silica the appropriate value of k is 6. For the fresh glass we found $\sigma_6 = 4 \times 10^{13}$ $(\mathrm{TW\,cm^{-2}})^{-6}\,\mathrm{cm^{-3}\,ps^{-1}}$ and for the memory saturated glass we found $\sigma_6 = 1.6 \times 10^{14}$ $(\mathrm{TW\,cm^{-2}})^{-6}\,\mathrm{cm^{-3}\,ps^{-1}}$, an increase of a factor of 4. These cross sections are of the same order as those predicted by Keldysh theory for a band gap of ~9 eV for ionization in the multiquantum absorption regime [15]. The drop in ionization cross section indicates a permanent change in the material that effectively reduces its band gap. The departure of the fit from the transmission results at high pulse energy is attributed to plasma defocusing that is not taken into account in the model.

Ionization thresholds are another useful approach to quantify changes in the nonlinear interaction. We obtain such thresholds I_{th} by alternatively fitting the transmission curve using a model that approximates $W(I)$ to a step function, i.e., $W(I) = 0$ for $I < I_{\mathrm{th}}$ and $W(I) = \infty$ for $I > I_{\mathrm{th}}$. For a Gaussian beam profile the transmission as a function of pulse energy can be described analytically [14] but to allow for the super-Gaussian beam profile used in our experiments we carry out the modeling numerically. Because this simple model does not include avalanche ionization and we are primarily interested in obtaining the ionization threshold, we fit only the early part of the transmission curve. The results are shown as the dashed lines in the figures. We find an ionization threshold of 1.2×10^{13} $\mathrm{W\,cm^{-2}}$ for fresh fused silica and a threshold of 9.5×10^{12} $\mathrm{W\,cm^{-2}}$ for material where the memory effect has been saturated.

Similar results are obtained with laser pulse energies up to at least 550 nJ, about 10 times the threshold. The only difference is that the rate at which the memory is established changes. The memory effect always saturates at a drop in threshold of ~20%. The memory effect is also observed with laser pulse widths of up to at least 2 ps.

From Fig. 2 and related plots made at other pulse energies we obtain first-order rate coefficients for the rate of change in transmission with number of laser shots. The results are plotted in Fig. 4. The rate constant first increases with pulse energy but then reaches a maximum value and remains constant. This is a signature of the self-controlled nature of energy deposition inside dielectrics by nonlinear absorption. The solid line on the same curve is the calculated peak plasma density in the focus of the laser pulse, calculated numerically when applying the self-limiting model as described above. The curve shown was obtained with the plasma generation rate given by Eq. (1) and using the same values of α and σ_k used to produce the fits to the transmission results plotted in Fig. 3. The plasma density saturates as a consequence of the pulse being depleted by nonlinear absorption before it reaches the focus. Clearly the data points fall almost on the plasma density curve given that one point is used to determine a scaling factor. The rate constant describing the change in threshold is proportional to the number of electron-holes that are generated.

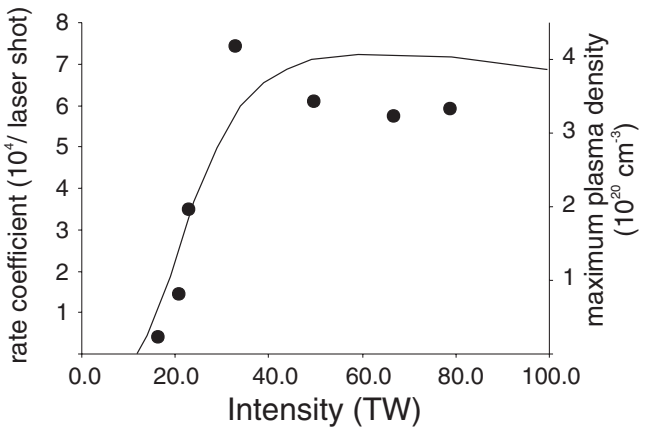

FIG. 4. The rate coefficient for the change of transmission with number of laser shots (referred to the left axis) as a function of the peak pulse intensity that would be obtained in the absence of absorption (●). The line (referred to the right axis) plots the calculated maximum plasma density reached per shot as obtained by numerical modeling as described in the text.

The nonlinear memory appears to have a common origin with femtosecond dielectric modification in SiO_2 and other dielectrics. In fact a lowering of the threshold for nonlinear absorption signals a lowering of the band gap in SiO_2 which would indeed increase the refractive index as is observed [16]. Raman experiments indicate that there is a chemical change in which the five and six membered rings that dominate the local order in amorphous SiO_2 shrink to predominantly from three to four membered rings [17,18]. The modified nonlinear threshold could arise from this modification, or from the many defects that are almost certainly generated by this process. Like the memory effect, both the refractive index changes and the changes in Raman response are known to show saturation with exposure [18,19].

In conclusion, we have measured a feedback mechanism in the nonlinear ionization of SiO_2 with ultrashort pulses. It manifests itself as a lowering of the ionization threshold. We have shown that the rate of reduction depends on the plasma density that is reached in the material. If this is correct at microscopic levels, then inhomogeneities in the breakdown will grow as a result of this positive feedback. We expect that such inhomogeneities can build into nanoplasmas whose interaction with strong fields can play a large role in the formation of ordered nanostructures during dielectric breakdown [7].

Nonlinear memory is likely to be a general feature of dielectric breakdown when it occurs inside the dielectric. We observe it in BK7 glass, where color centers play a partial role and in SiO_2 where chemical changes appear to dominate. It may occur in crystalline media where the crystalline structure is modified, or in polymers where more complex chemistry can occur. However, in all of these cases, if the laser pulse is very short the pulse contains insufficient energy for conventional damage. Unusual nonlinear phenomena are likely to occur.

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