

## Time-resolved study of laser-induced colour centres in $\text{SiO}_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 1281

(<http://iopscience.iop.org/0953-8984/8/9/018>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:50

Please note that [terms and conditions apply](#).

## Time-resolved study of laser-induced colour centres in SiO<sub>2</sub>

S Guizard†, P Martin†, G Petite†, P D'Oliveira‡ and P Meynadier‡

† Service de Recherche sur les Surfaces et l'Irradiation de la Matière, DSM, DRECAM, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires Saclay, 91191 Gif sur Yvette, France

‡ Service des Photons, Atomes, Molécules, DSM, DRECAM, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires Saclay, 91191 Gif sur Yvette, France

Received 10 July 1995

**Abstract.** We report the investigation of the onset of an absorption band in the UV in crystalline quartz ( $\alpha$ -SiO<sub>2</sub>) induced by an intense femtosecond laser pulse. Using a conventional pump-probe technique, we have measured the absorptions at 219 nm (5.66 eV) and at 240 nm (5.16 eV) as functions of time, at two different temperatures (10 and 300 K). The rise time of the absorption is measured to be 150 ( $\pm$ 50) fs. It is independent of probe wavelength and sample temperature. The absorption coefficients are similar at both probe wavelengths and the values at room temperature are about twice these at 10 K. We attribute the onset of the absorption to the ultra-fast formation of self-trapped excitons (STEs). The STEs recombine radiatively at a low temperature. At room temperature, we observe a cumulative effect. This demonstrates that, at 300 K, some of the STEs are converted to permanent colour centres, which we tentatively identify as neutral oxygen vacancies.

### 1. Introduction

The formation of colour centres induced by various types of radiation in quartz ( $\alpha$ -SiO<sub>2</sub>) and fused silica ( $\alpha$ -SiO<sub>2</sub>) has been the subject of numerous experimental and theoretical studies for almost 40 years. The most important intrinsic radiation defects are related to vacancies and interstitials in the oxygen sublattice. For instance, in 1956, Mitchell and Paige [1] measured the optical absorption spectra of neutron- and x-ray-irradiated crystalline and amorphous SiO<sub>2</sub> samples. They observed two absorption bands at 5.7 and 7.6 eV, which they attributed to the formation of an oxygen ion vacancy–interstitial pair. This hypothesis was confirmed by Weeks and Sonder [2] who showed a one-to-one correspondence between the optical density at 5.8 eV and the electron spin resonance signal in a series of fused silica samples irradiated with high-energy particles.

Yip and Fowler [3] have established a theoretical model of the positively charged oxygen vacancy—the E<sub>1</sub>' centre—the paramagnetic defect giving rise to the absorption centred around 5.8 eV. The experimental hyperfine constant can be theoretically reproduced with reasonable agreement by assuming an asymmetric relaxation of the lattice; one of the silicon atoms initially bonded to the vacant oxygen relaxes towards the plane formed by the three other oxygen atoms, while the unpaired electron is mainly localized on the other silicon atom.

More recently, several workers have studied the influence of prolonged irradiation with high-intensity excimer lasers on silica samples. In particular, the appearance of the E<sub>1</sub>' centre following irradiation with 5.0 eV (248 nm) or 6.4 eV (193 nm) photons has also

been demonstrated by optical absorption [4–6] and electron spin resonance (ESR) studies [7]. The formation of permanent defects is associated with a compaction of the irradiated area as shown by optical birefringence measurements [5, 6]. In this case, the electronic excitation leading to lattice rearrangement is assumed to occur via a two-photon absorption process. Indeed, Arai *et al* [4] noted that  $E'_1$  centres are formed when the 6.4 eV photons of an ArF laser or the 5.0 eV photons of a KrF laser are used to photoexcite the samples, while no effects are observed with the 4.0 eV photons of a XeCl laser, since the absorption of two photons is not sufficient to bridge the 9 eV band gap of SiO<sub>2</sub>. Finally, Leung *et al* [5] also pointed out that crystalline SiO<sub>2</sub> is much more radiation resistant than fused silica.

