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Exciton-seeded multiphoton ionization in bulk SiO_2

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In a femtosecond pump-probe experiment the pump pulse injects a modest density of free carriers by multiphoton absorption. Measuring the nonlinear absorption of the probe pulse we observe exciton-seeded multiphoton ionization. The excitons self-trap in SiO_2 in <300 fs following free-carrier injection and decay biexponentially with lifetimes of 34 ± 8 and 338 ± 67 ps at room temperature. The extent of the probe-pulse absorption provides a model-independent demonstration that avalanche ionization plays a significant role in free-carrier generation by laser pulses as short as 45 fs. Free-carriers injected into a dielectric from extreme-ultraviolet (XUV) sources created by high harmonic or attosecond pulse generation and then avalanched with a perfectly synchronized infrared (fundamental) probe pulse, can provide a route to nanoscale laser machining.

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The threshold for nonresonant absorption of high-intensity laser pulses in dielectrics is determined by the band gap of the material.[1] Prepopulating intraband states could, therefore, present a way of controlling light-material interaction. What is essential for control is to create more free carriers from trapped states than from valence-band to conduction-band transitions and to have these seed carriers dominate the subsequent absorption. This would be analogous to how preionization controls electrical breakdown.[2,3] One aim of this Brief Report is to show that seeded control is possible in dielectrics. As we will discuss in the conclusion, seeded control opens a path to precision guiding of laser machining, laser surgery, or laser material modification in much the same way one can guide lightning (electrical breakdown) in the atmosphere.[3]

We concentrate on self-trapped excitons (STEs) as the source of seed electrons. First we identify and isolate multiphoton absorption due to self-trapped excitons. This allows nonlinear absorption to be exploited as a new method to probe trapped excitons. We then measure room-temperature exciton dynamics in amorphous fused silica and establish that the free carrier to STE conversion has a yield that is close to unity and that the STEs decay biexponentially in under 1 ns. Finally, we use STE seeding for a model-independent measurement of avalanche ionization, showing that avalanche is important at intensities below the normal free-carrier generation threshold. The latter measurement confirms that seeded control is achievable.

Ours is not the first experiment to study exciton dynamics in dielectrics. SiO_2 has attracted particular attention due to its technological importance in photonics and electronics. In both crystalline quartz, c-SiO_2 and amorphous silica, a-SiO_2, it is accepted that free-carrier generation in the bulk by ionizing radiation leads to the production of metastable self-trapped excitons.[4] The situation is clearest in low-temperature steady-state experiments on c-SiO_2. Time-resolved luminescence, transient absorption and transient volume change measurements identify an STE, thought to consist of a nonbridging oxygen hole Si E' center pair that has a natural lifetime of 1 ms.[5] We concentrate on a-SiO_2 where a similar STE is also reported,[4] although the situation is more complex due to the greater interference of pre-existing permanent defects and the provision for a range of local environments. Multiexponential decay is typically observed.[6] Nevertheless, in both cases there is a thermally activated nonradiative decay channel that begins to open up above 160 K that has prevented study of STE dynamics at room temperature.

We are also not the first to apply femtosecond pump-probe methods to dielectrics. Using weak-field probes, experiments have shown that free carriers generated by femtosecond laser-multiphoton ionization (MPI) are captured in 150 fs.[7–9] We, in contrast, apply a high-energy probe pulse to specifically observe STE exciton formation and to study the effect of STEs on multiphoton ionization in a-SiO_2. It is the 3 eV difference in energy between creating free carriers from excitons (6 eV) and from the valence band (9 eV) that allows us to selectively interact with excitons by multiphoton ionization—without a noticeable contribution from the valence band.

Our experiment uses 800-nm laser pulses with a minimum duration of 45 fs. Details of the experiment are provided in the auxiliary material, including how collinearity between pump and probe beams is ensured.[10] By using modest fluence with tight focusing (0.25 NA) below the surface we ensure that we operate at powers below the self-focusing limit (<1.5 MW in a-SiO_2). Due to tight focusing and the local nature of the interaction, the intensity is low at the surface and we investigate unambiguously only bulk effects.

