OPTICAL PROPERTIES AND STRUCTURE OF DEFECTS IN SILICA GLASS

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Abstract

This paper reviews the structures of paramagnetic defects in silica glasses as they are understood from electron spin resonance (ESR) spectrometry. A synthesis of ESR and optical results found in the recent literature leads to the most probable assignments of several radiation-induced optical absorption bands in the visible, ultraviolet, and vacuum ultraviolet spectral regions.

1. Introduction

Silica glasses are exceedingly valuable optical materials which generally perform well even in stressing environments. Still, under high doses of ionizing radiations—or even high fluences of intense laser light—"color centers" are formed which cause the attenuation of transmitted light signals (see Fig. 1)[1] and may give rise to fluorescence emissions. In order minimize such unwanted effects, it has proved necessary to understand the microscopic natures of these color centers. This understanding is generally accomplished with the aid of structure-specific spectroscopies, such as electron spin resonance (ESR). The application of ESR to defect centers in silica glasses has been the subject of

a great many papers published over the past 35 years and some of the experimental correlations which link specific optical bands to specific ESR-active defect centers have been critically reviewed as of 1991[2]. The present paper is intended to serve as a condensed guide to the ESR literature and as an extended abstract to Ref. 2.

2. Information from ESR

ESR can only be applied to the subset of defect centers which are *paramagnetic*, i.e., those defects which are associated with an unpaired electron "spin". However, by means of carefully designed experiments, the amount of information which can be learned about these paramagnetic defects is enormous. Observations of hyperfine interactions with nearby "magnetic nuclei" (isotopes with non-zero nuclear magnetic moments) make it possible to map out the wavefunction of the unpaired spin and sometimes to infer the local atomic arrangements at the defect site. In pure silicon dioxide, the relevant magnetic nuclei are ^{29}Si and ^{17}O. These isotopes are 4.7 and 0.037% abundant in nature, respectively. Thus, isotopic enrichment experiments are generally necessary to obtain the all-important hyperfine information for Si and O. Additional background information on the ESR technique as applied to glasses is available elsewhere.[3-5]

The E′ centers comprise the best known family of paramagnetic defects in silicon dioxide.[6-12] Each of several known E′ species has in common the structure ≡Si•, where "≡" denotes three bonds with bridging oxygens and "•" represents the unpaired spin. The ^{29}Si hyperfine data demonstrate the unpaired spin for the E′ centers to be confined to a dangling sp^3 orbital of a single silicon atom. The

precursor of an E′ center is a usually diamagnetic oxygen vacancy, ≡Si-Si≡, which may preexist in the glass *or be created by the radiation*. Thus, the creation mechanism for the so-called E'_1 (E'_γ) center in crystalline α quartz[6,8] (silica glass)[9-12] can be written:

$$\equiv Si-Si\equiv \rightarrow \equiv Si\bullet \text{ }^+Si\equiv \text{ } + \text{ } e^-. \tag{1}$$

where the extracted electron, e^-, becomes trapped elsewhere in the material. The asymmetric relaxation which confines the unpaired spin to just one of the two silicons at the vacancy site has been explained theoretically.[13,14] One possible creation mechanism for the $E'_2{}^7$ (E'_β)[12] center can be expressed:

$$\equiv Si-Si\equiv \text{ } + \text{ } H^0 \rightarrow \equiv Si\bullet \text{ } \equiv Si-H, \tag{2}$$

where the presumed asymmetric relaxation of the ≡Si-H fragment is the result of theoretical calculation.[15] The atomic hydrogen appearing in Eq. (2) results from radiolysis of impurity hydroxyl groups according to[16-18]

$$\equiv Si-OH \rightarrow \equiv Si-O\bullet \text{ } + \text{ } \bullet H^0. \tag{3}$$