However, the detailed mechanism leading from the initial electronic excitation to a lattice defect remains unclear. A transient absorption band whose spectrum closely resembles that of the  $E'_1$  centre has been observed by Sigel [8] and Griscom [9] in crystalline and amorphous SiO<sub>2</sub> irradiated at a low temperature by electron pulses. This transient absorption was attributed to the formation of transient  $E'_1$  centres [8, 9]. It has been later suggested that the initial relaxation stage is the localization of an electron–hole pair (exciton) associated with a lattice distortion (self-trapped exciton (STE)) [10–12]. The existence of STEs in SiO<sub>2</sub> has been experimentally demonstrated by Tanimura *et al* [13] who have shown the link between the absorption at 5.5 eV, the luminescence at 2.8 eV and a volume change. The three phenomena were observed in crystalline and amorphous SiO<sub>2</sub> irradiated with a pulse of 2 MeV electrons and exhibited the same temperature lifetime dependences. Hayes *et al* [14] have carried out optically detected magnetic resonance measurements of x-ray irradiated  $\alpha$ -SiO<sub>2</sub> which show that the state emitting the 2.8 eV luminescence is a triplet state. They proposed that the transient defect is a close oxygen vacancy–interstitial pair. Recent theoretical investigations of the structure of the STE in SiO<sub>2</sub> clusters performed by Shluger [15], and Fischer *et al* [16] suggest that the STE can be considered as a transient Si–O bond breaking. In the triplet excited state of the exciton, the oxygen atom is displaced from its original position by 0.3–0.4 Å. The hole component of the exciton is primarily localized on the oxygen atom, while the electron is primarily localized on the silicon atom.

Almost all experimental investigations performed to date are *a posteriori* observations of radiation effects. This type of experiment gives no information about the dynamics of the process leading from the initial electronic excitation to the lattice rearrangement. The newly developed high-intensity short-pulse laser sources opens up the possibility of realizing time-resolved optical experiments. Using the pump–probe technique, it is possible, at intensities below the optical breakdown threshold, to create within a single laser shot a high excitation density and then to probe the modifications of the optical properties of the solid. Two experiments of this type have been carried out on SiO<sub>2</sub> recently. Saeta and Greene [17] have performed a time-resolved absorption experiment, in which they measured an absorption at 5.6 eV and a much weaker absorption at around 2 eV that they attributed to the formation of  $E'_1$  centres and of non-bridging oxygen hole centres, respectively. They deduced from their measurements that the close Frenkel pair is formed in an extremely short time of 250 fs. On the other hand, by measuring the transient modification of the refractive index following a high-intensity laser pulse, we have shown that the mean lifetime of the photoexcited free carriers in SiO<sub>2</sub> is 150 fs, after which the electrons are trapped roughly in the middle of the band gap [18, 19]. Both these results indicate that the trapping of carriers is extremely fast and corresponds to the onset of an absorption band in the UV, around 5–6 eV.

The aim of this work is to investigate further the possible link between the transient defect—namely the STE—and the permanent defect—the oxygen vacancy, neutral or ionized ( $E'_1$  centre). In particular, it has been observed that the sample temperature during irradiation strongly influences the efficiency of  $E'_1$ -centre formation; almost no  $E'_1$  centres

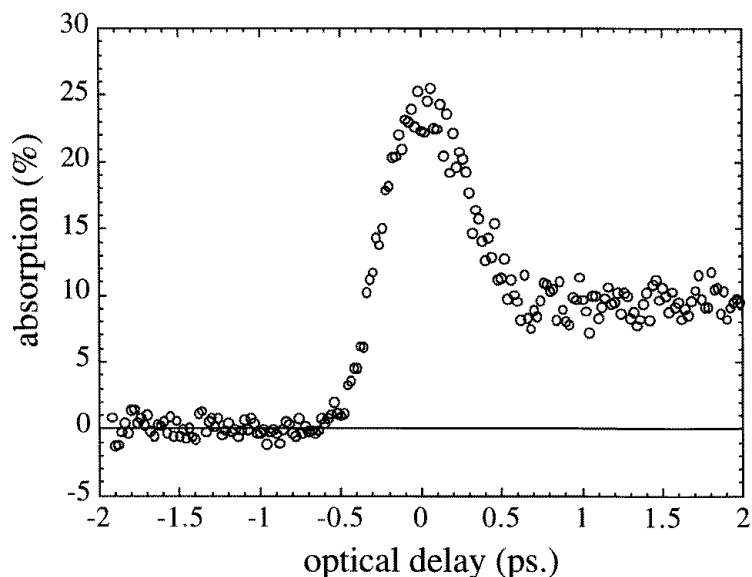
are created below the radiative recombination quenching temperature (150 K) of the STE [7, 20]. In order to investigate this problem, we have performed time-resolved studies of the absorption induced in the UV by high-intensity short laser pulses in crystalline SiO<sub>2</sub> ( $\alpha$ -SiO<sub>2</sub>), at temperatures above and below the quenching temperature of the radiative recombination of the STE. The probe wavelengths were chosen to match the maximum of the absorption bands of the E'<sub>1</sub> centre, and of the STE, observed at a low temperature by Tanaka *et al* [21] and Itoh *et al* [22].

