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Two types of oxygen-deficient centers in synthetic silica glass

Hiroaki Imai and Kazuo Arai
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba-shi, Ibaraki 305, Japan

Hiroshi Imagawa
Toyo University, 2100 Kujirai Nakanodai, Kawagoe-shi, Saitama 350, Japan

Hideo Hosono and Yoshihiro Abe
Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466, Japan
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The effects of ArF excimer laser irradiation on dehydrated high-purity silica glass were investigated on both the optical-absorption bands due to oxygen-deficient centers (ODC) and the formation of E' centers. With an intense uv flux from an excimer laser, an E'-center density of the order of 10^{15} cm^{-3} was created. The 7.6-eV absorption band remains at the original level, while the 5.0-eV absorption band having the 4.3-eV emission band decreased. Both bands were reduced by heat treatment in an O_2 atmosphere. These results suggest that there exist two types of ODC: ODC(I), which is responsible for the 7.6-eV band, and ODC(II), for the 5.0-eV band. The concentrations of ODC(I) and ODC(II) were evaluated to be 1×10^{18} cm^{-3} through an analysis of the gas treatment data and of the order of 10^{14} cm^{-3} through the growth curve of the E' centers, respectively. The structural origin of ODC(I) has been attributed to the Si—Si bond, judging from the fact that the peak energy and cross section of the absorption were in close agreement with those of the Si_2H_6 molecule. Theoretical calculations on defect energy levels by O'Relly and Robertson supported the structural model for IDC(I) and suggested an unrelaxed oxygen vacancy for ODC(II). These assignments were also consistent with the results of a quenching experiment in which the fictive temperature of samples was changed; the equilibrium between concentrations of ODC(I) and ODC(II) shifted in a reasonable manner.

Recently, we found correlations between the preparation processes of high-purity silica glass and transparency in the vacuum-ultraviolet (vuv) region. We have analyzed the extrinsic absorption due to defects such as oxygen-deficient centers (ODC), peroxygen linkages (POL), and the hydroxyl groups (OH).[1,2] We also showed that those defects have conspicuous effects on the production and decay of color centers during and after uv irradiation by excimer lasers.[1] Such investigations may yield an improved method to prepare silica-glass optical elements having superior transparency and durability for excimer laser applications.

Absorption bands at 7.6 and 5.0 eV are observed, for example, in silica glass which has been prepared by the chemical-vapor-deposited (CVD) soot method and subsequently dehydrated by chlorine gas treatment before sintering the CVD soot. Such a process is frequently used in the optical-fiber industry. Griscom, in his comprehensive review article,[3] has interpreted these two absorption bands as originating from one type of oxygen-deficient center with a Si-Si structure.

In the present Rapid Communication, we show that these two absorption bands arise from two different types of oxygen-deficient centers by examining the effects of excimer laser irradiation. We studied the above-mentioned dehydrated silica glasses prepared by the CVD soot method. The glass was cut and polished into plates or rectangular parallelepipeds having an optical path from 0.2 to 30 mm for optical measurements. Optical absorption measurements from 6.2 to 8.3 eV were carried out with a 1-m monochromator (Nikon McPherson) using synchrotron radiation from a storage ring at our laboratory as a light source. Absorption below 6.2 eV, luminescence, ir absorption, and Raman scattering were measured using commercial spectrometers. Heat treatment of the samples was carried out in H_2, O_2, and N_2 atmospheres at 800–900° C. The samples were exposed to an ArF excimer laser having a wavelength of 193 nm (6.4 eV) (Lambda Physik EMG102MSC) which was operated at 30 Hz with a pulse width of ~20 ns. The beam size was 8 mm high and 28 mm wide. Laser-induced paramagnetic defects were investigated by electron spin resonance (JEOL FElSG) at room temperature. We observed only the well-known E' centers.[4] Nonsaturating microwave power of 1×10^{-5} W was applied for the evaluation of the spin density of the resonance.

