Optical signatures of intrinsic electron localization in amorphous SiO$_2$

A-M El-Sayed$^1$, K Tanimura$^2$ and A L Shluger$^1$

$^1$ Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, Gower Street, London, WC1E 6BT, UK
$^2$ The Institute of Scientific and Industrial Research (ISIR), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

E-mail: al-moatasem.el-sayed.10@ucl.ac.uk

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Abstract
We measure and analyse the optical absorption spectra of three silica glass samples irradiated with 1 MeV electrons at 80 K, where self-trapped holes are stable, and use ab initio calculations to demonstrate that these spectra contain a signature of intrinsic electron traps created as counterparts to the holes. In particular, we argue that optical absorption bands peaking at 3.7, 4.7, and 6.4 eV belong to strongly localised electrons trapped at precursor sites in amorphous structure characterized by strained Si–O bonds and O–Si–O angles greater than 132°. These results are important for our understanding of the properties of silica glass and other silicates as well as the reliability of electronic and optical devices and for luminescence dating.

Keywords: electron traps, optical absorption, excited state

(Some figures may appear in colour only in the online journal)
The strong absorption peaking at 5.1 and 5.7 eV are associated with B2 and E′ centres (3-coordinated Si dangling bond), respectively. We note that the origin of the absorption bands around 4.5 – 6.0 eV depends critically on the samples employed. In fact, in the SZ sample with a significant amount of ODC(I), the dominant contribution comes from the B2 centre (see figure 1(a)). In the SCF sample, which includes almost no chemical impurities — concentrations of both Cl and OH ions are less than 1 ppm — however, it includes 500 ppm of oxygen deficiency (so-called ODC(II)) centres that exhibit a strong absorption peak at 7.6 eV and its fundamental absorption edge was measured at 8.0 eV. On the other hand, SCF has no Cl ions (less than 1 ppm), but includes about 1000 ppm of OH ions. All samples were cut and polished to a size of 8 × 10 × 1 mm and irradiated with electron beams (1 MeV, 20 ns duration) generated from a Febetron (HP43710A) at 80 K. The optical absorption spectra were measured after the irradiation using a spectrophotometer (Shimazu UV-3100). A Xe-arc lamp was used as the light source for optical excitation of the irradiated specimens. Red light with a wavelength range from 600 to 780 nm, and UV light with a peak at 320 nm (3.87 eV) and a band pass of 10 nm was generated by combining appropriate optical filters.

The black curve in figure 1(a) shows the optical absorption spectrum induced by the electron irradiation at 80 K in the SZ sample. Several peaks are clearly distinguishable. The lowest-energy peak at 2.2 eV has been attributed to self-trapped holes with two-centre type configurations (STH2) [17]. The peaks at 5.1 and 5.7 eV are associated with B2 and E′ centres (3-coordinated Si dangling bond), respectively. We note that the origin of the absorption bands around 4.5 – 5.0 eV depends critically on the samples employed. In fact, in the SZ sample with a significant amount of ODC(I), the dominant contribution comes from the B2 centre (see figure 1(a)). In the SCF sample, which includes OH ions, non-bridging oxygen hole centres, which show an absorption peak at 4.8 eV, are the dominant contributor, while in SW1, which includes dissolved oxygen, the ozone centres contribute primarily at 4.8 eV. These are typical examples of specimen-dependent features of absorption bands. On the other hand, the peak with a maximum at 3.7 eV is an, as yet, unattributed centre band (broken curve at 2.2 eV), a 3.7 eV band (thick solid curve), and the rest of the spectrum (solid green curve), which are decomposed further into a 4.7 eV band (thin red curve), the E′ centre band (broken curve centred at 5.8 eV) and the 6.6 eV band (thin solid curve).

experimental evidence of intrinsic electron trapping in a-SiO2 is still missing.

In this paper we measure and analyse the optical absorption spectra of three different silica glass samples irradiated at 80 K, where trapped electrons could co-exist with self-trapped holes, and use theoretical calculations to suggest that these spectra contain a signature of intrinsic electron traps.

