Structural origin of the 5.16 eV optical absorption band in silica and Gedoped silica

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The origin of the 5.16 eV absorption band observed in silica and Ge-doped silica was studied using optical and electron spin resonance (ESR) measurements. The band was observed only in samples containing Ge, suggesting that it is related to the Ge impurity in silica, while a lack of correlation between the ESR intensity of the induced hydrogen-associated doublet and the absorption coefficient of the 5.16 eV band indicates that it is not related to two-coordinated Si or Ge. The observation of the absorption coefficient increased as the square root of the Ge concentration demonstrates that the 5.16 eV band is not related to two-coordinated Ge defects but that it is an oxygen deficiency center of the divacancy type associated with Ge.

Synthetic silica are SiO_2 glasses prepared by hydrolysis of $SiCl_4$ in a hydrogen-oxygen or hydrocarbon-oxygen flame and fusion in an Ar or O_2 plasma. It is a high purity SiO_2 with very low optical absorption in the visible to near UV region.

The 5 eV ($\approx$245 nm) optical absorption band in silica, known as the B_2 band, was first proposed to be an oxygen deficiency center (ODC) by Arnold.[1] Later, Tohmon et al.[2] separated two types of B_2 bands: the $B_{2\alpha}$ band, normally observed in synthetic silica, has optical absorptions centered at 5.0 and 7.6 eV with a strong luminescence band centered at 4.3 eV and a weak one at 2.7 eV; and the $B_{2\beta}$ band, usually observed in fused quartz with an absorption at 5.16 eV, a weak luminescence at 4.3 eV, and a strong one at 3.1 eV.

Theoretical computer calculations by O'Reilly and Robertson,[3] recently confirmed by Dianov et al.[4] suggest that the $B_{2\alpha}$ band consists of two types of ODC: an unrelaxed ODC and relaxed ODC with an optical absorption at 5.0 and 7.6 eV, respectively, and distance between Si of about 4.3 and 2.7 Å, respectively. Experiments consistent with the existence of two types of ODC were reported by Imai et al.[5] A recent report by Tsai et al.[6] that the 5.0 eV absorption in silica can be reversibly changed, depending on the intensity of UV light, supports the structural model of an unrelaxed ODC for the 5.0 eV band in silica.

The report of Arai et al.[7] that the bleaching of the 5.0 eV band by UV light results in the generation of Si E' centers demonstrates conclusively that the $B_{2\alpha}$ band is an ODC type defect, in contrast to the two-coordinated Si proposed by Silin and Skuja.[8] However, the structural origin of the 5.16 eV $B_{2\beta}$ band is not yet understood. Two-coordinated Si in silica was recently proposed by Kohketsu et al.[9] and by Awazu et al.[10] to have an optical absorption at 5.16 eV. On the other hand, Skuja et al.[11] and Skuja[12] proposed a two-coordinated Ge defect for the 5.16 eV band in Silica containing Ge. Recently, Hosono et al. reported[13] that the 5.16 eV

band observed in Ge-doped silica consists of two bands: a 5.06 eV band associated with Ge-Ge ODC and a 5.16 eV band due to two-coordinated Ge.

In theory, these proposed two-coordinated defects can react with atomic hydrogen (H^0) to form hydrogen-associated paramagnetic centers through the following reaction:

$$—\ddot{T}—+H^0\rightarrow\ =\dot{T}—H, \tag{1}$$

where T is Si or Ge and · denote a nonbonding electron. When T is Si, the induced hydrogen-associated paramagnetic defects was shown by Tsai et al.[14] to have a 7.4 mT doublet electron spin resonance (ESR) spectrum. Radtsig and Bobyshev[15] proposed that when T is Ge, the hydrogen-associated paramagnetic defect has a 12.4 mT doublet. [Notice also that 11.9 mT doublet was found to be generated by the reaction of Ge(2) defects with H_2, as reported by Nagasawa et al.[16] and Tsai et al.[17]] Therefore, if two-coordinated Si or Ge defects exist, with high temperature baking, which changes the absorption coefficients of the 5 eV band,[18] we should be able to observe a correlated change of the 5.16 eV band and induced hydrogen-associated paramagnetic defects in accordance with Eq. (1). In this letter, experimental data are presented to demonstrate conclusively that the 5.16 eV $B_{2\beta}$ band is also an ODC type of defect in agreement with the general idea of an ODC defect proposed in Refs. 1 and 2.