## 2. Experimental set-up

The time-resolved absorption measurement is based on the classical pump-probe experiment scheme; the transmission through the sample is obtained by measuring the ratio of the probe beam intensity before to that after the sample as a function of the delay with the pump pulse. To obtain the desired wavelengths, we use a part of the output of an amplified Ti-Sa laser which delivers 120 fs pulses at a repetition rate of 20 Hz to generate two continua in water cells. One of the continua is amplified at 620 nm in four Rhodamine dye cells pumped by the second harmonic of a YAG laser. After frequency doubling in a BBO crystal, we obtain up to 40  $\mu$ J at 310 nm which will be used as pump pulses. The second continuum is amplified in three dye cells pumped by the third harmonic of the same YAG laser. There is no frequency-selective component in the amplification chain. The output wavelength is rather adjusted by selecting the appropriate dyes and solvents. We used Coumarin 440 diluted in methanol in all three dye cells for generating the 440 nm probe beam, and Coumarin 480 diluted in methanol in the first cell followed by Coumarin 481 diluted in dioxane in the last two cells to obtain 480 nm. The spectrum of the pulse is imposed by the spectral gain of the dyes and we obtain a spectrum approximately 10 nm broad at the output of the amplification. However, the probe beam is frequency doubled to obtain 5.66 eV (219 nm) or 5.16 eV (240 nm) photons, and we obtain a much narrower spectrum at the output of the BBO crystal (full width at half-maximum (FWHM), about 1 nm). It is then split into two beams; one is used as a reference beam and the other is focused on the sample together with the pump beam. The intensities of the two probe pulses are measured with two solar blind photomultipliers plugged into a Lecroy 9450 oscilloscope. The signal is digitized and sent to a microcomputer which also drives the stepping motor of the delay line. The samples are commercially available high-purity synthetic crystalline SiO<sub>2</sub> plates 500  $\mu$ m thick. They are cut perpendicularly to the Y axis (Y cut) and optically polished on both faces. Two samples are mounted with their Z axis perpendicular to each other in a helium compressor-type cryogenerator which allows the samples to be cooled to 10 K. The pump and probe beams are focused with silica lenses of 150 mm and 100 mm focal lengths, respectively. In a pump-probe experiment, a reproducible spatial overlap of the two beams is a key point for obtaining quantitatively reliable results, especially when the excitation depends non-linearly on the pump laser intensity, as in the present experiment. This is achieved for probe and pump beams by optimizing the intensity passing through a small pinhole (50  $\mu$ m diameter) mounted on the sample holder.

