Primary Relaxation Processes at the Band Edge of SiO_2

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The kinetics of photoinduced defect formation in high-purity silicas has been studied by femtosecond transient absorption spectroscopy in the visible and ultraviolet. Band edge two-photon excitation produces singlet excitons which decay in 0.25 ps into defects with the absorption spectra of nonbridging oxygen hole centers ($\equiv$Si$-$O$\cdot$) and silicon E' centers ($\equiv$Si$\cdot$). We identify these defect pairs with the self-trapped triplet exciton and the 0.25 ps decay with the motion of the photoexcited oxygen atom. Similar results were obtained with both crystalline and amorphous silica samples.

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The characterization of point defects in silica (SiO_2) has been a subject of continuous interest for well over three decades [1-6]. With the advent of fiber optic communications and the concomitant premium on the ultratransparent qualities of amorphous SiO_2, an understanding of the optical properties of defects has become of paramount importance. The microscopic structure as well as mechanisms of formation of a host of "primary" defects has been the subject of numerous studies and reviews [7,8]. Recent attention has focused on both mechanical [9] and photoinduced [10-12] (or radiation-induced [13]) mechanisms of *permanent* defect formation, as these are of particular technological relevance.

Of more fundamental interest, although by no means unrelated, has been a satisfactory explanation for the apparently intrinsic 2.8 eV luminescence observed in crystalline and amorphous silica following above band gap ($\gtrsim 8$ eV) photoexcitation [14]. The general notion of a self-trapped exciton has often been invoked [15], in which electronic excitation yields dramatically altered potential surfaces, thereby driving structural relaxation. While there has been considerable speculation in the literature regarding these events, to our knowledge there have been no reported experiments capable of directly resolving the relaxation process. Using the technique of femtosecond time-resolved absorption spectroscopy performed in the visible and ultraviolet (UV) regions of the spectrum, we have followed the course of 8 eV band edge excitations. The resultant visible and UV transient spectra agree well with those reported for the nonbridging oxygen hole center (NBOHC) and the silicon E' center, respectively.

The data described in detail below strongly suggest that the primary photophysical event following the absorption of band edge light in silica is the creation of a bound electron-hole pair (singlet exciton) that decays into a NBOHC-E' center defect pair in 0.25 ps. We suggest that this defect pair is in fact the self-trapped triplet exciton. Furthermore, we attribute the observed 0.25 ps decay to the initial lattice relaxation (self-trapping) process. These observations were qualitatively invariant over a variety of amorphous and crystalline SiO_2 samples, leading one to the conclusion that the relaxation can be directly associated with the gross electronic structure of the Si$-$O$-$Si network.

Femtosecond excitation and probe pulses were derived from the output of a colliding-pulse mode-locked dye laser amplified at 10 Hz, which produces 120 fs, 0.5 mJ pulses at $\lambda = 630$ nm. The 4.0 eV (315 nm) excitation pulses were generated by frequency doubling a portion of the laser output in a potassium dihydrogen phosphate crystal. The typical excitation pulse energy was ~ 30 μJ focused to a 100 μm diam spot at the sample. The remainder of the laser pulse was focused in a water cell to generate a continuum, from which a portion was used for probing. To measure transient absorption in the visible, a grating pair was inserted in the probe beam path after the continuum cell to remove the chirp caused by normal dispersion in the water and subsequent lenses. Kinetic traces were obtained by varying the path length of the probe beam with a micron stepping stage and recording the intensity of the transmitted light with silicon photodiodes as a function of probe delay. For transient absorption measurements in the UV, a β barium borate (BBO) crystal was inserted to frequency double the blue portion of the continuum, and the UV light was detected with solar-blind photomultiplier tubes. Both crystalline and amorphous silica samples were studied. To avoid accumulation effects, the samples were mounted on a translation stage that rocked them back and forth in plane. The samples were between 100 and 150 μm thick; thicker samples gave subquadratic intensity dependence, probably due to self-focusing effects. All measurements were performed at room temperature.