2. Experimental observations

Three different, high-purity a-SiO2 samples were used in this study to differentiate the results that are specific to only a given sample from those that are common to all samples. These include Suprasil W1 (SW1), Viosil-SCF (SCF), and Viosil-SZ (SZ); all fabricated by Shin-Etsu Quartz, LTD. SW1 has less than a few ppm of OH ions, but includes a considerable amount of dissolved O2. SZ includes almost no chemical impurities — concentrations of both Cl and OH ions are less than 1 ppm; however, it includes 500 ppm of oxygen deficiency (so-called ODC(II)) centres that exhibit a strong absorption peak at 7.6 eV and its fundamental absorption edge was measured at 8.0 eV. On the other hand, SCF has no Cl ions (less than 1 ppm), but includes about 1000 ppm of OH ions. All samples were cut and polished to a size of 8 × 10 × 1 mm and irradiated with electron beams (1 MeV, 20 ns duration) generated from a Febetron (HP43710A) at 80 K. The optical absorption spectra were measured after the irradiation using a spectrophotometer (Shimazu UV-3100). A Xe-arc lamp was used as the light source for optical excitation of the irradiated specimens. Red light with a wavelength range from 600 to 780 nm, and UV light with a peak at 320 nm (3.87 eV) and a band pass of 10 nm was generated by combining appropriate optical filters.

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and SCF samples, which contain almost no oxygen vacancies (see figure 2 in [17]).

To reveal the origin of the 3.7 eV band, we measured its growth kinetics as a function of electron dose. In figure 2, the growth characteristics of the E′ centres (5.7 eV), STH2 (2.2 eV), and the 3.7 eV absorption band are shown. The yield of E′ centres increases linearly with the dose, while those of the STH2 and the unattributed centre are strongly correlated and show a tendency to saturate at doses greater than ≈1.5 × 105 Gy, indicating that the STH2 and 3.7 eV peak grow concurrently. One of the reasons for saturation could be that the number of precursor sites for trapped holes is limited and smaller than the number of oxygen vacancies in SZ samples.

The thermal stability of the defects responsible for the optical absorption spectrum in figure 1(a) was studied by a pulse annealing method. The red line in figure 1(a) shows the absorption spectrum after warming the irradiated sample up to 186 K (at which STHs are mobile) for 5 min, followed by an absorption measurement at 80 K. One can see that the peaks at 2.2 and 3.7 eV are completely annealed out, which is also demonstrated by the blue curve showing the difference
3. Theoretical calculations

To further investigate the atomistic origins of the 3.7 eV and other absorption bands in figure 1, we calculated the optical transitions of intrinsic electron trapping centres in a-SiO₂ using an embedded cluster method implemented in the GUESS code [21]. The effect of structural disorder in glass samples on inhomogeneous broadening of absorption spectra is included by using seven independent models of a-SiO₂. These were produced using the ReaxFF forcefield [22] and molecular dynamics simulations to melt samples of crystalline β-cristobalite at 5000 K and then quench them to 0 K. This procedure is explained in detail in a previous publication [16].

These models were then adapted for use in an embedded cluster model where each a-SiO₂ matrix was represented as a spherical nanocluster divided into two regions—I and II. Region I is located in the centre of the nanocluster and is further subdivided into three concentric regions of different physical descriptions. The centre of region I consists of a cluster of atoms which are treated using density functional theory (DFT) implemented in the Gaussian09 code. The Si and Ge atoms are described with a 6-31G* basis set and the O atoms with a 6-31G basis set and the O atoms with a 6-31G basis set.

Figure 2. Growth kinetics of the optical absorption bands of electron irradiated a-SiO₂ measured at 80 K. The 2.21 eV and 3.70 eV peaks show a trend to saturate at a dose greater than 1.5 × 10⁵ Gy.

of negatively charged oxygen vacancies is at about 3.3 eV [19] and they can contribute to the 3.7 eV absorption in SZ samples which include a considerable amount of oxygen vacancies. Some oxygen excess silica samples exhibit a relatively weak absorption band at 3.8 eV. This band had initially been attributed to peroxy linkages, but was later shown to be due to interstitial Cl₂ molecules [20]. However, as noted above, the 3.7 eV band is induced in all of the SW1, SZ and SCF samples regardless of whether they include dissolved oxygen, OH ions or pre-existing oxygen vacancies. Therefore, we can exclude these defects from being the source of the 3.7 eV band in this study. The remaining candidate is an electron trapped by the amorphous SiO₂ network [16].
the well-known Ge electron centre (GEC) in \( \alpha \)-quartz, which has a similar structure to the electron trap considered here [16]. It is responsible for the Ge(I) EPR signal [29]. This signal strongly correlates with an optical absorption band at 4.2 eV, which is now universally attributed to this centre [17, 30–32]. Optical absorption spectra of Ge-doped SiO\(_2\) include additional bands that peak at \( \approx 5.8 \) eV and higher energies, which have also been tentatively assigned to GEC [33].