## 3. Experimental results

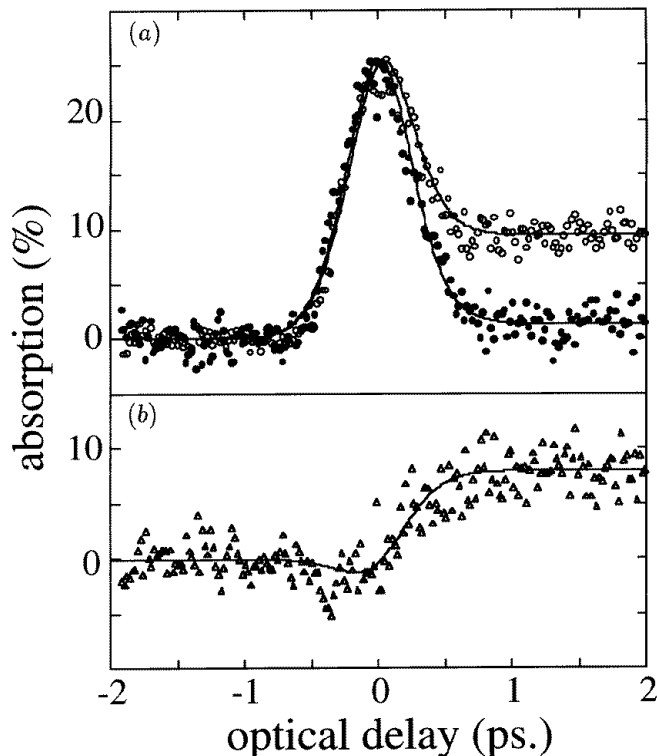
A typical result of our absorption measurements is shown in figure 1. Three different regimes can be distinguished. For negative time delays, the probe pulse is incident on the sample before the pump pulse and therefore no absorption is observed. For time delays



**Figure 1.** Absorption at 219 nm as a function of the time delay between the pump pulse and the probe pulse. The pump laser intensity is  $2 \text{ TW cm}^{-2}$ ; the sample temperature is 10 K.

close to zero, the probe and pump pulses overlap in time within the sample. In this case, simultaneous absorption of one probe photon and one pump photon occurs. Indeed, the sum energy of one pump photon and one probe photon is 9.2 eV; this is sufficient to bridge the band gap of  $\alpha\text{-SiO}_2$  which is 9 eV. Then, after this absorption due to the simultaneous presence of the pump and probe pulses in the sample, we observe an absorption due to the formation of colour centres in  $\alpha\text{-SiO}_2$ . The intensity of this absorption depends strongly on the excitation intensity; this non-linear dependence reflects the multiphoton absorption process necessary to create electron-hole pairs.

A good estimate of the absorption rise time can be obtained by a detailed comparison of low- and high-intensity results. When we decrease the pump intensity, the induced absorption decreases more rapidly than the  $1 + 1$  absorption process. Thus the experimental temporal width can be directly deduced from the low-intensity absorption measurement, as shown by the full circles in figure 2(a). The FWHM is measured to be 525 fs. This is much larger than expected from the convolution of the probe and pump pulse duration, measured before frequency doubling with an autocorrelator to be 40 fs and 130 fs, respectively. This temporal broadening is most probably due to the group-velocity dispersion in the  $500 \mu\text{m}$  thick BBO crystal used for frequency doubling the probe beam. Figure 2(a) also shows the absorption as a function of time for a higher intensity (open circles). The high-intensity result has been divided by a normalization factor adjusted in such a way that the  $1 + 1$  absorption matches the low-intensity result. Both curves have been fitted by assuming a  $\text{sech}^2$  (standard description of the temporal behaviour of the laser envelope) shape (FWHM, 525 fs) and the best agreement has been obtained with a rise time of 150 fs for the absorbing centre. By subtracting the low-intensity from the high-intensity data, one obtained a direct time-resolved view of the onset of the absorption band. This is presented in figure 2(b). The line is the difference between the two former fits for the low- and high-intensity absorption. Due to the limited temporal resolution, the rise time of the absorption (150 fs) is known with



**Figure 2.** (a) Absorption at 219 nm as a function of time for two different laser intensities:  $\circ$ ,  $I = 2 \text{ TW cm}^{-2}$ ;  $\bullet$ ,  $I = 0.4 \text{ TW cm}^{-2}$ . The data have been normalized to match the  $1 + 1$  absorption at high and low intensities. (b) Difference between the above two curves.

an accuracy of  $\pm 50$  fs. This result is in good agreement with our recent measurement of the lifetime of laser photoexcited free carriers in amorphous and crystalline SiO<sub>2</sub> [18, 19]. The shapes of the curve representing the absorption as a function of time are the same for the two probe wavelengths used in this experiment, 219 nm and 240 nm and neither depends on the sample temperature (10 or 300 K). This means that the kinetics of the transformation leading from the initial electron-hole pair to the colour centre are the same, within our experimental uncertainty, in all cases. This result indicates that the same phenomenon is observed in all the experimental conditions that we considered.

