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Excimer-laser-induced emission bands in fused quartz

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The characteristics of KrF (5.0 eV) and ArF (6.4 eV) -excimer-laser-induced luminescence in type-I ($[\mathrm{OH}] < 5$ ppm) and type-II ($[\mathrm{OH}] = 120$ ppm) fused quartz were investigated. These two types of fused quartz have an absorption band near 5 eV, called the B_2 band. Comparing the absorption and the emission bands under excitation by these excimer lasers, we found that the B_2 bands in these types of fused quartz derived from different origins: In type-II fused quartz, the B_2 band is the $B_2\ \beta$ band caused by silicon lone-pair center ($=\mathrm{Si}:$), which can be annealed out in air. The B_2 band in type-I silica consisted of two types of B_2 bands: the main component of this band is the $B_2\ \alpha$ band caused by an oxygen-deficient center ($\equiv \mathrm{Si} \cdots \mathrm{Si} \equiv$) and the other component is a small amount of the $B_2\ \beta$ band. We proposed a model in which these defects are located on the grain boundary, which is a trace of the contact between silica and silica particles.

I. INTRODUCTION

Vitreous silicas are widely used in optical materials in the uv region,[1] because these materials have high optical transmission in the uv region. Recently, a number of studies concerned with excimer-laser-induced absorption and emission bands in various types of vitreous silica were reported.[2-15] These studies showed that the excimer-laser-induced optical properties provide a useful tool to clarify defect structures in vitreous silicas.

We can classify vitreous silicas into two groups:[1,16] fused quartz produced by melting natural quartz powder, and synthetic fused silicas synthesized chemically from silicon tetrachloride or other appropriate silicon compounds.

Fused quartz are further classified into two types by their OH content;[1,16] containing OH (type II) and no OH (type I). Type-I silica is produced by melting natural quartz powder in an electrical furnace or in a plasma torch. Type-II silica is produced by fusing the quartz powder in a hydrogen-oxygen flame.

There are several types of synthetic fused silicas: Type-III fused silica[17] is synthesized by flame hydrolysis of silicon tetrachloride in a hydrogen-oxygen flame containing about 1000 ppm of OH. Type-IV silica[1] is produced by plasma torch chemical vapor deposition (CVD) and contains less than 5 ppm of OH. The other types of synthetic fused silica are soot remelted silica such as synthesized by the VAD (vapor-phase axial deposition)[18] method, and made by use of the sol-gel method.[19]

Defect structures in vitreous silica depend on the types of silica and the history of the material processing.[2,20] Such structural differences strongly affect excimer-laser-induced optical properties.[3-15] Most studies on excimer-laser-induced absorption and emission are concerned with synthetic fused silicas, because optical vitreous silica is mostly type III and soot remelted silicas. The former are mainly used in the uv region such as with excimer lasers and the latter are mainly used in optical fibers in telecommunications.

This work is a report on the excimer-laser-induced optical properties of fused quartz. The optical properties of fused quartz in uv region seems to be inferior to those of synthetic fused silica for the following reasons.

(i) Metallic impurities in the fused quartz (0.1–10 ppm) are higher than those of the synthetic fused silicas (<0.1 ppm).[21] Because of the impurities, the optical transmission near 200 nm (6.2 eV) in the fused quartz are less than that of the synthetic fused silica, i.e., transmission of samples 10 mm thick are greater than 85% in synthetic fused silica, but 10–80 % in fused quartz.[1,21]

(ii) In addition to the metallic impurities, transmission at less than 300 nm in fused quartz is lower than in synthetic fused silica because of the existence of an absorption band near 5 eV called the B_2 band.[1,22]

(iii) Grain structure, which is trace of the contact of between quartz powder, is observed by projecting pinhole light through a polished sample onto a screen.[1]

Because of the optical properties mentioned above, fused quartz is inappropriate for use as a fine optical material such as lenses for a microlithography process. However, it can be used in some optical material in the uv region. For example, optical cells for uv spectrophotometers can be made of type-II fused quartz. Although an as-manufactured material of type-II fused quartz has a B_2 band, this band can be annealed out and a optical fused quartz in the uv region obtained.[1,21] Type-I fused quartz also possesses the B_2 band, but this latter band is hard to anneal out.

