Space-Time Observation of an Electron Gas in SiO_2

P. Audebert,[1] Ph. Daguzan,[2] A. Dos Santos,[3] J. C. Gauthier,[1] J. P. Geindre,[1] S. Guizard,[2] G. Hamoniaux,[3] K. Krastev,[2]
P. Martin,[2] G. Petite,[2] and A. Antonetti[3]
[1]*LULI, Ecole Polytechnique, 91128 Palaiseau, France*
[2]*Commissariat à l'Energie Atomique, DRECAM/SRSIM, 91191 Gif sur Yvette, France*
[3]*Laboratoire d'Optique Appliqueé, École Nationale Supérieure de Techniques Avancées, Batterie de l'Yvette,*
91120 Palaiseau, France

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We report the first space-time observation of the ultrafast excitation and relaxation of an electron gas pumped into the conduction band of a wide band-gap insulator by an intense subpicosecond laser pulse. The experiment is based on a new phase-sensitive technique which allows a resolution of 120 fs in time and 5 μm in space. In crystalline and amorphous SiO_2, no evidence of gas expansion has been observed and a mean trapping time of 150 fs for the photogenerated carriers is measured.

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When an ultrashort and intense laser field propagates inside a dielectric medium, it induces a strong polarization field and, if the intensity is high enough, it produces a high density of electrons and holes. This space-time dependent problem is extremely intricate because it involves a number of nonlinear effects such as multiphoton excitation, free carrier absorption, photoemission, electron-phonon interaction, exciton generation, and carrier-carrier interaction, all these basic processes occurring in the presence of a high intensity laser field. Moreover, these quasi-free charges and the likely presence of ultrafast created defects, as well as self-induced effects such as self-phase modulation or self-focusing, can dramatically affect optical wave propagation [1,2]. Understanding the fundamental aspects of laser-dielectric interaction requires detailed knowledge of the energy balance between the laser field, the electrons, and the lattice. Indeed, this is the cornerstone of crucial problems such as the creation of intrinsic defects such as self-trapped excitations [3,4], E' centers in SiO_2 [5,6], or laser heating of free electrons which can lead to optical breakdown [7–9]. Recently, pump-probe experiments with subpicosecond resolution have been carried out to observe the onset of absorption bands attributed to laser-induced intrinsic defects [6,10,11]. This type of experiment can give valuable information about the dynamics of the relaxation process. It is, however, focused on the analysis of a particular defect and the resulting information is restricted to the imaginary part of the index which is proportional to the absorption cross section at a given frequency, while the real part of the index is hidden. Moreover, to our knowledge, the very first parts of the relaxation process, concerning the photogenerated carriers in the conduction band, remain unexplored in wide band-gap insulators.

In this Letter, we apply a new and very sensitive technique [12,13] allowing us to measure the induced polarization and the excitation density during and after a pump pulse with a temporal and spatial resolution of 120 fs and 5 μm, respectively. The principle of this experiment is based on interferences in the frequency domain. The target is probed with two collinear femtosecond pulses separated by a fixed time delay Δt ($\Delta t = 1$ ps in this experiment). These two pulses are then analyzed in a spectrometer. The power spectrum of this sequence of twin pulses is a fringe system whose period is inversely proportional to the pulse separation Δt. It can be written $I(\omega) = 2I_0(\omega)[1 + \cos(\omega\Delta t)]$, where $I_0(\omega)$ is the envelope of a single pulse. If a high intensity pump pulse is focused on the sample at some time between the two probe pulses, the second probe pulse will experience a disturbed dielectric constant. This will induce a phase shift ($\Delta\Phi$) between the two probe pulses and eventually a partial absorption of the second probe pulse. In this case, the spectrum is given by

$$I(\omega) = I_0(\omega)[1 + T + 2T\cos(\omega\Delta t + \Delta\Phi)],$$

where T is the ratio of light transmitted after the pump pulse. The phase shift thus induced can be measured as a function of time by changing the delay between the pump pulse and the probe pulses; the absorption of the probe pulse is obtained simultaneously by measuring the fringe contrast directly on the interference pattern. The experimental setup is given in Fig. 1. For this experiment, we use as a pump a colliding-pulse mode-locked (CPM) dye laser emitting 70 fs pulses at 620 nm. Those pulses are amplified in 5 rhodamine 6G dye cells to energies up to 3 mJ. Probe pulses are produced with part of this beam by continuum generation in a water cell. Frequencies around 560 nm are selected and amplified in three dye cells. Probe pulse duration is 60 fs. The temporal resolution is the sum of two terms: The first is given by the cross correlation of the probe and pump pulses (90 fs in our case), and the second arises from the fact that the two refracted beams propagate with an angle θ. This second term is equal to $n_0\phi(1 - \cos\theta)/(c\sin\theta)$, where n_0 is the refractive index, ϕ the diameter of the pump beam, and c the speed of light.