The high nonlinearity of both pump and probe interactions is revealed by the dependence of the absorption of the laser pulses on their energy shown in Fig. 1. For single-pulse (pump only) experiments (curve a), there is characteristically no absorption until a threshold energy that corresponds to an intensity of $\sim1\times10^{13}$ W cm^{-2} is reached. Thereafter the absorption increases with pulse energy. This behavior is characteristic of multiphoton ionization.[1] In dielectrics the nonlinear ionization rate is strongly dependent on the bandgap, Δ, just as it is dependent on the ionization potential (IP) in isolated atoms and molecules. Excited states of atoms and molecules ionize more easily than their ground states because the IP is decreased. Similarly, we expect STE states in

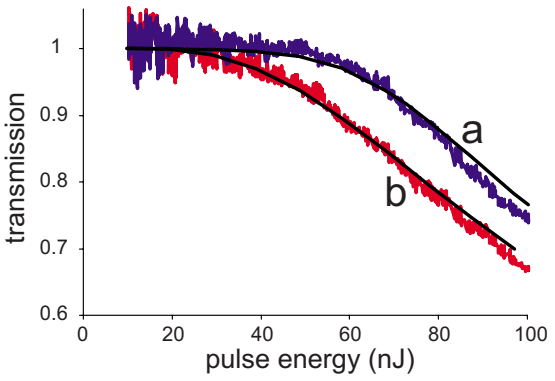

FIG. 1. (Color online) Nonlinear absorption of a focused (NA 0.25), 800 nm, and 45-fs laser pulse in a-SiO_2 as a function of pulse energy. Curve (a) is obtained with a single-laser pulse. Curve (b) is obtained for the probe pulse of a pump-probe pair separated by 3 ps. The pump energy was 70 nJ. The smooth curves are fits from numerical modeling of the pulse propagation taking into account nonlinear absorption due to multiphoton and avalanche ionization as described in the text.

dielectrics to ionize more easily than the unexcited bulk. In curve (b) of Fig. 1, when a STE population is prepared 3 ps in advance by a 70-nJ pump pulse, we observe a significant reduction in the absorption threshold that demonstrates this effect. Once absorption starts there are three contributions to the energy extracted from the beam: (1) energy expended to create free carriers from self-trapped excitons; (2) energy expended through inverse Bremsstrahlung and avalanche ionization, and (3) energy expended to create free carriers by valence to conduction-band ionization.

The contribution of avalanche to nonresonant femtosecond laser absorption in dielectrics remains a matter of debate. Some argue that avalanche plays no role for pulses <100 fs.[8,11] We have presented evidence for a field-assisted avalanche mechanism[12] that explains how avalanche signatures can be observed well below 100 fs.[12,13] However, the controversy persists because all investigations have been indirect, relying on modeling of the complex interplay in time and space of nonlinear processes through the focus to relate to experimental observables.

The results in Fig. 1 provide a *model-independent* confirmation that avalanche must play a significant role for 45 fs pulses. In the absence of avalanche when pump and probe have the same energy, energy conservation requires a probe absorption $A_{probe} \leq A_{pump}(1+j/k)$, where k and j are the multiphoton orders of ground state and STE ionization, respectively. Figure 1 shows that this does not hold. For instance, at 70-nJ probe energy we find $A_{pump}=0.07$ and $A_{probe}=0.16$. With the order ratio $j/k=4/6$, appropriate for an STE energy above the valence band, E_{STE} of ~ 3 eV (Ref. 14) and a band gap of 9 eV, the measurement exhibits large extra-absorption ($\approx 30\%$) that can only be attributed to avalanche seeded by STE ionization. Even more absorbed energy must come from avalanche if the STE ionization is not saturated.

To understand Fig. 1 more quantitatively and to develop the concept of our multiphoton pump-multiphoton probe experiment requires that we take both MPI and avalanche ionization into account. The fit to the single-pulse curve in the figure is obtained by numerical modeling of the pulse propagation through the focus with the free-carrier generation described by

$$\frac{dn}{dt} = \sigma_k I^k + \alpha I n. \tag{1}$$

Here n is the carrier density and I is the intensity. We model MPI through the term $\sigma_k I^k$ where k is the multiphoton order and σ_k is the kth order cross section, and avalanche ionization through the second term where α is the avalanche coefficient. Setting $k=6$ to correspond to the band gap of a-SiO_2 (9 eV), we adjust σ_6 and α to fit the model to the experiment. As seen in the figure the transmission curve is described well by this approach with $\sigma_6 = 4 \times 10^{13} (\mathrm{TW\ cm^{-2}})^{-6}\ \mathrm{cm^{-3}\ ps^{-1}}$ and $\alpha = 4\ \mathrm{J^{-1}\ cm^2}$ as has been found in previous experiments.[12,15]

To model the drop in threshold observed in curve (b) of Fig. 1 we take into account that electrons from exciton ionization buildup and can act as seed electrons for avalanche. With excitons present, the carrier generation rate must be formulated as

$$\frac{dn}{dt} = \sigma_j' I^j N_{\mathrm{STE}} + \sigma_k I^k + \alpha I n, \tag{2}$$

where σ_j' is the cross section for the STE ionization (the prime distinguishes it as the cross section for an individual exciton rather than a unit volume of bulk dielectric) and N_{STE} is the exciton concentration.