The B_2 band can be also observed in type-IV fused silica made by plasma torch CVD or soot remelted silica.[23]

Several models of the B_2 band are proposed: Skuja[24] proposed that the structure being responsible for the B_2 band is twofold-coordinated silicon atom ${}_2\mathrm{O}{=}\mathrm{Si}$:. Arnold[25] suggested that the B_2 band is caused by an oxygen vacancy. Nagasawa, Hoshi, and Ohki[26] showed that the E' center ($\equiv$Si$\cdot$) is induced by fiber drawing only in fused silica having the B_2 band. They proposed that the structure responsible for the B_2 band is a $\equiv$Si-Si$\equiv$ structure. Imai *et al.*[27] reported that fused silicas having the B_2 band show an emission band at 4.3 eV. They showed that the structure being responsible for the B_2 band is an unrelaxed oxygen vacancy $\equiv\mathrm{Si}\cdots\mathrm{Si}\equiv$.

Guzzi *et al.*[22] showed that emission bands at 4.1 and 3.1 eV are induced by exciting the B_2 band. Tohmon *et al.*[23] showed that there are two kinds of B_2 band in fused silica synthesized under various conditions in VAD and type-IV fused silicas. They named these bands the $B_2\ \alpha$ and the $B_2\ \beta$ bands, respectively. The peak position of the $B_2\alpha$ band is at 5.02 eV and emission bands are at 4.42 and 2.74 eV. The peak position of the $B_2\ \beta$ band is at 5.15 eV and the emission bands at 4.24 and 3.16 eV are observed. Kohketsu *et al.*[28,29] showed that in a SiO_2-GeO_2 glass there are two kinds of B_2 band: those which have a 5.06-eV absorption and 4.6-eV emission bands, and those which have a 5.17-eV absorption and 3.8-eV emission bands.

Awazu, Kawazoe, and Muta[30] proposed, by comparing the B_2 band and ${}_2\mathrm{O}{=}\mathrm{Si}$: molecule in a gas phase, that the $B_2\ \beta$ band is caused by a silicon-lone-pair center ($=$Si:).

Most of the studies shown above are concerned with the synthetic fused silicas (the soot remelted and type-IV silica), and studies concerned with fused quartz are scarce.[22] Thus we studied in this paper the excimer-laser-induced emission bands and effects of annealing on these properties in type-I and type-II fused quartz and specifically the types of the B_2 band in both types of fused quartz. We also discussed the creation mechanism of these bands.

II. EXPERIMENT

A. Samples

A type-I fused quartz made by melting of natural quartz powder in a plasma torch, and a type-II fused quartz made by fusing natural quartz powder in a hydrogen-oxygen flame were used. These vitreous silicas contain about 5 and 120 ppm of OH by weight, respectively; we call them sample I and sample II.

Samples were cut into size of $10\times10\times30$ mm^3, and all surfaces were polished.

B. Annealing

The samples were annealed in air at 1150 °C for 1 hour and cooled to 700 °C at a cooling rate of 6 °C/h. Then they were cooled to room temperature without temperature control.

C. Luminescence and absorption measurement

Luminescence spectra were measured by using the same method as in previous papers.[9–14]

A Questek SQL 2240 type excimer laser was used. The energy density of the beam was controlled to 200 mJ/cm^2 using a fused silica lens ($f=500$ mm). The diameter of the beam was adjusted to 3 mm by using an iris.

The luminescence was detected from the direction perpendicular to the excitation beam. Emission spectra were measured shot by shot monochromatically (using a Jasco CT-10) by a diode array image sensor with image intensifier (a Hamamatsu Photonics C280-03).

Absorption spectra were measured by a UV-Visual spectrophotometer (a Shimadzu UV-250).

III. RESULTS AND DISCUSSION

A. Effects of annealing on absorption spectra

Absorption spectra of both types of fused quartz are shown in Fig. 1. Both types of samples have B_2 bands before annealing. The optical transmission of these samples at 200 nm (6.2 eV) are considerably different: The transmission is 76% in the type-II sample: it is 15% in the type-I sample.

The B_2 band in sample II was annealed out with air.

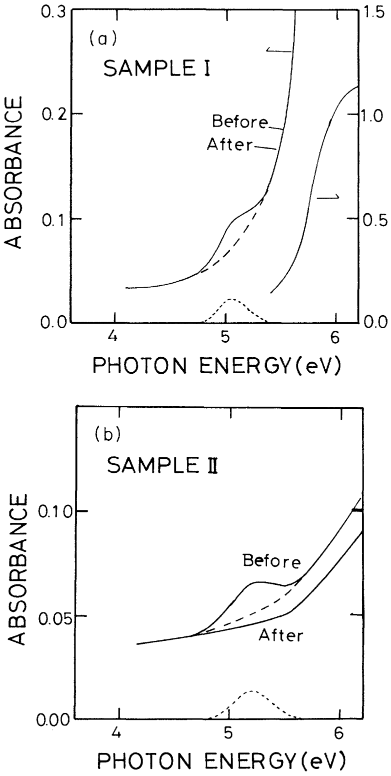


FIG. 1. Absorption spectra of (a) type-I and (b) type-II fused quartz before and after annealing. The solid curve indicates the absorption spectra before and after annealing, and the dotted curve indicates the B_2 bands in the samples obtained by subtracting the base line indicated by dashed lines.