As illustrated in Fig. 1, the optical-absorption behavior at the band edge was well characterized by the dominant defects ODC, POL, and OH.[1,2] The dominance of each defect in a particular silica glass seemed to be definitely related to the preparation procedure. The dehydrated silica glass prepared by the CVD soot method shows a 7.6-eV band and a 5.0-eV band having a 4.3-eV emission. These bands have been shown to originate from oxygen-deficient centers on the basis of the following experimental results.[1,2] When the sample was annealed in H_2 at 800 °C

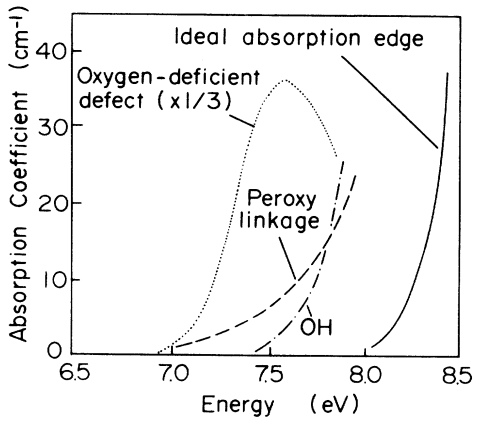

FIG. 1. Typical absorption edge characteristics of various synthetic silica glasses with dominating preparation-dependent defects. The ideal absorption edge included in the figure corresponds to the Urbach tail explained by the electron-phonon interaction [I. T. Godmanis, A. N. Trukhin, and K. Hubner, Phys. Status Solidi B **116**, 279 (1983)].

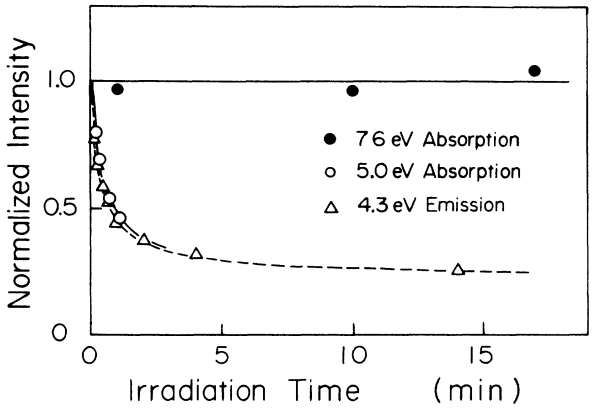

FIG. 2. The effect of the ArF laser irradiation on the 7.6- and 5.0-eV absorption bands along with the 4.3-eV luminescence. The laser was operated with a power of 30 mJ/pulse at 30 Hz.

or in O_2 at 900 °C, these bands were reduced with an increase in the annealing time. After the H_2 treatment, a weak band due to the Si-H mode was observed at 2200 cm^{-1} in Raman scattering spectra whereas no Si-OH mode was seen in ir spectra. Thus, the reaction with the H_2 treatment is expressed by the following formula:

$$\text{ODC}+H_2 \rightarrow 2{\equiv}\text{Si}-\text{H}\,. \tag{1}$$

As for the reaction with O_2, formula (2) is expected,

$$\text{ODC}+\tfrac{1}{2}O_2 \rightarrow {\equiv}\text{Si}-\text{O}-\text{Si}{\equiv}\,, \tag{2}$$

since the other candidate, namely a POL, has been ruled out for the following reasons. First, the O_2 treatment created no characteristic absorption of POL as shown in Fig. 1. Secondly, no Si-OH was detected in a specimen which underwent a two-step heat treatment in O_2 followed by H_2. Since both the 7.6-eV band and the 5.0-eV band with the 4.3-eV emission diminished at a similar rate with the annealing, it agrees with Griscom's suggestion that both bands originate from point defects with oxygen deficiency.

In contrast to the annealing effects on the optical band, we found that the two bands show an entirely different response to exposure from the excimer laser. While the ArF laser irradiation did not modify the intensity of the 7.6-eV band at all, the 5.0-eV band decreased with the irradiation as shown in Fig. 2. The relative intensity of 4.3-eV emission decreased along with that of the 5.0-eV band and became almost constant. These decreases induced by the laser did not recover at room temperature. Thus, it is concluded that these two absorption bands arise from different types of oxygen-deficient centers with different atomic configurations, the ODC(I) is assigned to the 7.6-eV band, and the ODC(II) is assigned to the 5.0-eV band.

The generation of the E' centers by the laser may also be explained by formula (3) which has been used for x- or γ-ray irradiation,

$$\text{ODC}\rightarrow {\equiv}\text{Si}^{\cdot}+{\equiv}\text{Si}^{+}+e^{-}\,, \tag{3}$$

where the $\equiv Si^+$ relaxes into a planar configuration as predicted by the theory.[5] Such a local structural relaxation upon capture of a hole prevents recombination, thus stabilizing the resulting E' centers. Recently, defect formation by excimer formation by excimer laser irradiation has been investigated.[6,7] The photon energy of the laser light, which is much less than that of x or γ rays, does not directly break the Si—O≡Si bonds and does not cause the displacement of atoms in the network. Therefore, laser-induced effects might provide a better understanding of the intrinsic defect properties. We found that the E' centers can be created mainly via a two-photon process by excimer laser irradiation with an energy much less than the band-gap energy.[1,8]

In the following discussions, both ODC(I) and ODC(II) are deduced to be precursors of the E' centers. The spin density, in the range up to 10^{15} cm^{-3}, of the E' centers increased almost linearly with the laser dose and did not saturate as shown in Fig. 3. This behavior is in contrast to the nonlinear decreasing behavior of the 5.0-eV band in Fig.2 to ODC(II). This fact suggests that the induced E' centers come from not only ODC(II) but also ODC(I).