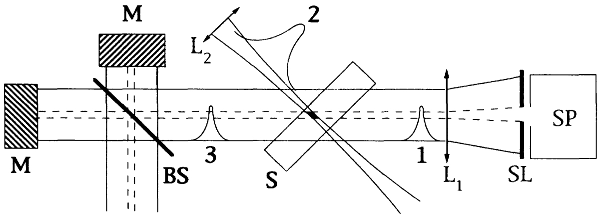

FIG. 1. Principle of the experiment. M: mirror; BS: beam splitter; S: sample; SL: slit, SP: spectrometer; 1,3: probe pulses; 2: pump pulse; L_1: imaging lens, L_2: focusing lens. The black area represents the interaction region imaged on the slit SL by L_1. The corresponding light rays are symbolized by the dashed lines.

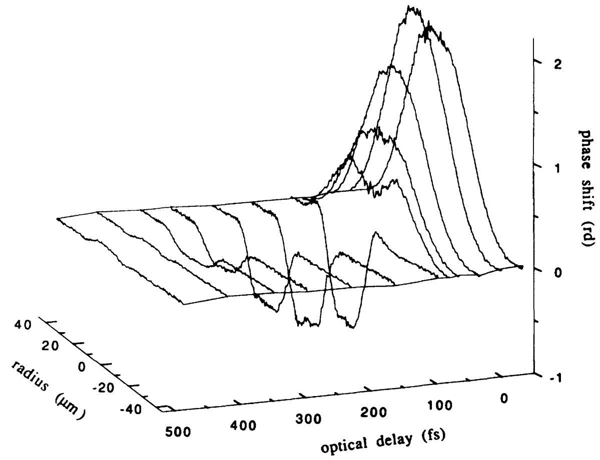

FIG. 2. Phase shift as a function of time and space. The first five curves have been divided by 1.5. The pump intensity is 2.7×10^{13} W/cm^2.

The total estimated resolution is thus 120 fs. The samples are 100 μm thick high-purity [impurity concentration below 1 ppm (parts per 10^6)] amorphous (a-SiO$_2$) and crystalline (α-SiO$_2$) silicon dioxide. The α-SiO$_2$ is cut perpendicularly to the optical axis. The pump beam is nearly at normal incidence, while the probe pulse incidence angle is 45°. Pump intensity is selected by changing the aperture at the entrance of the focusing lens. It ranges from 10^{12} W/cm^2 to a few 10^{13} W/cm^2. At such high intensities, damage may occur at the surface. To avoid this and cumulative effects, we move the sample between two laser shots. The area of the sample under study is imaged with a magnifying lens on a slit at the entrance of the spectrometer. The interference pattern is visualized at the output of the spectrometer on a CCD camera interfaced with a microcomputer. The horizontal axis of the two-dimensional image represents the frequency, while the vertical axis (parallel to the slit, i.e., perpendicular to the plane of Fig. 1) represents the radial (vertical) dimension. In order to obtain a reference for the phase shift, the magnifying power is selected so that the focal spot of the pump beam (25 μm FWHM) fills approximately 70% of the vertical axis. By a Fourier-transform treatment of the spectrum displayed by each horizontal line, we obtain the radial variation of the phase shift and of the absorption. The result for a-SiO$_2$ is presented for various time delays in Fig. 2 (phase shift). We observe a very rapid evolution of the phase shift as a function of the time delay between the pump pulse and the second probe pulse. It is positive for time delays close to zero, becomes suddenly negative, and finally goes back to a value close to zero. Concerning the space dependence, we observe that the positive phase shift occurs in a broader region, the half-width of the signal being larger than in the case of negative phase shift.

We interpret the above result as follows: The phase shift is proportional to the variation of the real part of the sample index (Δn); it is given by $\Delta\Phi = 2\pi \Delta n L/\lambda$, where L is the effective length over which the index is modified (diameter of the pump beam seen at a 45° incidence, 35 μm) and λ is the wavelength of the probe beam. The positive phase shift is due to an induced phase modulation and occurs as far as the pump pulse and the second probe pulse overlap in time. In this case, $\Delta n = n_2 I$, where n_2 is the nonlinear refractive index and I the intensity of the pump pulse. Note that the temporal resolution can be directly deduced from Fig. 2, and we checked that the measured value coincides with the estimated value within experimental errors. On the other hand, a free electron population, produced by multiphoton absorption, induces a negative phase shift which becomes visible even before the pump pulse has ended.