Both species on the right hand side of Eq. (3) are paramagnetic and can be monitored by ESR in the course of isochronal or isothermal annealing experiments. These experiments have indicated that much of the radiolytic atomic hydrogen dimerizes to form H_2, thus inhibiting the back reaction of Eq. (3) at temperatures below ~180 K.[16-18] The species ≡Si-O• is the nonbridging oxygen hole center (NBOHC), whose structure has been verified by ^{17}O and ^{29}Si isotopic

enrichment experiments.[19-21]

An additional oxygen-associated paramagnetic defect center is the peroxy radical. One particular peroxy radical species, $\equiv$Si-O-O$\bullet$, has been well characterized by observation of its ^{17}O and ^{29}Si hyperfine structures.[20,22] Two possible creation mechanisms for this peroxy radical are:

$$\equiv\text{Si-O-O-Si}\equiv \;\rightarrow\; \equiv\text{Si-O-O}\bullet \;^{+}\text{Si}\equiv \;+\; e^{-} \tag{4}$$

and

$$\equiv\text{Si}\bullet \;^{+}\text{Si}\equiv \;+\; O_2 \;\rightarrow\; \equiv\text{Si-O-O}\bullet \;^{+}\text{Si}\equiv. \tag{5}$$

The latter mechanism, i.e., the reaction of an E'_γ center with an interstitial O_2 molecule,[23] has been unambiguously demonstrated by employing silica samples "stuffed" with calibrated amounts of dissolved molecular oxygen.[24,25]

3. ESR-Optical Correlations

Perhaps the best ESR-optical correlation found in the literature is that linking the E'_γ center with an absorption band centered at 5.85 eV: A linear relationship between the optical absorption coefficient at 215 nm and the E' center ESR signal amplitude was demonstrated for variations of both quanties over nearly two orders of magnitude.[26] Another E' center—presumably E'_β—has been correlated with an optical band centered at ~5.4 eV.[27] These bands are among those included in the Gaussian resolutions of the radiation-induced spectra of Fig. 2.[28]
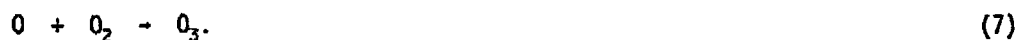
The origin(s) of a much weaker band centered near 2.0 eV (see Fig. 1) have been strongly debated in the literature,[29-35] due to the seemingly contradictory natures of the ESR-optical correlations which had been obtained.[30,32] A possible resolution of this problem has been developed in ref. 2, where it is proposed that the NBOHC is the primary contributor to the 2.0-eV band, while the peroxy radical must also have a band (of lower oscillator strength) near the same position. A band at 7.7 eV has also been correlated with the peroxy radical.[19]

4. Absorption Bands Due to Diamagnetic Defects

Absorption bands near 5 and 7.6 eV are conventionally assigned to diamagnetic oxygen-vacancy-type defects, since such bands are commonly observed—in the absence of an ESR spectrum—in certain as-manufactured (unirradiated) silicas which are oxygen deficient. In one view,[36] both bands are optical transitions of the simple oxygen vacancy, $\equiv$Si-Si$\equiv$. In a second view,[37] the 5-eV band arises from an unrelaxed vacancy, $\equiv$Si$^\frown$Si$\equiv$, while the 7.6-eV band is due to $\equiv$Si-Si$\equiv$ homobonds. In a third view,[38] the 5-eV band is ascribed to a two-coordinated silicon, -O$^\diagup$$^{Si}_\diagdown$O-. Adding to the complexity of this debate is the fact that *two* 5-eV "B$_2$" bands have been isolated:[39] the B$_2\alpha$ band at 5.02 eV and the B$_2\beta$ band at 5.17 eV. Only the former appears in conjunction with the 7.6-eV band; however, the B$_2\alpha$ band can be bleached by excimer laser light while the 7.6-eV band is unchanged.[37] The available evidence reviewed in ref. 2 is still inconclusive on the question of which model is correct but leans toward the third view on the strength of photoluminescence studies.[38]
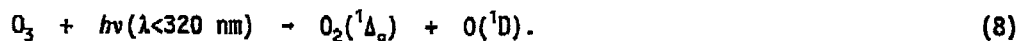
The intensity 4.8-eV band is seen in Fig. 2 to vary widely from sample to sample, particularly in relation to the intensities of the E′ bands at 5.4 and