The spectrum of the visible induced absorption for a UV grade a-SiO_2 sample (OH ~ 1000 ppm) immediately following excitation is shown in Fig. 1 in units of optical density [O.D. $= -\log_{10}(T/T_0)$, where T is the sample transmission and T_0 the transmission prior to excitation]. The absorption spans the wavelength range 500-750 nm (1.65-2.48 eV), peaking at ~ 630 nm (2.0 eV). The low signal-to-noise ratio, particularly at long wavelengths, arises from shot-to-shot fluctuations in the spectrum of the continuum, which are normalized by averaging approximately 100 pulses in the optical multichannel ana-

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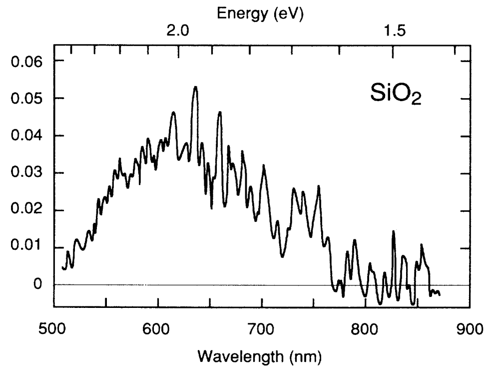

FIG. 1. Spectrum of the transient visible absorption induced in amorphous SiO_2 by intense 4 eV pulses. This spectrum is in good agreement with that of the NBOHC.

lyzer. This spectrum agrees quite well with that of the NBOHC [4,5].

The kinetics of the induced absorption was studied at several wavelengths in the range 500–700 nm using 10 nm bandpass filters and at 630 nm using the laser fundamental without continuum generation. A representative trace is shown as × in Fig. 2, which was taken with $\lambda = 630$ nm probe light. The absorption is seen to rise rapidly, then decay somewhat more slowly to a persistent value roughly 7% of the peak absorption. Scans out to 100 ps showed some modest further recovery ($<15\%$). Substantially the same kinetics was observed at other wavelengths and with crystalline samples. Also plotted in the figure is the induced absorption at 220 nm (5.63 eV) (shown as ◇), which shows an $\sim$1 ps rise to a steady value, but, significantly, no transient peak. We were unable to take a spectrum of the UV absorption because of the narrow bandwidth of the light produced by the BBO doubling crystal. However, we verified that the induced absorption at 235 nm (5.27 eV) was a factor of 3 lower than at 220 nm, in excellent agreement with the spectrum of the Si E' center [1].

The intensity dependence of the induced absorptions was measured using calibrated UV neutral density filters in the excitation beam. Absorption levels were measured in the steady state several picoseconds after excitation. The results are shown by the circles (5.6 eV) and squares (2.0 eV) in Fig. 3. The lines are quadratic fits to the data, which demonstrate that the fundamental excitation with 4 eV light is two-photon absorption.

The density of photoinduced defects was estimated from the absorption data of Fig. 2 (after the fast transient, in the case of the NBOHC). Based on the absorption data of Weeks and Sonder [1], the density of E' centers corresponding to the 0.28 O.D. steady-state absorption was calculated to be 1×10^{18} cm^{-3}. The NBOHC density was estimated to be 4×10^{18} cm^{-3}, based on the absorption and electron spin resonance (ESR) data of Hibino and Hanafusa [6]. Given the uncertainty in spot size, the variation in UV pump intensity, and the uncertainty in absorption of the NBOHC, these values are approximately equal within experimental error. This is consistent with a defect creation mechanism in which the absorption of two photons of 4 eV light leads to the production of a NBOHC-E' center pair. Such pairwise generation of NBOHC-E' centers was recently observed in γ-irradiated silica glass following appropriate fluorine doping to remove precursors of the E' center [16].

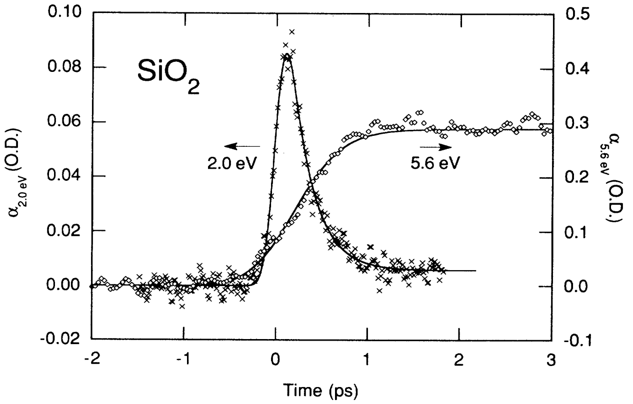

FIG. 2. Kinetic traces of the transient absorption in the spectral regions of the NBOHC (2.0 eV, 630 nm) and the silicon E' center (5.6 eV, 220 nm) induced in silica by $\sim$0.1 ps 4 eV pulses. The smooth curves through the data points are fits to a simple three-level model (see text). From the decay of the 2.0 eV absorption, a 0.25 ps lifetime for the singlet exciton is deduced. The slower response in the UV most likely arises from a temporally broadened probing pulse.