Samples used in this study consist of synthetic silica containing no detectable Ge, fused quartz containing 1 ppm Ge, and 100 and 180 ppm Ge-doped silica. High temperature baking of the samples was carried out either in vacuum or in air at high temperature for various lengths of time in an electric furnace. Rods (1–1.9 cm diam) of various length were cut from samples and polished to an optical finish for optical measurements. Optical absorption measurements were carried out using a UV-VIS-NIR spectrometer (Varian Cary 2400). The absorption coefficients of the 5.16 eV band of the samples were obtained by Gaussian fit of their optical

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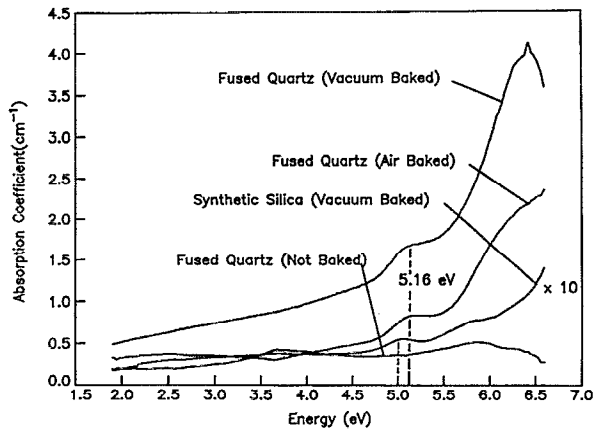[a]Also at Virginia Polytechnic Institute, Blacksburg, VA 24061.

FIG. 1. Optical absorption spectra of synthetic silica and fused quartz (containing 1 ppm Ge).

spectra. The typical error in the absorption coefficient is estimated to be about ± 0.02 cm^{-1}.

ESR samples of size 2 mm$\times$2 mm$\times$(4−8) mm were cut from the as-prepared and high-temperature baked samples and were irradiated with KrF excimer laser (EMG 103 MSC, Lamda Physik) with 10 Hz repetition rate and 120 mJ/pulse at room temperature. The average power of the laser was measured with a power meter (Lamda Physik, model EPM 300). The induced paramagnetic defects were studied at room temperature by X-band ESR ($\approx$9.4 GHz) employing 100 kHz field modulation using a Bruker ER 200D-SRC spectrometer.

Figure 1 shows typical optical absorption spectra of high temperature baked synthetic silica and both baked and unbaked fused quartz. The 5.0 eV band is induced only in high temperature baked synthetic silica containing no detectable Ge while the 5.16 eV band occurs in silica containing 1 ppm Ge (fused quartz), indicating that the 5.16 eV band is related to Ge impurities, in agreement with the observation of a 5.16 eV band in Ge-doped silica.[19]

Consistent with the above conclusion, Fig. 2(c) shows that the 5.16 eV band is observed in silica doped with 180 ppm Ge, either baked or unbaked. The absorption coefficient of the 5.16 eV band in the high temperature baked sample is higher (about 50%) than in the unbaked sample, in agreement with the report[18] of Awazu et al. The room temperature ESR spectra of both baked and unbaked samples irradiated with a KrF excimer laser to saturation in the concentration of the hydrogen-associated doublet are shown in Figs. 2(a) and 2(b). Paramagnetic defects clearly observed are Ge(1) and Ge(2) centers,[17] and the 11.9 mT hydrogen-associated doublet.[16,17]

Since no 7.4 mT doublet can be distinctly observed, the 5.16 eV band is likely not related to the two-coordinated Si defects in silica, in contrast to the proposal of Refs. 9 and 10.