5.85 eV. The 4.8-eV band does not correlate with any ESR center and, in particular, its exclusive association with NBOHCs has been ruled out.[40] In silicas known to contain dissolved O_2 molecules, the 4.8-eV band can be induced by both 7.9- and 6.4-eV excimer laser light,[41,42] as well as by γ irradiation. The best explanation[42] of the 4.8-eV band seems to be that it arises from interstitial molecular ozone generated according to the reactions:

$$O_2 + h\nu(\lambda < 242\ nm) \rightarrow 2O, \tag{6}$$

$$O + O_2 \rightarrow O_3. \tag{7}$$

In support of this assignment, it has been noted that the position and width of the 4.8-eV band are virtually identical with those of the Hartley bands[43] of atmospheric ozone.

An interesting observation concerns the ability to excite the well-known 1.9-eV photoluminescence by illuminating into the 4.8-eV band, since the luminescence certainly arises from NBOHCs. It has been proposed[40] that the 4.8-eV band is associated with an "energy donor center" which transfers the excitation to an "energy acceptor center" (the NBOHC). Recent evidence[42] now suggests that the "energy donor center" is interstitial ozone. It is known from atmospheric photochemistry[43] that ozone can be photodissociated for $h\nu > 3.9$ eV:

$$O_3 + h\nu(\lambda < 320\ nm) \rightarrow O_2(^1\Delta_g) + O(^1D). \tag{8}$$

The $O(^1D)$ excited state may decay to the $O(^3P)$ ground state by emission of a 1.97-eV photon, but the intrinsic lifetime (147 s)[44] is very long, so that in the

atmosphere the luminescence is quenched by collisions with O_2 molecules. This time is also much longer than the decay of time of the 1.9-eV luminescence in silica (~20 μs).[40,41] The explanation proposed in ref. 2 is that the $O(^1D)$ atom diffuses to the site of an NBOHC where it transfers its energy of excitation resonantly. The observed temporal dependence[40] of the 4.8-eV-excited 1.9-eV luminescence is consistent with this model. Moreover, the excitation spectrum[42] for one oxygen-rich silica sample was virtually identical with the quantum yield curve[43] for Eq. (8).

Figure 3[45] illustrates several vacuum ultraviolet bands observed in different types of as-manufactured (unirradiated) silicas. None of these bands is associated with an ESR spectrum. As noted above, the 7.6-eV band is found in oxygen-deficient silicas and is almost universally attributed to simple oxygen vacancies, ≡Si-Si≡. Indeed, the peak energy and absorption cross section of the 7.6-eV band agree well with those of the Si-Si bond in the Si_2H_6 molecule.[46] Annealing these silicas in H_2 gas results in the destruction of the 7.6-eV band due to the reaction:[45]

$$≡Si-Si≡ \; + \; H_2 \; → \; 2(≡Si-H). \tag{9}$$

The band tail labeled "OH" has been shown[45] to vary in strength in proportion to the hydroxyl content of the glass as determined by infrared spectroscopy at 2.73 μm. Finally, it has been pointed out[42] that the band tail labeled "O_2" is identical in shape with the Schumann-Runge bands[43] of O_2 molecules in the gas phase. That these bands in silica glass are also due to molecular oxygen was deduced[42] from the results of annealing in a hydrogen environment according to the reaction:

$$\tfrac{1}{2}O_2 \;+\; H_2 \;+\; \text{=Si-O-Si=} \;\rightarrow\; 2(\text{=Si-OH}), \tag{9}$$

where the resulting hydroxyl was monitoring at 2.73 μm.