We first use Eq. (1) with values of σ_6 and α from the single-pulse experiment, to calculate the carrier distribution in the focal region as produced by the pump pulse. Next we assume a linear relationship between initial free-carrier and exciton populations, and that the decay to STE is complete in 3 ps (confirmed below). This provides the starting exciton distribution of N_{STE} needed to model the probe absorption using Eq. (2). We treat σ_j' and the yield of STE from free electrons, Φ as variables. The solid curve fitted to the probe absorption curve (b) in Fig. 1 is obtained with $j=4$, $\sigma_4' = 0.0025 (\mathrm{TW\ cm^{-2}})^4\ \mathrm{ps^{-1}}$ and $\Phi=1$.

Figure 1 shows that it is possible to model the pump-probe experiment in a manner that is entirely consistent with what we know about nonlinear absorption in dielectrics. The value required for σ_4' is reasonable, lying between that estimated from Keldysh theory for an effective band gap of $\Delta - E_{\mathrm{STE}}$ and that predicted for an isolated atom having an equivalent IP by Perelomov, Popov, and Terent'ev theory. A second conclusion comes from a sensitivity analysis that shows that we are required to use values for Φ of 1 or close to it. We note that orders of magnitude smaller yields for the conversion of free carriers to STEs have been assumed in some discussions of dielectric modification.[16] The third conclusion is that STEs have a characteristic influence on probe absorption that we now show can be used to follow their dynamics down to the femtosecond time scale.

Figure 2 shows the results of pump-probe experiments over the early time range where free carriers are decaying to produce STEs. Curve (a) is obtained with a weak (low intensity) probe pulse. Its absorption can only be single-photon

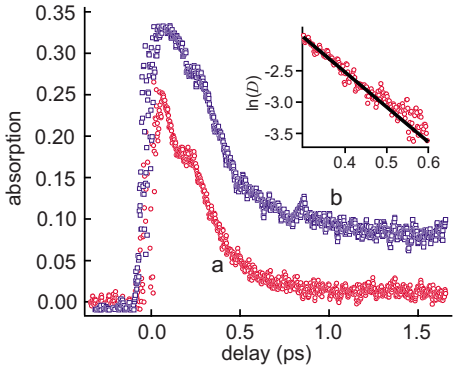

FIG. 2. (Color online) Probe absorption in a-SiO_2 as a function of pump-probe delay. The pump energy was 70 nJ and pulse duration 45 fs. Curve (a) is obtained with a weak-probe pulse (5 nJ) and curve (b) with a strong probe (50 nJ). The inset shows a plot of the log of the optical density, D, as a function of time for the weak probe case showing that the decay of the absorbing species, which are free electrons as discussed in the text, is first order with a lifetime of 179 ± 6 fs.

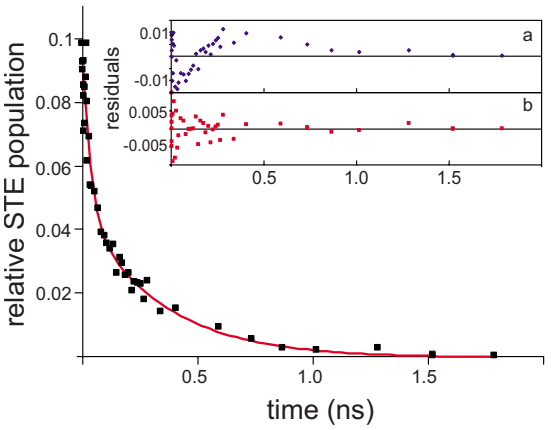

FIG. 3. (Color online) Relative STE population, determined from multiphoton-probe absorption as a function of time. The pump energy was 70 nJ and the probe energy 52 nJ. The inset shows the residuals obtained from (a) single exponential and (b) biexponential nonlinear least-squares fits. The curve through the data points in the main figure is the result of the biexponential fit.