We now concentrate on the intensity of the induced absorption, which appears as a constant value after the  $1 + 1$  absorption signal, i.e. for time delays longer than 1 ps. The optical density has been measured for two different probe wavelengths (219 and 240 nm) and two sample temperatures (10 and 300 K). We have also changed the linear polarization of the pump beam, which is perpendicular or parallel to the polarization of the probe beam, the latter being vertically polarized in all cases. Measurements were also made on vertically and horizontally oriented identical Y-cut samples; this is equivalent to rotating the polarization of the probe beam. As already pointed out, the comparison between different sets of experiments is reliable provided that the overlap between the pump and probe beams on the one hand and the intensity of the pump beam on the other hand remain constant. The first condition is achieved with the alignment procedure described above and the fulfillment of

the second is checked by measuring the laser intensity just before and after each experiment. An ultimate *a posteriori* verification is possible with the 1 + 1 photon absorption process, which of course also critically depends on the beam overlap and pump pulse intensity. Finally, our optical density measurements are reproducible from day to day within  $\pm 20\%$ . The results of the absorption measurements for both wavelengths and temperatures are summarized in table 1.

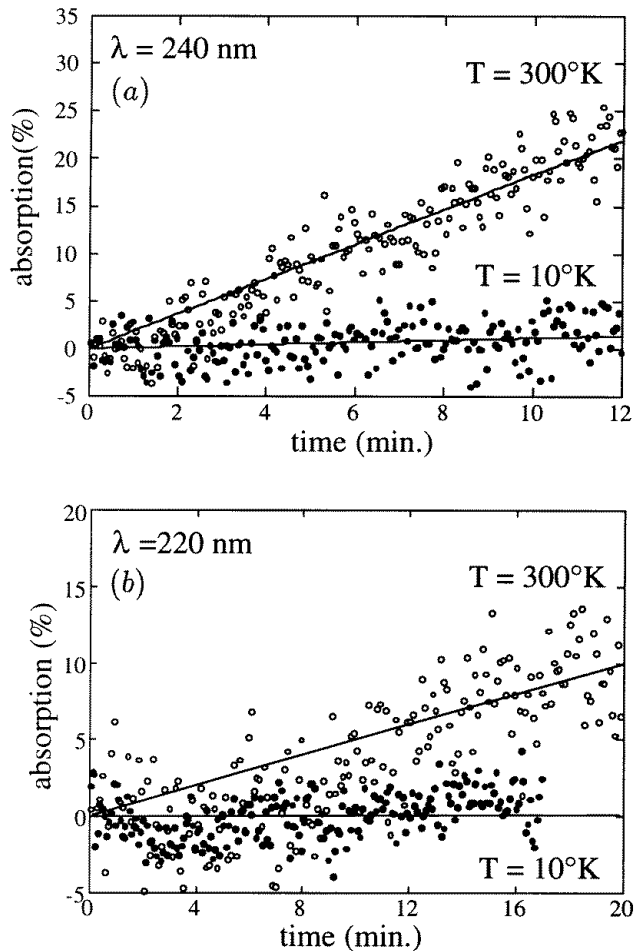
**Table 1.** Absorption measured at short time delays (between 1 and 2 ps), at two different probe wavelengths and two sample temperatures. The results are given as a percentage of absorption or as absorption coefficient (the sample's thickness is 500  $\mu\text{m}$ ).

Wavelength (nm)	Temperature (K)	Absorption (%)	Absorption coefficient ( $\text{cm}^{-1}$ )
219	300	17.0	3.7
219	10	10.4	2.2
241	300	15.7	3.4
241	10	11.5	2.4

Concerning the temperature dependence, the optical density is about 50% higher at 300 K than at low temperatures. It should be noted, however, that the 1 + 1 absorption process, which is proportional to the initial density of electron-hole pairs, also decreases with decreasing temperature. This may be due to the lower probability that phonon-assisted indirect transitions from the valence band to the conduction band occur at low temperatures, or to a broadening of the effective band gap at 10 K, thereby forbidding the possibility of lower-order multiphoton excitation processes. It is possible to take into account the lower initial excitation density by correcting the measured optical densities according to the 1 + 1 photo absorption signal. Although this normalization procedure adds some uncertainty, the ratio of the optical density obtained at 300 K to that at 10 K decreases but remains in all cases higher than one. We conclude that the probability that an electron-hole pair forms a colour centre decreases with increasing sample temperature.