Other optical absorption bands in the ultraviolet and vacuum ultraviolet may arise from chlorine impurities which are present up to levels of several tenths of a weight percent in certain synthetic silicas.[47] Radiation-induced defects associated with chloride impurities have been observed by ESR.[48]

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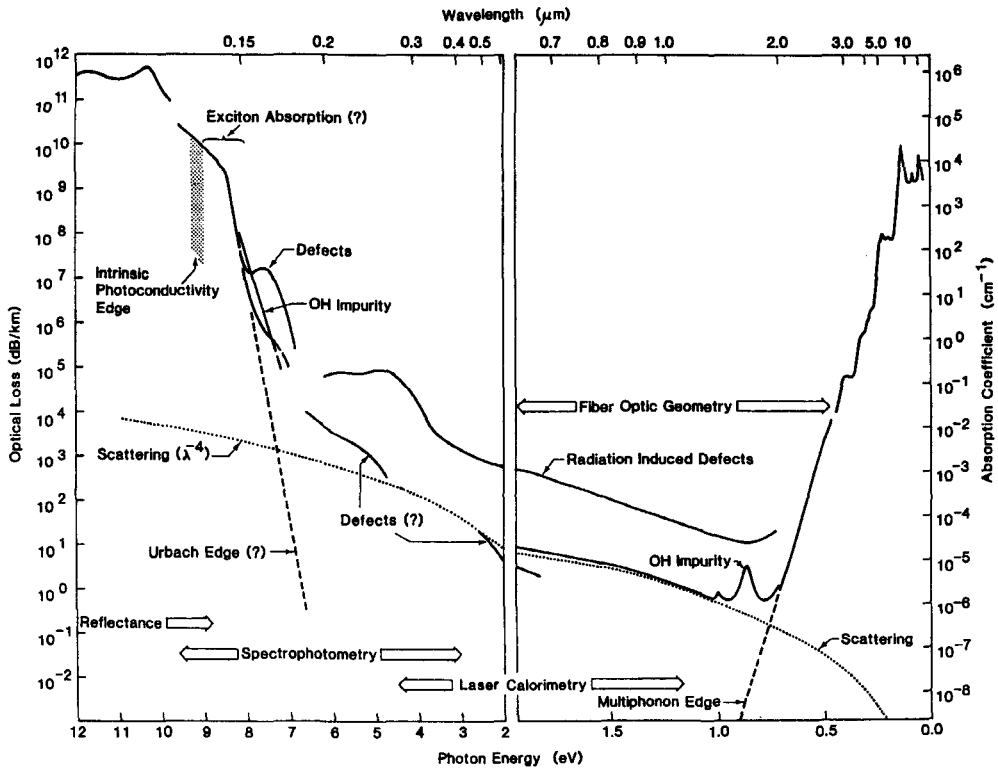
Fig 1.   Optical attenuation spectra of pure silica. Radiation-
induced spectrum pertains to Suprasil W1. Sources of
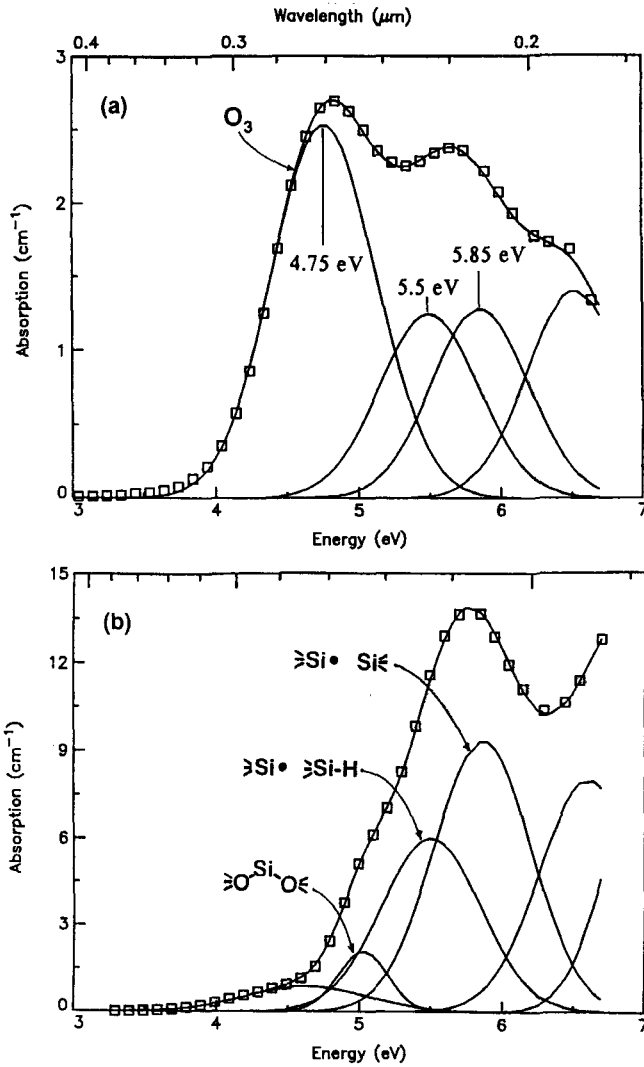original data are cited in ref. 1.