(linear) absorption by the free carriers produced by the pump pulse. The absorption rises on the time scale of the pump duration (45 fs) and decays exponentially with a lifetime of 179 ± 6 fs. This is consistent (within error) with the decay time of 150 fs attributed to free carriers by time-resolved phase-shift measurements.[7] Curve (b) is obtained when the probe energy is raised to 50 nJ, close to the threshold for single-shot multiphoton ionization of a-SiO_2. A fast decaying component remains but a slow one, stable on a 1-ps time scale is observed. Because of the absorption by high-lying free-exciton states into which the electrons initially trap, the fast component is now slightly longer ($\sim$300 fs) than the weak probe result. This is consistent with a decay time of 250 fs of free-exciton states populated by direct band-edge UV absorption.[17] The slow component is consistent with the probe absorption observed in Fig. 1. It is due to the presence of STEs detected through multiphoton absorption.

Varying the pump-probe delay further, Fig. 3 shows that the STE population, produced by a 70-nJ pump pulse, decays in under a nanosecond. The raw absorption curves and details of how we extract the STE population from the absorbance, taking nonlinear absorption and the nonuniform spatial distribution into account are provided in the auxiliary material.[10]

The accompanying residual plots in Fig. 3, obtained by nonlinear least-square fitting, show that at least a double-exponential function, having the form $P_{\mathrm{STE}} = P_1 e^{t/\tau_1} + P_2 e^{t/\tau_2}$ is required to describe the decay. The fit is obtained with $\tau_1 = 34 \pm 8$ ps, $\tau_2 = 338 \pm 67$ ps, $P_1 = 0.047 \pm 0.006$, and $P_2 = 0.046 \pm 0.006$. The two rates are much faster than heat diffusion from the absorbing volume, meaning they relate to a temperature above room temperature due to the energy released as the free carriers relax to STEs. For relaxation to STEs with $E_{\mathrm{STE}} = \sim 3$ eV, we estimate from the calculated electron density, that this is 350 K. Although a number of models might be applicable to describe the biexponential behavior, we note that τ_1 and τ_2 are significantly faster than the limiting high-temperature rates interconversion of the zero-field spin-split states of the triplet STE in c-SiO_2, as estimated from low-temperature emission measurements.[18] It is possible that we are observing the independent nonradiative decay of such states.

If we extrapolate the low-temperature results for STE decay obtained from luminescence, transient absorption, and optical-rotation experiments in c-SiO_2 (Ref. 5) to 350 K we find a nonradiative rate one or two orders of magnitude slower than the measured rates. This may indicate a departure from Arrhenius behavior but may also be due to differences between c-SiO_2 and a-SiO_2.

Before concluding we would like to comment on two issues that are important for technology. First, when modeling multiphoton free-carrier generation and laser machining in dielectrics some authors include a term describing free-carrier trapping while others ignore trapping. Our results show that while the intense laser pulse is present either trapping should be ignored or exciton breakup should be included. Second, we have worked in the injected carrier-density range of $<10^{20}$ cm^{-3}, well below the density required for machining,[13] dielectric modification, or nanoplane formation.[19] If we increase the number of carriers injected then the probe absorption changes dramatically. Absorption abruptly becomes dominated by single-photon absorption which lasts for >30 ns (at 350-nJ pump energy).

In conclusion, we have investigated how the presence of self-trapped excitons modify the response of dielectrics to intense field laser pulses. It has allowed us to time resolve the lifetime of deep traps in SiO_2 at room temperature. These trapped excitons can provide seed electrons for collisional absorption and ionization. Without recourse to any model, these seed electrons allow us to measure that collisional absorption and ionization (avalanche ionization) account for at least 30% of the energy absorption from our $<$50-fs probe pulse. Our measurements show that avalanche can be driven via self-trapped excitons with a probe pulse energy that is below the threshold for multiphoton absorption in unexcited material.

Looking forward, it seems feasible to inject seed-free carriers into a dielectric from extreme-ultraviolet (XUV) sources created by high-harmonic or attosecond pulse generation. Such an XUV pump pulse would allow seed-electron injection to be controlled in space and in time to nanometer and attosecond precision, respectively. These seed electrons can then be multiplied with the perfectly synchronized infrared (fundamental) probe pulse. From a fundamental physics perspective, precisely injected seed electrons would allow avalanche ionization to be studied in unprecedented detail. From a technology perspective, it seems realistic to extend laser machining or modification of dielectrics to spatial dimensions of 10 nm or less. Controlled laser ablation on a 10 nm scale would open the door to nanosurgery of cells (or of DNA), and to nanopatterning/nanolithograpy of dielectric surfaces with unprecedented resolution.

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