A simple-man model allows us to write the phase shift between the two probe pulses as [14]

$$\Delta\Phi(\mathbf{r}, z, t) = 2\pi \frac{L}{\lambda} \left(n_2 I(\mathbf{r}, z, t) + \sqrt{n_0^2 - \frac{\omega_p^2(\mathbf{r}, z, t)}{\omega^2}} - n_0 \right). \quad (1)$$

In the above expression, n_0 is the usual linear refractive index, I the pump intensity, and ω_p the plasma frequency. As is well known, the square of this plasma frequency is proportional to the excitation density. These quasi-free electrons have been promoted in the conduction band by a five-photon-absorption process necessary to cross the band gap of such materials, which is approximately 9 eV—large in silicon dioxide. This excitation density has been modeled by using a simple rate equation for a three-level system,

$$\frac{dn(\mathbf{r}, z, t)}{dt} = n_i \sigma^5 I^5(\mathbf{r}, z, t) - \frac{n(\mathbf{r}, z, t)}{\tau_p}. \quad (2)$$

n_i is the initial valence electron density which is 2.2×10^{22} cm^{-3} in silicon dioxide. σ^5 and τ_p represent, respectively, the five-photon-absorption cross section and electrons mean trapping time. We will go back to this point later. We stress that these two quantities are introduced in an *ad hoc* way. Our aim is to show that one of the main physical points in the observation in Fig. 2 results from the competition between the nonlinear induced polarization (phase modulation induced by the pump beam) and the free electron density. The dependence of the intensity on the z coordinate (through the sample) is disregarded because no self-focusing or filamentation has been observed for a 100 μm thick sample. We disregard pump and probe absorption since it cannot affect the phase shift, but only the contrast. For n_0 and n_2, we used, respectively, 1.6×10^{-16} and 3×10^{-16} cm^2/W which are standard values for both quartz and fused silica at this probe wavelength [2]. The result of this model is given in Fig. 3. Note that the spatial width of the phase shift reflects the nonlinearity order of the process. After the pump pulse, this width decreases because the dominant process is no longer the induced phase modulation (I dependence) but results from the free electron density (I^5 dependence) as Eqs. (1) and (2) show.

In Fig. 4 we present the phase shift for various times after the excitation pulse for α-quartz and silica and for a pump intensity of 2.7×10^{13} W/cm^2. We could not observe any measurable difference between the two materials. Note that a decrease in the phase shift implies a decrease in the free electron density. More specifically, electrons must be trapped at levels deeper than the photon energy; otherwise they would be seen as free by the laser field. The trapping of the gas is extremely fast and its time dependence can be fitted by an exponential law, with a time decay of 150 fs. As a consequence, the gas has "disappeared" before expanding in a measurable proportion. Moreover, we find that this mean time does not depend on the pump intensities we consider. The observed phase shift of 1.2 rad corresponds to an excitation density of 3×10^{19} cm^{-3}. The traps must therefore have an intrinsic character since this density is at least 2 orders of magnitude higher than the density of extrinsic defects in our samples.

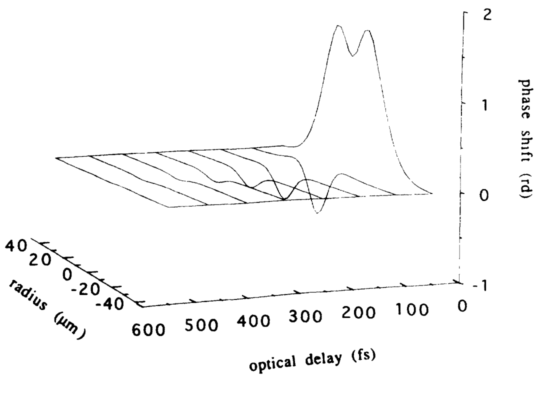

FIG. 3. Phase shift as a function of time and space as calculated from Eqs. (1) and (2).

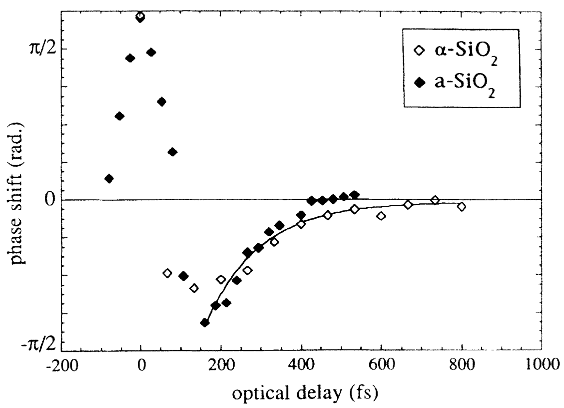

FIG. 4. Phase shift as a function of time for α-SiO$_2$ and a-SiO$_2$. Solid line: exponential fit, with a time decay of 150 fs. The data points represent the space-integrated phase shift (area of the curves in Fig. 2). They are normalized to the peak phase shift.