The quantum cluster containing 72 atoms and representing the \( \alpha \)-quartz structure was embedded in the rest of the crystal as described above. A single Si atom at the centre of the quantum cluster was substituted for a Ge atom and the geometry of the system was optimized in the neutral charge state. The relaxation resulted in an extension of the Ge–O bonds to 1.72 Å compared to the Si–O bonds (1.64 Å) in \( \alpha \)-quartz; however, the GeO\(_4\) tetrahedron remains intact. The calculated band gap of the system is 7.2 eV with a Ge unoccupied state located just below the conduction band and strongly localized on the Ge atom.

An extra electron was then added to the system followed by full geometry optimization. This resulted in a strong local relaxation, where the O–Ge–O angle opened from 109° up to 148° and the extra electron highly localized on the Ge atom, as shown in figure 3(a). The Ge–O bond lengths extend asymmetrically, so that two bonds measure 1.83 Å while the other two bonds measure 1.87 Å. This defect introduces an occupied electron state which sits 5.0 eV below the \( \alpha \) quartz conduction band.

The optical transition energies and oscillator strengths of the Ge electron trap in \( \alpha \) quartz were then calculated using TDDFT. The obtained optical absorption spectrum is plotted as a solid black line in figure 3(b) along with the experimental spectrum which is plotted as a dashed black line. The experimental spectrum was obtained by 1 MeV electron irradiation of Ge-doped \( \alpha \)-quartz at 6 K followed by a measurement, also performed at 6 K. The 4.2 eV band can clearly be seen and this is the band that has been attributed to the GEC, while there is another band at 2.2 eV for the GEC’s hole counterpart which is not considered in the calculation. The bar plot shows all calculated one-electron transitions. Each absorption line is Gaussian broadened by 0.3 eV in order to simulate homogeneous broadening. The total spectrum shown by the black line is a sum of broadened excitation energies, weighted by their respective oscillator strengths. The optical transitions can be categorised into two types. The transitions of the first type are highlighted as red bars while those of the second type are highlighted as blue bars. The first type is caused by transitions of the unpaired electron localized on the wide O–Ge–O angle into quasi-local states at the bottom of the a-SiO\(_2\) conduction band (see also transition 1 in the inset of figure 4(b)). It exhibits a peak with a maximum at 4.2 eV, in excellent agreement with experiment. The second type is due to transitions of a \( \beta \)-spin electron from the occupied non-bonding oxygen ‘p’ orbitals, which have broken away from the top of the a-SiO\(_2\) valence band due to the structural distortion introduced by the defect, to the unoccupied state which is localized on the wide O–Ge–O angle (see also transition 2 in the inset of figure 4(b)). They comprise 2 peaks with maxima at around 5.8 eV and 7.1 eV. The O ‘p’ states, which split from the top of the valence band, are localized around the wide O–Ge–O angle, similar to the O ‘p’ states of the nearest O neighbours highlighted in figure 3(a). The 5.8 eV peak agrees very well with the band recently assigned to the GEC in a-SiO\(_2\) [33].

3.2. Optical absorption of the electron trapping centre

As has been shown in previous calculations [16], extra electrons can trap at certain (precursor) sites in amorphous SiO\(_2\) networks without a barrier. These sites are characterized by
strained Si–O bonds and O–Si–O angles greater than 132°. Although these angles are at the extreme of the distribution of O–Si–O angles in a-SiO₂, which peaks at ≈109.5°, we have estimated that the concentration of such precursor sites in our glass models is ≈4 × 10¹⁹ cm⁻³ [16]. The electron trapping at network sites with O–Si–O angle less than 132°, requires overcoming an energy barrier and hence is less probable. After finding these sites in seven different a-SiO₂ models, a quantum region in an embedded cluster calculation was centred at a wide O–Si–O angle and included between 96 and 114 atoms. Due to the disorder in a-SiO₂ and the rather stringent criterion of O–Si–O angles greater than 132°, it was not possible to standardize the numbers of atoms described quantum mechanically across the seven different glass models. The quantum region was then interfaced with a classically polarizable region which contained between 910 and 933 atoms. The diameter of the entire system is ≈50 nm while the quantum regions are ≈1.5 nm in diameter. The positions of all atoms in region I were optimized in the neutral charge state. We also checked that the size of the region I is sufficient to accommodate the distortion induced by the electron localization in the amorphous network. The one-electron band gap averaged over the seven different samples in the embedded cluster model is 7.7 eV, ranging from 7.4 eV to 8.1 eV.

