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T. E. Tsai, J. M. Jewell, and J. S. Sanghera

Citation: *Applied Physics Letters* **62**, 3396 (1993); doi: 10.1063/1.109028

View online: <http://dx.doi.org/10.1063/1.109028>

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Dynamics of the 5 eV optical absorption in SiO₂ glass

T. E. Tsai,^{a)} J. M. Jewell, and J. S. Sanghera
Code 5605, Naval Research Laboratory, Washington, DC 20375

(Received 14 December 1992; accepted for publication 9 April 1993)

The optical absorption at 5 eV in SiO₂ glass was observed, using laser calorimetry, to change reversibly depending on the intensity of UV light. The generation and bleaching of an absorption band at 5 eV by two- and one-photon absorption processes, respectively, can explain these reversible changes. This observation supports the structural model of unrelaxed oxygen deficiency center for the 5 eV absorption band in silica.

The 5 eV band is the most well known optical absorption of SiO₂ glass in the ultraviolet wavelength region. When induced by ion irradiation, its bandwidth is approximately 0.5 eV and was attributed to the oxygen deficient center (ODC).¹ The 5 eV optical absorption of the ODC was termed $B_{2\alpha}$ band by Tohmon *et al.*² and shown to have a strong emission band at 4.42 eV and a weak one at 2.74 eV. However, the structural origin of this absorption band in SiO₂ is not yet understood. Imai *et al.*³ showed that two types of ODC exist in synthetic silica glass. Tohmon *et al.* proposed² that it is due to the ground-to-triplet transition at ODC. Skuja *et al.*⁴ proposed a twofold coordinated Si for the absorption band.

In agreement with the calculation of O'Reilly and Robertson,⁵ a semiempirical calculation recently carried out by Dianov *et al.*⁶ shows two types of ODC defects: relaxed $\equiv\text{Si}-\text{Si}\equiv$ with Si-Si bond length of 2.7 Å and unrelaxed $\equiv\text{Si}-\text{Si}\equiv$ with bond length 4.25 Å. The one with bond length of 4.25 Å (unrelaxed ODC) has optical absorption at 5 eV. This result is in agreement with the two types of ODC reported by Imai *et al.*³ In this letter we report for the first time the observation of a reversible change in the 5 eV absorption band in silica using laser calorimetry and optical transmission measurements. This provides additional experimental evidence supporting the unrelaxed ODC model for the 5 eV absorption in silica.

Synthetic silica rods 4 mm in diameter and approximately 23 mm in length containing 1200 ppm OH (Suprasil 2) and <5 ppm OH (Suprasil W) manufactured by Heraeus Amersil were placed lengthwise in the direction of an unfocused beam (3 mm in diameter) of a multigas excimer laser (Model MEG 103 MSC, Lambda Physik) with KrF ($\lambda=248$ nm, 5 eV) as the lasing medium. A differential thermocouple was placed on the side face of the glass rods to measure the temperature (T) change of the sample in which only the central portion of 3 mm in diameter was exposed to the 5 eV photons. The incident laser power (10–200 mW) was determined independently using a pyroelectric joulemeter (Molelectron Model J25). The absorption coefficient, β , at 248 nm was calculated from the heating rate (dT/dt) of the sample according to the technique described by Hass *et al.*⁷ and Jewell *et al.*⁸ The typical error in the absorption coefficient is estimated to be about ± 0.003 cm⁻¹.

Optical transmission spectroscopy measurements of both the high and low absorption states at 5 eV were measured using a UV-VIS-NIR spectrometer (Model Cary 2400, Varian).