As can be observed in Fig. 2(c), the high temperature baked sample has absorption coefficient about 50% higher than that in unbaked sample. Since both samples have about the same amount of OH, similar amounts of H^0 can be photo-induced. It is then expected, according to Eq. (1), that the
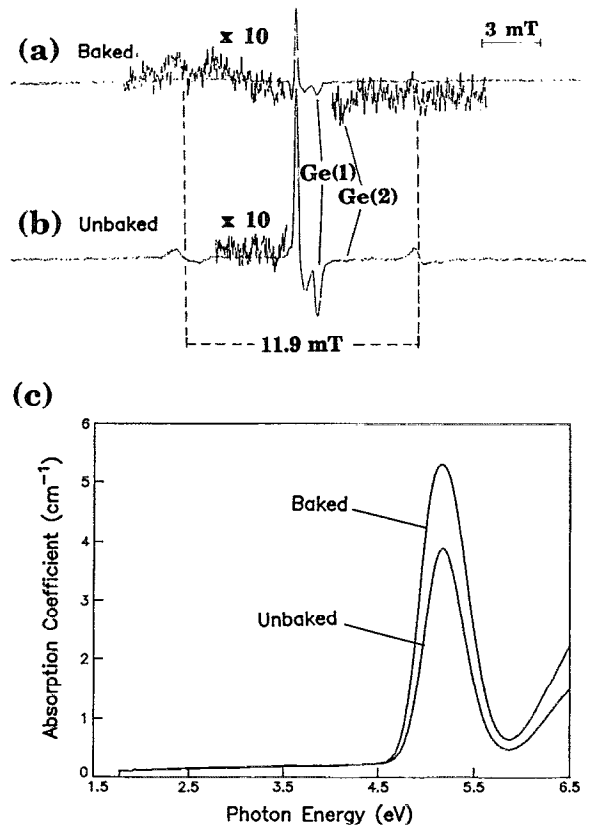

FIG. 2. Room temperature ESR spectra of 180 ppm Ge-doped synthetic silica irradiated with a KrF excimer laser to a fluence of 2$\times$10^6 mJ/cm^2: (a) high temperature baked sample of size 2 mm$\times$2 mm$\times$4 mm and (b) unbaked sample of size 2 mm$\times$2 mm$\times$8 mm. (c) Optical absorption spectra of baked (63 ppm OH) and unbaked (66 ppm OH) synthetic silica doped with 180 ppm Ge. The absorption coefficients are arbitrary normalized at 1.77 eV (700 nm).

11.9 mT hydrogen-associated doublet will be about 50% higher in the baked sample than in the unbaked one if the 5.16 eV absorption band is associated with two-coordinated Ge. In contrast, the concentration of the hydrogen-associated 11.9 mT doublet estimated from the ESR spectra of Fig. 2(a) for the high temperature baked sample is at most half that estimated from Fig. 2(b) for the unbaked sample. Thus, the concentrations of induced hydrogen-associated 11.9 mT doublets in baked and unbaked samples are in disagreement with the prediction of Eq. (1) that their concentration be proportional to the product of the absorption coefficient of the 5.16 eV band and OH concentration. Similar results are also observed in 100 ppm Ge-doped fused quartz. This suggests that the hydrogen-associated 11.9 mT doublet is not generated via the reaction of Eq. (1) and that the 5.16 eV band is not associated with two-coordinated Ge, in disagreement with Refs. 11–13. Our observation of the 11.9 mT hydrogen-associated doublet along with a minor concentration of Ge(2) [see Figs. 2(a) and 2(b)] implies that the doublet is generated by reaction of induced hydrogen with Ge(2), in agreement with Refs. 16 and 17.