We now compare the results obtained for the two probe wavelengths. At room temperature, the absorption is slightly higher at 5.66 eV than at 5.16 eV, while the opposite situation is observed at 10 K. In both cases, the difference is of the order of only 10% and, given the precision of such measurements, the results can be considered as almost equivalent for both probe wavelengths. Our result is in contradiction with the observation of Saeta and Greene [17] on amorphous  $\text{SiO}_2$  that the absorption measured in similar conditions (at room temperature) is lower by a factor of 3 at 235 nm (5.27 eV) than at 220 nm (5.63 eV). It shows that the colour centre observed in  $\alpha\text{-SiO}_2$  at short time delays is not the  $E'_1$  centre, for which the absorption at 5.7 eV is higher than at 5.2 eV by a factor of at least 2 [1, 4–6]. Although it is difficult to compare full spectra with data obtained at only two different wavelengths, it seems, however, that the spectrum of the colour centres observed in our experiment is more closely connected to the STE. Indeed, the absorption spectrum of the STE is red shifted in comparison with the absorption spectrum of the  $E'_1$  centre [21, 22].

We have already mentioned that the formation of  $E'_1$  centres has been observed in  $\text{SiO}_2$  after prolonged irradiation with the UV light of excimer laser [4–7]. In order to investigate such cumulative effects, we have carried out the following experiment: we let the laser irradiate the same area of the sample and we measured the optical density as function of time. The probe laser impinges the sample *before* the pump pulse in order to avoid transient effects (at least those having a lifetime shorter than the delay between



**Figure 3.** Absorption at (a) 240 nm and (b) 219 nm as functions of irradiation time, at two temperatures: ●, 10 K; ○, 300 K. The pump laser intensity is  $2 \text{ TW cm}^{-2}$ .

two consecutive pulses, i.e. 50 ms). The result is shown in figures 3(a) and 3(b) for probe wavelengths of 240 nm and 219 nm, respectively. Obviously the onset of permanent centres is occurring at room temperature (open circles), while no effect is observed at 10 K (full circles). Moreover, at room temperature, the absorption increases about four times more rapidly at 240 nm than at 219 nm.

#### 4. Discussion and conclusion

We shall first focus on the short-time behaviour revealed by the time-resolved absorption measurements. The striking feature is the similarity of the results obtained at low temperatures and room temperatures. The spectral characteristics of the absorption—as far as we can conclude from the comparison of measurements performed at two wavelengths—and the temporal evolution are, within experimental errors, identical. We are thus led to conclude that the colour centres which appears in a time of 150 fs after the creation of



electron–hole pairs by the pump laser pulse are the same at 10 and 300 K. The observation of an absorption slightly higher at 5.16 eV than at 5.66 eV at 10 K is in good agreement with the published transient absorption spectra of the STE [21, 22]. Moreover, the fact that no cumulative effect is observed at this temperature indicates that the colour centre disappears between two laser shots, i.e. in 50 ms. This is compatible with the measured lifetime of the STE, which recombines radiatively at temperatures below 150 K with a lifetime of 1 ms [13]. Indeed, we observe a strong blue luminescence when the sample is irradiated at 10 K, and we have shown that this luminescence exhibits all the characteristics of the STE luminescence [23]. Finally, the most recent theoretical models describe the STE as a localization of the trapped electron–hole pair on a broken Si–O bond, the oxygen atom being displaced (by 0.4 Å) from its original position [15, 16]. The time necessary for such a small motion is compatible with the formation time of 150 fs that we measure.