The kinetic of formation of the E' centers was measured recently [6]. In this experiment, the authors used a 4 eV excitation pulse generated by frequency doubling a portion of a CPM laser. The excitation was done by a two-photon-absorption process. Their probe pulse in the UV (5.6 eV) was produced by doubling the blue portion of a continuum generated with a part of the CPM laser. These authors found a strong absorption band at 5.6 eV, with a rise time of 250 fs, which was attributed to the E' center. This transient defect, laying in the band gap at an energy level deeper than 2.2 eV, can explain the "annihilation" of the initial electronic density. The time discrepancy between their result (250 fs) and ours (150 fs) could be due, as mentioned by the authors themselves, to a temporal broadening of their UV probe pulse.

In Fig. 5, we present the time-dependent absorption of the probe pulse. As in Fig. 4, the function is well fitted by an exponential time decay, similar for both materials and independent from the intensities we consider. However, note that the absorption kinetic is slightly slower: 200 fs instead of 150 fs. At short time delay, when the excitation density is in the order of 3×10^{19} cm^{-3}, the probe absorption is very high (25%). We attribute this absorption to free carriers. This is supported by a Monte Carlo simulation, based on an approach similar to [15], in which we included electron-phonon collisions (optical and acoustical) and electron-photon-photon collisions [16,17]. Electrons are injected with a mean excess energy of 1 eV above the bottom of the conduction band. The result is given in the inset of Fig. 5. Although no traps have been included in the simulation, we found that free carrier absorption is strongly dependent on the energy relaxation due to electron-phonon collisions, which means that the observed decay time in Fig. 5 is the result of two processes, namely,

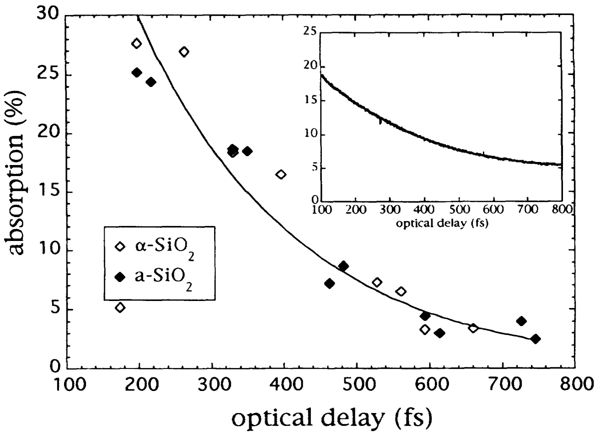

FIG. 5. Probe-free carrier absorption as a function of time for α-SiO$_2$ and a-SiO$_2$. Solid line: exponential fit with a time decay of 200 fs. Inset: Monte Carlo simulation of probe free carrier absorption. Solid line: exponential fit with a time decay of 210 fs.

the energy relaxation of the electron gas and the trapping of the free electrons. A more accurate model for the trapping process will be needed to identify precisely the contribution of each mechanism. Furthermore, it seems that a residual absorption in the order of 4% remains for a long time decay (1 ps), although the absorption data are more sensitive to shot-to-shot fluctuations. It has been suggested [18] that in the strong electron-phonon coupling regime, low kinetic energy electrons can be trapped in levels very close to the bottom of the conduction band and then form the so-called small polarons. This model explains quite well the carrier trapping-detrapping process. One of its main consequences, which can be seen easily in photoemission experiments, is to build up a macroscopic charge appearing or disappearing as a function of the sample temperature [19]. It shows that these trapped levels, sensitive to sample temperature, are located a few hundred meV below the conduction band. They can make a significant contribution to the probe absorption without inducing a significant variation in the phase shift.

In conclusion, we present the first experimental observation of the primary excitation and relaxation processes in the conduction band of a wide band-gap insulator, during and just after the pump pulse, with a temporal resolution of 120 fs. This experimental method is very powerful and promising. Indeed, it can be applied to any transparent medium. Space-time dependent nonlinear polarization due to the action of an intense laser field and to the presence of photogenerated quasi-free electrons has been observed in two wide band-gap insulators, namely, amorphous and crystalline silicon dioxide. We show that the mean lifetime of the electron gas in the conduction band is in the order of 150 fs in both materials. No evidence of gas expansion has been observed even for pump intensities as high as 60 TW/cm^2. Most electrons are trapped into deep levels and form the well-known E' centers.

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