Figure 3 shows the 5.16 eV absorption coefficient as a function of Ge concentration in silica. The solid line with a slope of 0.46 is a linear regression fit of the data. It demon-
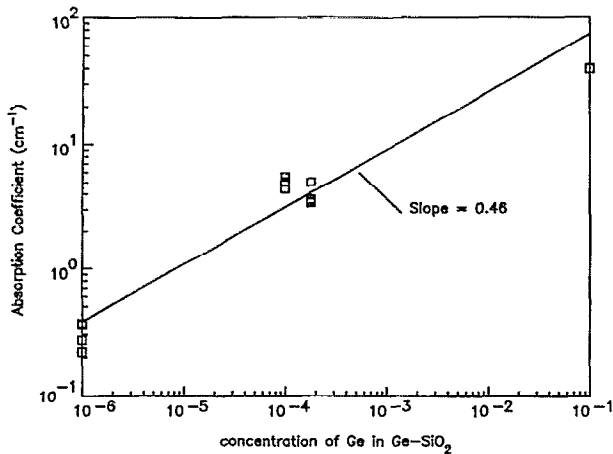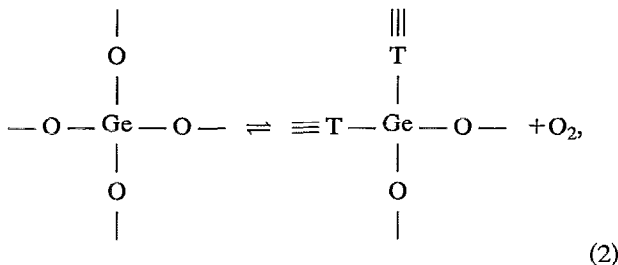
FIG. 3. Optical absorption coefficient of the 5.16 eV band in Ge-doped silica vs Ge concentration. The 40 cm^{-1} data point is from Ref. 19. The solid line with slope=0.46 is a regression fit to the data.

strates that the 5.16 eV absorption coefficient increases approximately as the square root of Ge concentration (0.46 ≈0.5). (Small deviations suggest that although the 5.16 eV absorption coefficient depends mainly on the GeO$_2$ concentration, it also depends on other factors, such as oxygen stoichiometry, etc.)

If the 5.16 eV band is associated with two-coordinated Ge defects, its absorption coefficient should increase linearly with GeO$_2$ concentration because at high temperature during the glass manufacturing processes, only one two-coordinated Ge is in thermochemical equilibrium with a GeO$_2$ in silica. The square root dependence shown in Fig. 3 establishes conclusively that the 5.16 eV band is not associated with two-coordinated Ge.

On the other hand, if the 5.16 eV band is an ODC defect associated with Ge, then our observation of the absorption coefficient increasing approximately as the square root of the Ge concentration (see Fig. 3) suggests that it is a divacancy type ODC similar to that reported recently by Kinser et al.[20] At high temperature during the glass manufacturing processes, two ODCs of a Ge divacancy are in the thermochemical equilibrium with a GeO$_2$ in silica according to Eq. (2),

$$
\begin{array}{ccc}
| & & ||| \\
O & & T \\
| & & | \\
-O-Ge-O- \rightleftharpoons \equiv T-Ge-O- & +O_2, \\
| & & | \\
O & & O \\
| & & | \\
\end{array}
\tag{2}
$$

where T is Ge or Si. Since each divacancy defect contains two ODCs, the thermochemical equilibrium constant, K, for Eq. (2) is

$$K = [ODC]^2[O_2]/[GeO_2], \tag{3}$$

where [ODC] is the concentration of ODC, [O$_2$] is the partial pressure of O$_2$ during the glass manufacturing processes, and [GeO$_2$] is the concentration of GeO$_2$. Therefore, the square of the ODC concentration is linearly proportional to [GeO$_2$]. Thus, our observation of the absorption coefficient of the 5.16 eV band increasing with the square root of GeO$_2$ concentration in silica clearly illustrates that the 5.16 eV band is an ODC divacancy type defect, rather than a two-coordinated Ge, as proposed in Refs. 11-13. The recent report of Poirier et al.[21] that the blue photoluminescence associated with the 5.16 eV band can be photobleached is consistent with this conclusion. This is also consistent with the observation of Skuja[12] that photoluminescence lifetimes of the 5 eV band in pure GeO$_2$ and Ge-doped silica are different.

In summary, we have found that the 5.16 eV band can only be observed in silica containing GeO$_2$, implying that it is associated with a Ge impurity. Although the absorption coefficient of the 5.16 eV band can be changed by high temperature baking, no corresponding changes in the photoinduced hydrogen-associated paramagnetic defects are observed. This suggests that the band is likely not associated with a two-coordinated defect. By contrast, our observations that the 5.16 eV band absorption coefficient increases as the square root of the GeO$_2$ concentration affords strong evidence that it is associated with a Ge-related ODC defect of divacancy type rather than a two-coordinated Ge.

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