Although the value of the band gap of silica is not very well known, there is general agreement (based on reflectivity and photoluminescence excitation spectra) that it is approximately 9–11 eV independent of allotrope, with a Wannier exciton state lying $\sim$1.3 eV below the conduc-

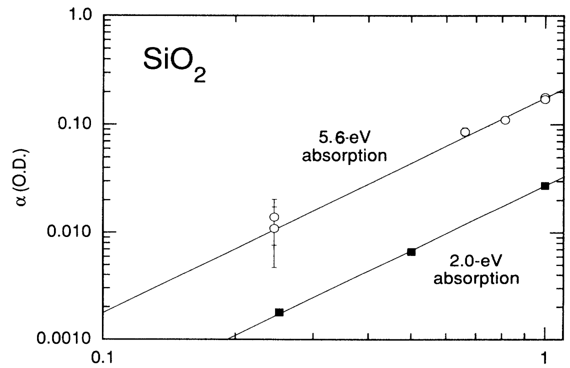

FIG. 3. Dependence of the induced absorption in the visible (2.0 eV) and the UV (5.6 eV) on the intensity of the 4 eV excitation pulse. Lines are quadratic fits to the data.

tion minimum [17]. The Urbach tail [18] of this excitonic state extends to appreciably lower energies and gives rise to the two-photon absorption with 4 eV pulses [11,19]. The data of Fig. 3 show that the creation of defects depends quadratically on the exciton intensity, indicating that the initial step in the excitation process is the creation of an exciton by two-photon absorption. Since the electric dipole operator is independent of spin, optical excitation produces singlet excitons.

The size of the singlet exciton can be estimated from the character of the band edge states. Those at the top of the valence band are most likely nonbonding oxygen p states [20], and are characterized by a large hole effective mass $m_h \approx (5\text{-}10) m_e$ [21]. Those of the conduction band are primarily silicon s states, although they appear to have a finite admixture of silicon-oxygen antibonding character [21], and have an effective mass of $(0.3\text{-}0.5) m_e$. Assuming a static dielectric constant of 2.3, a simple hydrogenic model yields an exciton radius of 0.28 nm [22], which is larger than the Si-O separation of 0.16 nm. Because of its large mass, the hole of the exciton is localized on the oxygen atom, while the electron is appreciably delocalized over the nearby silicon atoms.

Consistent with the finite antibonding character of the electron state, it is envisioned that electronic excitation reduces the Si—O bond strength [17] and facilitates exciton self-trapping, i.e., the electron and hole become a localized Frenkel pair. The low-temperature 2.8 eV luminescence of the self-trapped exciton in crystalline quartz was shown by optically detected magnetic resonance experiments to derive from an excited triplet state [23]. Fisher, Hayes, and Stoneham have calculated equilibrium configurations for small Si- and O-centered silica clusters in the triplet excitonic state that indicate that the oxygen atom on which the hole is centered is displaced an appreciable fraction of a Si—O bond length compared to the unexcited state [17,24]. Similar calculations of the potential surface of the triplet exciton show that as the oxygen atom moves the exciton energy is reduced by ~ 1.7 eV compared to the unexcited equilibrium configuration [14]. Furthermore, the triplet exciton in the relaxed configuration is calculated to have the 5.8 eV absorption characteristic of the Si E' center [14]. These theoretical studies suggest, therefore, that as the oxygen atom on which the hole is located moves away from one of the silicon atoms to which it was bonded the associated electron becomes localized on that silicon atom and undergoes a spin flip. Similar single-to-triplet exciton conversions have been observed on the subpicosecond time scale in other materials, such as polydiacetylene [25].