Concerning the formation of permanent defects observed in the cumulative experiment, a similar influence of the temperature on the creation efficiency has already been reported for the formation of the  $E'_1$  centre monitored by the ESR signal in  $\alpha$ -SiO<sub>2</sub> irradiated by 5 eV photons [7] and in  $\alpha$ -SiO<sub>2</sub> irradiated by 1.7 MeV electrons [20]. In both cases the induced  $E'_1$ -centre density is almost zero when the irradiation takes place at 150 K and increases irradiation temperature. All these observations, which concern different samples and irradiation types, demonstrate the existence of a competition between different relaxation channels in which the sample temperature plays a key role.

Regarding the ratio of transient to permanent colour centres measured at room temperature, we observe that irradiation for 10 min at 20 Hz (i.e. 12 000 laser shots) is needed to obtain the transient absorption induced by a single laser shot (about 10%) in identical experimental conditions (same pump laser intensity and polarization, same probe wavelength and same sample and temperature). Keeping this in mind, we can formulate two hypotheses to explain the cumulative effect. First, if we suppose that the absorption coefficients at the probe wavelength for transient and permanent absorbing centres are not notably different, the branching ratio for this thermally activated transformation is also very weak, of the order of  $10^{-4}$ . It is interesting to compare our result with the yield of  $E'_1$ -centre formation following electron–holes pair creation by two-photon absorption of excimer lasers. The efficiency of  $E'_1$ -centre formation was estimated to be  $7.5 \times 10^{-4}$  by Rothschild *et al* [6], while Arai *et al* [4] found a value of  $1.3 \times 10^{-3}$ . The apparent discrepancy between these values is not surprising if one considers that they are estimated from the two-photon absorption coefficient, a quantity usually known with a poor accuracy, and that the result—and thus the attached error—depends quadratically on the laser intensity. The second hypothesis is that all the initially created defects transform to permanent centres. This implies that the oscillator strength decreases by four orders of magnitude. A possible explanation for such a huge decrease could be transformation of the multiplicity of either the ground state or the excited state involved in the optical absorption. This has been observed by Tohmon *et al* [24] who have studied the correlation of absorption bands at 5.0 and 7.6 eV with oxygen vacancies. They attribute the band at 7.6 eV to a singlet-to-singlet transition and the band at 5.0 eV, which is at least three orders of magnitude weaker, to a singlet-to-triplet transition.

Finally, we recall that the absorption increases approximately four times more rapidly at 5.16 eV than at 5.66 eV. This result is in contradiction with all the published data concerning the absorption band of the  $E'_1$  centre. On the contrary this seems to indicate the formation of a neutral oxygen vacancy [24, 25]. The shape of the radiation-induced absorption in the UV strongly depends on the irradiation type [26] and Guzzi *et al* [27] have shown that the absorption spectra in the range 5–6 eV is a composite of several bands. Concerning

UV laser irradiation, all the published results are for amorphous silica irradiated with long (20 ns) pulses [4–6]. In all cases the absorption spectra are peaked between 210 and 220 nm and this is attributed to the formation of E<sub>1</sub>' centres. The experimental conditions in our case are obviously quite different; the pulse duration and intensity are five orders of magnitude larger and smaller, respectively, in the case of excimer lasers. It is therefore *a priori* not surprising to find different results. Indeed, in our case the pump laser is already turned off before an appreciable amount of colour centres is created, while the use of excitation pulses in the nanosecond range dramatically increases the probability of sequential events. This has been shown by Tanaka *et al* [21] who have observed that a nanosecond laser pulse eliminates both the transient absorption and the luminescence of the STE. Another example is given by Arai *et al* [4] who measured the absorption in the range 4–9 eV in amorphous SiO<sub>2</sub> irradiated with an ArF excimer laser. They observed the evolution of the absorption spectrum as a function of irradiation time. The absorption band at 5.0 eV, attributed to oxygen defect centres, decreases while the absorption band at 5.8 eV, attributed to E<sub>1</sub>' centres, increases.