Figure 1 shows the typical absorption coefficient determined calorimetrically of a high OH containing silica, Suprasil 2, as a function of KrF excimer laser fluence at various laser pulse energies and repetition rates. The absorption coefficient at 5 eV for an average pulse energy of 50 mJ (≈ 25 mJ/cm²) and repetition rate of 40 Hz increases from about 0.02 cm⁻¹ with laser fluence and subsequently exhibits saturation at about 0.045 cm⁻¹. At the saturated state, there is no change in absorption coefficient even when the repetition rate is increased from 40 to 160 Hz. However, when the average laser pulse energy is decreased from 50 to 20 mJ, the absorption coefficient at 5 eV decreases with laser fluence and then exhibits saturation at

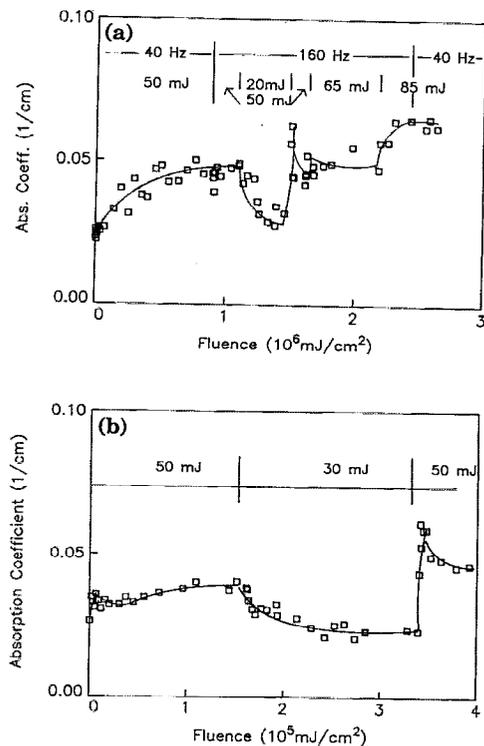


FIG. 1. The absorption coefficient at 5 eV for (a) Suprasil 2 and (b) Suprasil W at room temperature vs KrF laser fluence for various pulse energies and repetition rates. The solid line is drawn as an aid to the eye. Typical error is estimated to be about ± 0.003 cm⁻¹.

^{a)}Also with Virginia Polytechnic Institute, Blacksburg, VA 24061.

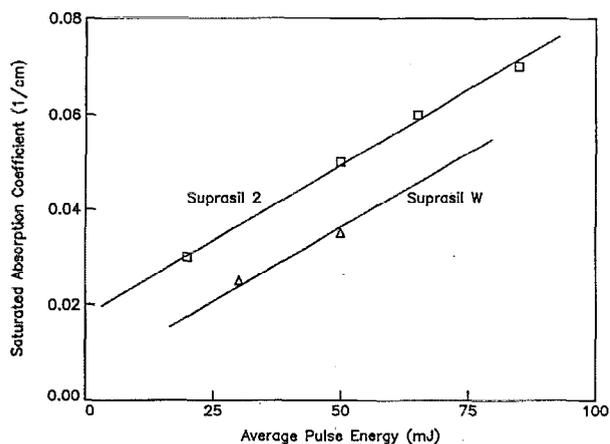


FIG. 2. Saturated absorption coefficient of Suprasil 2 and W vs average laser pulse energy from Figs. 1(a) and (b). Solid lines are arbitrary drawn to aid the eye.

about 0.025 cm^{-1} . Clearly, the absorption coefficient at 5 eV varies with the laser pulse energy and not with the laser repetition rate, as demonstrated in Fig. 1(a). Similar results are also observed in a low OH-containing silica, Suprasil W as shown in Fig. 1(b) for a repetition rate of 160 Hz. Thus, irrespective of the OH concentration in silica, the absorption coefficient at 5 eV depends reversibly on the average laser pulse energy and is independent of the repetition rate. It is to be noted that the absorption coefficient shows an initial spiking at laser repetition rates of 160 Hz when the average pulse energy is increased [see Figs. 1(a) and 1(b)]. The origin of this phenomenon is unknown but likely is related to some form of perturbation from equilibrium subsequently relaxing.

The saturated absorption coefficients, β_{sat} , of Suprasil 2 and W [i.e., plateau regions in Figs. 1(a) and 1(b), respectively] are shown as a function of laser pulse energy in Fig. 2. It demonstrates that β_{sat} increases linearly with laser pulse energy.