The kinetics of the defect-formation process can be understood with a simple three-level rate-equation model. Two-photon absorption of the pump pulse produces bound electron-hole pairs (singlet excitons). These decay either by relaxing to the ground state, with characteristic time k_1^{-1}, or by transforming into a triplet exciton and self-trapping to produce NBOHC-E'-center pairs, with characteristic time k_2^{-1}. The decay rate of the exciton, and the observed rate of defect formation, is given by the sum $k = k_1 + k_2$. The singlet exciton population is then given by $\dot{N}_s = \beta I^2(t) - k N_s$, where $I(t)$ is the excitation pulse intensity, and the defect pair population is given by $\dot{N}_{dp} = k_2 N_s$. We assume that the red absorption arises from both excitons and NBOHC's. We are aware of no calculations of the optical absorption of the singlet exciton to support this assumption. However, the assumed red absorption of the exciton is made plausible by noting the structural similarity of the exciton and NBOHC, in both of which the hole is strongly localized on an oxygen atom. The smooth curve of Fig. 2 is a fit to the data assuming a Gaussian pulse shape for the pump and probe beams, yielding $k^{-1} = 0.25$ ps for the decay of the exciton and the formation of the defect pair, and $\tau = 0.13$ ps for the $1/e$ time of the cross correlation of the pump and probe, i.e., $\int_{-\infty}^{\infty} I_{\text{pump}}^2(t') I_{\text{probe}}(t - t') dt' \propto e^{-t^2/\tau^2}$.

To fit the UV absorption data, it was assumed that only the E' centers cause UV absorption. This assumption seems reasonable since the delocalized electron of the singlet exciton does not resemble the localized electron of the Si E' center. The values of τ and k determined from the fit to the visible data resulted in a rise that was much more rapid than observed for the UV data of Fig. 2. The smooth curve through the UV data was therefore obtained by letting the cross correlation increase to 0.49 ps. This situation most likely results from temporal broadening of the UV probe pulse due to significant dispersion at 220 nm in our apparatus.

An interpretation that cannot be supported by the combined UV-visible data, however, is that the fast relaxation of the visible signal corresponds to the geminate recombination of instantaneously created NBOHC-E' centers. If such were the case, the UV data would also display a fast transient which, even with the degraded time resolution, would have been observed.

We have assumed that the fast transient in the visible data arises from absorption by the singlet exciton. It is conceivable, though unlikely, that the peak is a coherent effect that reflects the cross correlation of the pulses, not the kinetics of exciton decay. To rule out this possibility, we have taken kinetic traces with pump and probe polarizations orthogonal (as in Fig. 2) and parallel. When the polarizations are parallel, a bump appears roughly halfway up the rising edge of the signal, which appears to be precisely such an artifact. Furthermore, the peak in the visible data of Fig. 2 is clearly asymmetric, whereas the cross correlation of the pulses would be symmetric. Finally, the same kinetics was obtained at different wavelengths when the probe was produced by continuum generation, and was therefore not coherent with the excitation pulse. The peak could conceivably arise from free-carrier absorption by ionized excitons, but the spectrum of such an absorption would be broad and would not have a high-energy cutoff as observed in Fig. 1. Nor is it likely to be due to excitation of preexisting defects or impurities, both because of the spectrum and because of the high density of excited defect states ($\sim 10^{18}$ cm^{-3}).

While the present experiments strongly suggest that band edge absorption in pure silica produces excitons that decay rapidly to produce triplet NBOHC-E' defect pairs, and that this process is essentially independent of the allotrope, the production of *permanent* defects may depend upon the presence of preexisting defects. In this context "permanent" means stable at room temperature on the time scale of days. A recent ESR study of defects produced in high-purity silicas by ArF laser irradiation (6.4 eV) found that permanent NBOHC and E' center defects can in fact be correlated with the presence of precursor defects, such as oxygen vacancies and peroxy linkages [11], although the point is controversial [26]. Furthermore, we have observed a more rapid recovery of the relaxed red absorption in high-OH than in low-OH ($\sim$5 ppm OH) silicas, suggesting that the presence of hydrogen reduces the barrier to exciton recombination.

In conclusion, we have presented data that for the first time visualize the process of exciton self-trapping in SiO_2. The spectral signature of the relaxed species resulting from 8 eV band edge excitation bears a strong similarity to the previously well-characterized NBOHC and E' center, which is consistent with theoretical models of the lowest energy triplet exciton state. These observations are largely independent of allotrope, suggesting that subpicosecond exciton self-trapping is fundamental to the Si−O−Si network.

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