The density of ODC(II) should be less than that of the E' centers induced by the laser because the major decrease of the 5.0-eV band occurred in the initial stages of the irradiation. The formation of E' centers from the ODC(II) may be reflected in the growth curve of the defect as shown in Fig. 3. A rather steep increase in the density is seen initially, which may correspond to the contribution from the ODC(II). As depicted in Fig. 3, the growth curve may be resolved into two processes on the assumption that the spin density (i) due to ODC(I) is proportional to the dose and (ii) that due to ODC(II) grows in a manner which follows the decrease of the relative intensity of the 5.0-eV band. The density of the ODC(II) is roughly estimated to be 0.3×10^{15} cm^{-3}.

On the other hand, the density of ODC(I) was con-

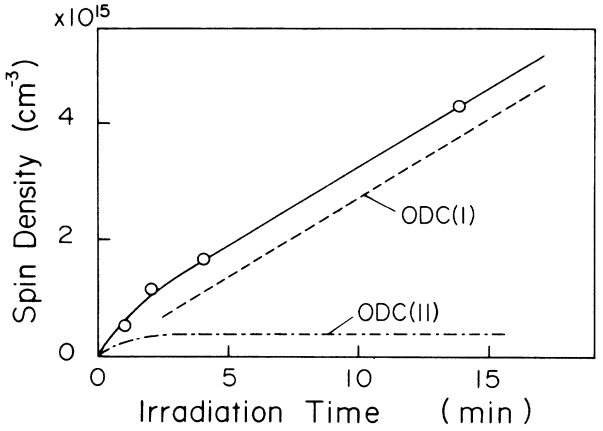

FIG. 3. The spin density of the induced E' center with irradiation time of ArF laser with 30 mJ/pulse at 30 Hz. The growth curve was resolved into two curves on the assumption that the spin density due to ODC(I) is proportional to the time and that due to ODC(II) grows in a manner which follows the decrease of the relative intensity of the 5.0-eV band. The density of ODC(II) is estimated to be 0.3×10^{15} cm^{-3}.

sidered to be much larger than that of the induced E' centers since this induced density did not appear to saturate. From an analysis of the decrease in the 7.6-eV band after the O_2 treatment, the density of ODC was estimated to be of the order of 10^{18} cm^{-3}.[1,2] The analysis was made according to the method of Shelby assuming a tarnishing reaction,[9] where the reaction of defects with molecules such as H_2 is completely controlled by gas diffusion. Since, in this case, the reaction front moves after all reactive sites are eliminated, both ODC(I) and ODC(II) are removed simultaneously. The reaction rate of the centers with O_2 and H_2 molecule is, of course, dominated by the majority, ODC(I). Thus, the density obtained by the analysis substantially corresponds to that of ODC(I). Because the density of ODC(I) is much greater than that of the induced E' centers, the decrease in ODC(I) resulting from the E' center formation corresponds to $\sim$0.1% of the total number of ODC(I). This percentage is far below the accuracy of the conventional vuv optical absorption method employed here.[10]

The optical absorption coefficient of the 7.6-eV band, ($\sim1\times10^{2}$ cm^{-1}), is larger by four orders of magnitude than that of the 5.0-eV band ($\sim1\times10^{-2}$ cm^{-1}). The difference may be attributable not to the difference in the absorption cross sections but to that in the density of the centers. Using the density estimated above, the cross section at the peak of the former band is estimated to be 8×10^{-17} cm^2 while that of the latter to be 2×10^{-17} cm^2, respectively.