To understand the origin of the reversible change in the absorption coefficient at 5 eV with laser pulse energy, absorption spectroscopy was performed at different absorption saturation states. The optical absorption spectra of a Suprasil 2 at high and low saturated absorption states are shown in Fig. 3 along with that of the unirradiated sample. It is to be noted that the absorption coefficient measured in this optical transmission method is higher than those shown in Figs. 1 and 2 measured by laser calorimetry because only the nonradiative part of the absorption measured in transmission method is detected in calorimetry measurement. These two saturation states were prepared by subsequently irradiating the sample with KrF laser pulse energy of 55 and 17 mJ/cm^2 . The difference spectrum for the two saturation states is shown in Fig. 3(b). The solid line in Fig. 3(b) is a least-squares fit to the difference spectrum. The figure demonstrates clearly that the variation in the absorption coefficient at 5 eV measured calorimetrically is due to the change in the intensity of the 5 eV optical absorption band.

The possibility that part of this change in absorption

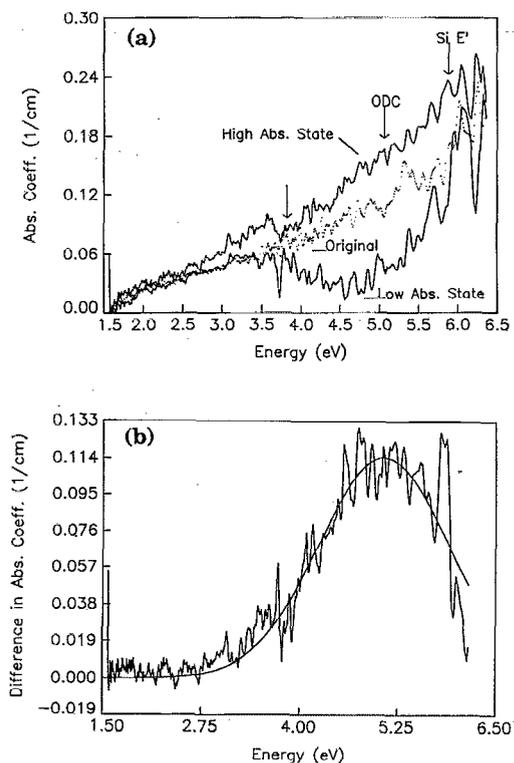


FIG. 3. (a) The optical absorption spectra of unirradiated Suprasil 2 (dotted line) and at high and low absorption states, and (b) the difference absorption spectrum of the high and low absorption states of (a). The solid line in (b) is a least squares fit to the data. The absorption band at 3.8 eV, assigned either as peroxy linkage (-O-O-) or Cl_2 are from Refs. 13 and 14, respectively.

coefficient at 5 eV is due to the formation of ozone, which has an absorption band at 4.8 eV (Ref. 9) can be ruled out because no 4.8 eV absorption band is observed in Suprasil 2 even when irradiated with 7.9 eV photons,¹⁰ and photons of energy greater than 5.1 eV are required to dissociate O_2 to form an ozone.^{8,11} (The induced absorption of $0.015/\text{cm}$ for the 4.8 eV absorption band reported by Devine *et al.*¹² in oxygen-containing Suprasil W irradiated with 5 eV photons is one order of magnitude smaller than the change we report here.) Since Suprasil is stoichiometric silica and has photoluminescence bands excited by 6.4 eV (Ref. 13) and by 7.8 eV (Ref. 14) similar to that of ODC, we then assigned the induced 5 eV band to ODC.

Since our sample is nonuniformly irradiated, local stress can build up.¹⁵ The ≈ 2 eV absorption width observed can then be attributed to the stress induced broadening [The $B_{2\alpha}$ band observed in as-sputtered SiO_2 film has width ≥ 1 eV as reported by Hickmott,¹⁶ which is in contrast to the ≤ 0.5 eV width observed in ion (uniformly) irradiated silica.¹⁷] Notice that the bleaching of the ODC results in the appearance of an absorption band centered at 3.8 eV, which can be associated with a peroxy linkage (-O-O-) defect center¹⁸ or Cl_2 .¹⁹ This, to the best of our knowledge, is the first report on the observation of 3.8 eV absorption band in Suprasil. Comparing the width reported for peroxy linkage¹⁸ or Cl_2 (Ref. 19) in silica, similar stress-induced broadening as that observed on the 5 eV

band can also be noticed for this 3.8 eV band due to non-uniform irradiation in our sample.