Fig. 2.   γ-ray-induced ultraviolet absorption spectra of two
commercial fused silicas: (a) O_2-containing Suprasil W1
and (b) Mitsubishi Diasil. The probable origins of
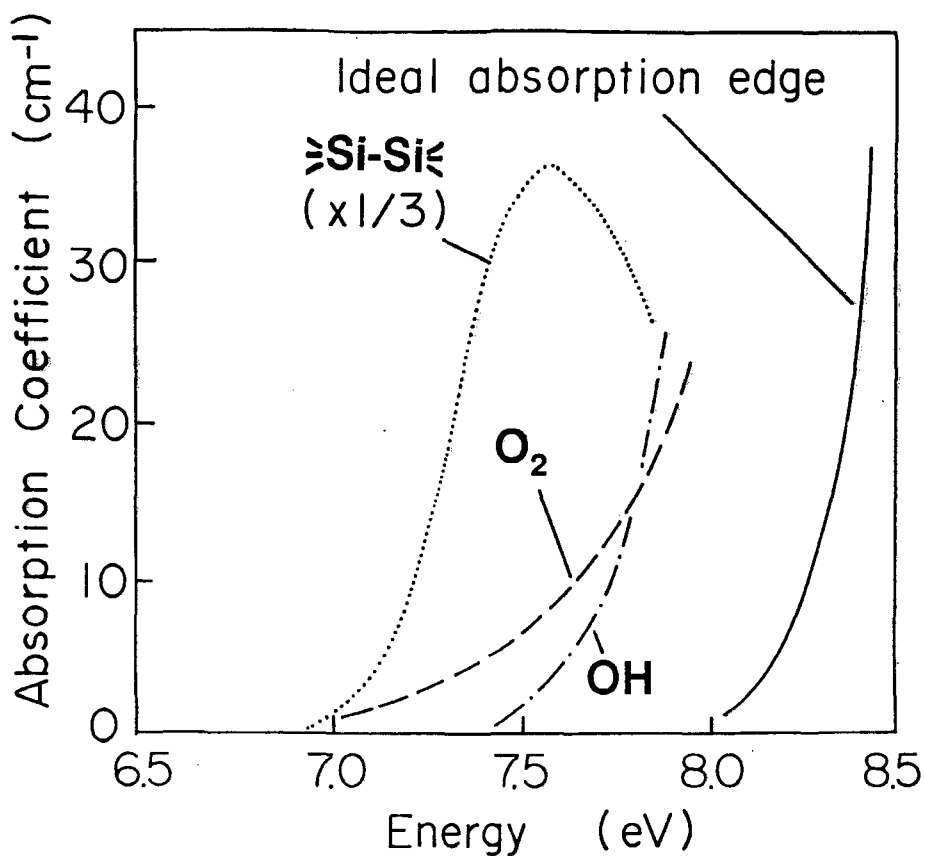several bands are indicated. Figure adapted from ref.
28.

Fig. 3.   Vacuum ultraviolet spectral features of unirradiated high-purity silicas arising from oxygen vacancies (=Si-Si=), dissolved O_2, and OH impurities. Figure adapted from ref. 45.