The values of the peak energy and absorption cross section due to the ODC(I) agree well with those of the Si_2H_6 molecule with the Si–Si bond, (i.e., 7.56 eV and 6.0 $\times10^{-17}$ cm^2,[11] respectively). Due to the localized nature of the defective bond in the glass network, this agreement supports the structural model that the ODC(I) is related to the Si–Si bond. According to the calculation of the bond energy,[12] the σ-σ^* transition of the Si–Si bond corresponds to an energy gap of 7.7 eV, while an unrelaxed oxygen vacancy corresponds to 4 eV. These results suggest that stereoconfigurations of ODC(I) and ODC(II) are attributable to these two as illustrated in Fig. 4, respectively. It is well understood that in the case of the Si–Si bond, the formation of the E' centers following formula (3) will require extra relaxation in the local network configuration to produce a planar counterpart of Si^+, compared with that of the unrelaxed oxygen vacancy. The rapid decrease in the ODC(II) with laser dose may reflect the higher efficiency for the E' center creation from the ODC(II).

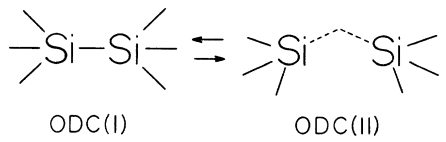

FIG. 4. Defect configurations for the oxygen-deficient center proposed in Ref. 12. Since equilibrium between the two states can be attained in the liquid state, the density of each defect will be changed depending on the quenching temperature.

The free energy of the Si–Si bond is reasonably assumed to be lower than that of the oxygen vacancy state. Localized orbital energies belonging to the ODC(I) and ODC(II) in the ground state, which may provide most of the free energy, have been estimated to be 1.2 and 3.0 eV, respectively.[12] On this basis, our assignment to the two types of defect configurations was also supported by an additional quenching experiment intended to change the fictive temperature (T_f) of the glassy samples. We found that the 4.3-eV emission intensity due to ODC(II) was reduced by one-third when the T_f of the samples was

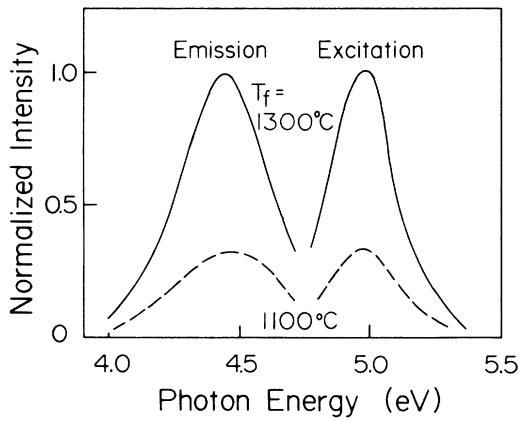

FIG. 5. The fictive temperature (T_f) dependence of the 4.3-eV emission intensity. The samples were quenched by dipping them in water after keeping them at 1300 °C for 8 h or at 1100 °C for 210 h. The keeping time to reach the equilibrium state was determined by considering the structural relaxation time at each annealing temperature reported by the literature [A. E. Geissberger and F. L. Galeener, Phys. Rev. B **28**, 3266 (1983)]. The emission intensity of as-received samples, the thermal history of which was not clear, was weaker than that of T_f = 1300 °C by about one order of magnitude.

lowered from 1300 to 11000 °C, as shown in Fig. 5. This indicates that a part of the unstable oxygen vacancies which could exist at higher T_f were converted into the more stable Si—Si bond, resulting in the attainment of equilibrium at the lower T_f between the concentrations of these two centers. The lack of a change observed for the 7.6-eV band intensity can be explained again by the high concentration of ODC(I). The concentration change of the 4.3-eV emission gives the enthalpy difference between the two configurations, 1.0 eV, which fairly agrees with the calculated value of 1.8 eV cited in Ref. 12.

We have provided direct evidence substantiating the presence of the two types of oxygen-deficient centers, ODC(I) and ODC(II), in dehydrated synthetic silica glass. The former, of which the density is estimated to be of the order of 10^{18} cm^{-3}, produces the 7.6-eV absorption band and has a lower efficiency for E' center formation by ArF laser irradiation. The latter, of which the density is estimated to be of the order of 10^{14} cm^{-3}, produces the 5.0-eV band having the 4.3-eV luminescence and has a higher E' center formation efficiency. Although both definitely have an oxygen deficiency, their atomic configurations have not yet been identified. The similarity between the band characteristics due to ODC(I) and those of the Si_2H_6 molecule indicates that ODC(I) is attributable to the Si—Si bond. A recent theoretical calculation on the local levels of their electronic structures strongly supports the present assignment and suggested ODC(II) to be the unrelaxed oxygen vacancy. The change in the concentrations of the two centers as a function of T_f was consistent with this model.

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*On leave from Japan Oxygen Co. Ltd., 4-320 Tsukagoshi, Saiwai-ku, Kawasaki, Japan.

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