Our observation that β_{sat} is independent of the laser repetition rate suggests that ODC generated by atomic movement following the absorption of high power UV light is stable. Indeed, no change in 5 eV absorption coefficient have been observed on all the samples measured overnight.

Since the band gap of silica is approximately 9 eV (Ref. 5) and therefore the generation of ODC via the dissociation of an Si—O bond requires the absorption of at least two 5 eV photons, we suggest that the generation of these ODCs is through a two-photon absorption process. This is consistent with the report²⁰ that the initial absorption coefficient at 5 eV increases linearly with laser pulse energy. The result of Fig. 2 that β_{sat} , which is proportional to the concentration of ODC at saturation state, increases linearly with average laser pulse energy then implies that the bleaching of ODC involves the absorption of one 5 eV photon. This is in contrast to the bleaching of 5 eV absorption band to generate Si E' center by two-photon absorption processes reported by Arai *et al.*²¹ It is also consistent with our observation that the concentrations of the Si E' center at high and low absorption states, estimated from the absorption band at 5.85 eV from the spectra in Fig. 3(a), are approximately the same. Thus, in these one-photon bleachings of the 5 eV absorption band, no Si E' centers are generated, which is in contrast to the reports of Tsai *et al.*²² and Arai *et al.*²¹ that Si E' centers are generated in two-photon absorption processes. This, together with the fact that ODC can be reversibly generated in silica (see Figs. 1) suggests that the recovery of the displaced oxygen to form Si-O-Si is likely the process in the one-photon bleaching of the ODCs.

Since the oxygen atom is comparable in size to atomic hydrogen,²³ which is known to be mobile²⁴ in silica at temperatures as low as 130 K, we can presume that atomic oxygen is also mobile in silica at room temperature. To form stable ODC at room temperature, the displaced oxygen must either form O₂ molecules or be bound to the glass network. However, if all the displaced oxygen form molecular O₂, the bleaching of ODC to form Si-O-Si in the glass network cannot be a one 5 eV photon process because O₂ cannot be dissociated by one 5 eV photon.¹¹ [The weak 4.8 eV absorption band induced in oxygen containing silica (Suprasil W), reported by Devine *et al.*¹² is likely the result of two-photon absorption processes, due to very high pulse energy (300 mJ/cm²) used.] Therefore, the above conclusion that the bleaching of ODC is a one-photon process suggests that some of the displaced oxygen is weakly bound in the glass network and can be dissociated with one 5 eV photon. It is likely that these oxygen atoms are bound to oxygen in the glass network via a dative bond, i.e., O→O (network). The absorption of one 5 eV photon at that site dissociates this O→O (network) bond and results in a mobile oxygen atom that can move to and subsequently bleach a nearby ODC.

To recover the ≡Si—O—Si≡ network by reacting the displaced oxygen with ODC, extra lattice energy is needed for relaxed ODC but not for unrelaxed ODC. Therefore,

the relaxed ODC is likely not involved since thermal energy of the sample during measurements (≈ 300 K) is only about 0.025 eV. Nor can the model of two coordinated Si atoms of Skuja *et al.*⁴ satisfactorily explain the reversible change in the 5 eV absorption band. We thus conclude that the ODC we observed is unrelaxed ODC [ODC(II)] reported by Imai *et al.*³

In summary, we have found that the optical absorption at 5 eV in high purity SiO₂ glass can be changed reversibly by high intensity UV laser light. This is due to the generation and bleaching of an optical absorption band centered at 5 eV by two- and one-photon absorption processes, respectively. Consistent with previously reports,^{21,22} no Si E' was generated in this one 5 eV photon bleaching processes. Likely, the dissociation of the dative bond [O→O (network)], formed by the displaced oxygen from the SiO₂ glass network, is responsible for the one-photon bleaching phenomenon. More works are in progress to help understand the transient phenomena observed and will be reported in future publication.

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