In conclusion, using time-resolved absorption with subpicosecond resolution, we have shown that the primary relaxation process following the laser excitation in  $\alpha$ -SiO<sub>2</sub> is independent of the sample temperature. We attribute the onset of absorption in the UV to the ultra-fast formation of a STE. The measured rise time for the absorption, 150 fs is in agreement with our recent measurements of the free-carrier lifetime in SiO<sub>2</sub>. At a low temperature (10 K), the STE recombines radiatively, and the crystal recovers its original structure. At room temperature, we observe the formation of permanent colour centres. The induced optical density is larger at 5.16 eV than at 5.66 eV by a factor of 4. This indicates that the permanent defect is a neutral oxygen vacancy rather than the E<sub>1</sub>' centre observed in the case of excitation with long (nanosecond) pulses. Further work is needed to determine the conversion efficiency from transient to permanent defects. This quantity could be extracted from our measurements, provided that the oscillator strength of the optical transitions is known.

## References

- [1] Mitchell E W and Paige E G 1956 *Phil. Mag.* **1** 1085
- [2] Weeks R A and Sonder E 1963 *Paramagnetic Resonance* vol II, ed W Low (New York: Academic) p 869
- [3] Yip K L and Fowler W B 1975 *Phys. Rev. B* **11** 2327
- [4] Arai K, Imai H, Hosono H, Abe Y and Imagawa H 1988 *Appl. Phys. Lett.* **53** 1891
- [5] Leung W P, Kulkarni M, Krajnovich D and Tam A C 1991 *Appl. Phys. Lett.* **58** 551
- [6] Rothschild M, Ehrlich D J and Shaver D C 1989 *Appl. Phys. Lett.* **55** 1276
- [7] Devine R A B, Fiori C and Robertson J 1986 *Defects in Glasses (Mater. Res. Soc. Symp. Proc. 61)* ed F L Galeener, D L Griscom and M J Weber (Pittsburgh, PA: Materials Research Society) p 177
- [8] Sigel G H 1973–4 *J. Non-Cryst. Solids* **13** 372
- [9] Griscom D L 1979 *Proc. 33rd Frequency Control Symp.* (Washington, DC: Electronic Industries Association) p 98
- [10] Tsai T E, Griscom D L and Friebele E J 1988 *Phys. Rev. Lett.* **61** 444
- [11] Tsai T E and Griscom D L 1991 *Phys. Rev. Lett.* **67** 2517
- [12] Devine R A B 1989 *Phys. Rev. Lett.* **62** 340
- [13] Tanimura K, Tanaka T and Itoh N 1983 *Phys. Rev. Lett.* **51** 423
- [14] Hayes W, Kane M J, Salminen O, Wood R L and Doherty S P 1984 *J. Phys. C: Solid State Phys.* **17** 2943
- [15] Shluger A L 1988 *J. Phys. C: Solid State Phys.* **21** L431
- [16] Fischer A J, Hayes W and Stoneham A M 1990 *J. Phys.: Condens. Matter* **2** 6707
- [17] Saeta P N and Greene B I 1992 *Phys. Rev. Lett.* **70** 3588
- [18] Audebert P *et al* 1994 *Phys. Rev. Lett.* **73** 1990

- [19] Guizard S, Martin P, Daguzan Ph, Petite G, Audebert P, Geindre J P, Dos Santos A and Antonetti A 1995 *Europhys. Lett.* **29** 401
- [20] Jani M G, Bossoli R B and Halliburton L E 1983 *Phys. Rev. B* **27** 2285
- [21] Tanaka T, Eshita T, Tanimura K and Itoh N 1985 *Cryst. Latt. Defects Amorph. Mater.* **11** 221
- [22] Itoh C, Tanimura K and Itoh N 1988 *J. Phys. C: Solid State Phys.* **21** 4693
- [23] Joosen W, Guizard S, Martin P, Petite G, Agostini P, Dos Santos A, Grillon G, Hulin D, Migus A and Antonetti A 1992 *Appl. Phys. Lett.* **61** 2260
- [24] Tohmon R, Mizuno H, Ohki Y, Sasagane K, Nagasawa K and Hama Y 1989 *Phys. Rev. B* **39** 1337
- [25] Imai H, Arai K, Imagawa H, Hosono H and Abe Y *Phys. Rev. B* **38** 12772
- [26] Antonini M, Camagni P, Gibson P N and Manara A 1982 *Radiat. Eff.* **65** 281
- [27] Guzzi M, Pio F, Spinolo G, Vedda A, Azzoni C B and Paleari A 1992 *J. Phys.: Condens. Matter* **4** 8635