An extra electron was added into each of the seven samples and their respective geometries optimized, resulting in seven different intrinsic electron trap configurations, where an electron has localized at a precursor Si site and the O–Si–O angle has opened from 132° to an average of 174°, ranging over 5°. These electron traps introduce an occupied one-electron state located on average 4.3 eV below the bottom of the conduction band in the a-SiO₂ matrices, ranging between 3.7 and 4.8 eV. The spin density of this system is shown in figure 4(a).

The transition energies and oscillator strengths of all seven electron trapping configurations calculated using TDDFT are plotted together with equal weights in figure 4(b). The bar plot shows all optical transitions corresponding to the two types explained in the inset of figure 4(b) with their respective oscillation strengths. Each absorption line is Gaussian broadened by 0.3 eV to simulate homogeneous broadening and the black line in figure 4(b) is produced as a sum of all Gaussian broadened optical transitions in seven electron trapping centres weighted by their respective oscillation strengths. Transitions of the first type are highlighted as red bars while the second type are highlighted as striped blue bars. The first type is caused by the electron localized on the wide O–Si–O angle (see figure 4(a)) being excited into quasi-local states at the bottom of the a-SiO₂ conduction band composed of ‘d’ orbitals of nearby Si atoms and nearby O ‘s’ orbitals. These transitions cause peaks with maxima at 3.7 and 4.7 eV. The second type is due to the excitation of a β-spin electron from the occupied non-bonding oxygen ‘p’ orbitals, which have broken away from the top of the a-SiO₂ valence band due to the structural distortion introduced by the intrinsic electron trap, into the unoccupied states in the band gap localized on the wide O–Si–O angle. They comprise a peak with a maximum at around 6.4 eV. These non-bonding O ‘p’ states are localized around the wide O–Si–O angle, similar to the O ‘p’ states of the nearest O neighbours highlighted in figure 4(a). The whole spectrum is much broader than that of the GEC in figure 3(b) because the transitions in each local defect configurations have different energies due to the disorder of a-SiO₂.

We note that the calculated spectrum exhibits transitions in the energy range of 3–7 eV. This is consistent with both the anneal and spectral bleaching data, which show a significant reduction of the optical density at energies exceeding 4 eV (see figure 1). The nature of both types of transitions is the same as in the GEC. The results of the thermal anneal at 186 K shown in figure 1(a) demonstrate that hole mobility causes complete bleaching of the optical absorption up to about 4.0 eV and partial depletion of bands at higher energies. This is consistent with our suggestion that the 3.7 eV band originates from the trapped electron centre created as a counterpart to self-trapped holes and indicates that the higher energy
bands are composites of optical absorption bands of trapped electrons as well as other defects. The first type of electron excitation would create electrons at the bottom of the a-SiO$_2$ conduction band, which would then recombine with holes and react with other defects. This explains why the optical excitation with 3.87 eV photons results in the bleaching of the 2.2 eV band and some of the E’ centres.

4. Conclusions

Our results provide the strongest evidence yet for the formation of intrinsic localized electron centres in a-SiO$_2$ as a counterpart to self-trapped holes and support a detailed theoretical model of a strongly localized electron in a disordered oxide. This localization is promoted by strained Si–O bonds and results in distorted SiO$_4$ tetrahedra. Therefore, one can expect that similar electron traps can exist in other types of silica glasses [34], feldspar and tectosilicates based on networks of SiO$_4$ tetrahedra. Many of these materials contain, as yet unexplained, deep electron centres responsible for thermo-luminescence employed in e.g. luminescence dating [1]. Therefore, we believe the optical signatures of intrinsic electron traps revealed here will be useful for understanding the properties and stability of other silicates, and electronic and optical devices utilizing a-SiO$_2$.

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