In sample I, however, the B_2 band did not change within our experimental accuracy by annealing. The peak position and the full width at half maximum (FWHM) are estimated by using the baseline drawn in Fig. 1 as a dashed line.

The peak position of the B_2 band in sample II is at 5.18 eV, and the FWHM is 0.46 eV; these values correspond to the reported value of the B_2 β band[23] in that the peak position is 5.15 eV and FWHM is 0.48 eV. Therefore this band is mainly derived from the B_2 β band. In sample I, the peak position and FWHM are 5.05 and 0.32 eV, respectively. This band is the B_2 α band because the reported value[23] of their peak position and FWHM are 5.02 and 0.35 eV, respectively.

The difference of the types of the B_2 band can be seen in the luminescence spectra. Thus we compared luminescence spectra of both types of samples irradiated with excimer lasers.

B. Excimer laser induced emission bands

Figure 2 shows luminescence spectra of both types of fused quartzes irradiated with the ArF (6.4 eV [193 nm]) and KrF (5.0 eV [249 nm]) excimer lasers. Since the photon energy of the KrF laser (5.0 eV) is near the peak position of the B_2 band, an emission band excited directly by the KrF laser will be observed. In sample II, emission bands at 4.2 eV (290 nm) and 3.2 eV (390 nm) are observed by irradiating with ArF and KrF excimer lasers. These emission bands are characteristic of the B_2 β band,[23] i.e., the reported values being 4.24 and 3.16 eV, respectively. The ratio of these two peaks are different between different types of excimer lasers; the ratio between the intensities of the 4.2- and 3.2-eV bands are stronger in the case of the KrF laser than the ArF laser. The intensity of the 3.2-eV band in the case of two types of excimer lasers are almost the same. The luminescence spectrum of sample-II irradiated with ArF laser is much closer to the luminescence spectra reported by Tohmon *et al.*;[23] they measured the luminescence excited by monochromatized D_2 lamp of 5.0 eV. This fact suggests that the luminescence intensity of the 3.2-eV band was saturated because the photon density of the excimer lasers are much higher than that of the D_2 lamp. Therefore the intensities of the 3.2-eV bands are almost the same. In the case of KrF laser irradiation, the intensity of the 4.2-eV band is stronger than that of ArF laser irradiation because the photon energy is almost equal to the peak position of the B_2 band and the photon energy of the ArF laser (6.4 eV) is higher than the peak position of the B_2 β band.

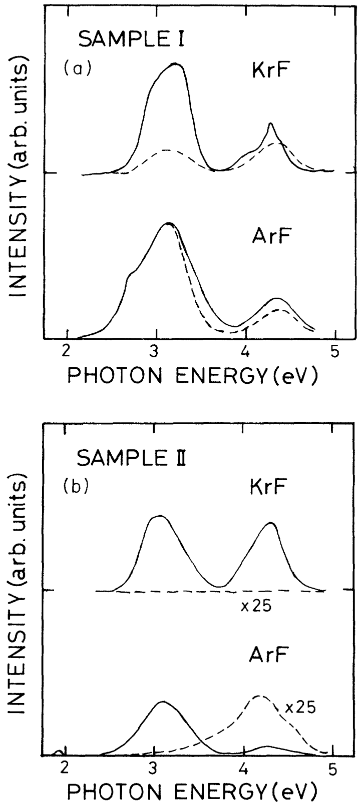


FIG. 2. Luminescence spectra of (a) type-I and (b) type-II fused quartz irradiated with KrF and ArF lasers (200 mJ/cm^2, 50 Hz) before and after annealing. Solid curve, before annealing; dashed curve, after annealing.

Sample-I irradiated with the ArF laser shows emission peaks at 4.4 eV (280 nm) and 3.2 eV (390 nm) and a shoulder at 2.7 eV (450 nm). Under irradiation with the KrF laser, the emission spectra near 4 eV is different from that of the ArF laser irradiation; a sharp band at 4.2 eV and broad peak at 4.4 eV are superimposed. The reported values of the emission bands of the B_2 β band are 4.24 and 3.16 eV, respectively. Therefore, the B_2 α and B_2 β bands coexist in type-I silica. The fact that the peak position and the FWHM of the absorption band in sample I indicate that amount of the B_2 β band in the sample is considerably smaller than that of the B_2 α band.

C. Annealing effect on the emission bands

After annealing, sample I irradiated with the KrF laser shows emission bands at 3.1 and 4.4 eV. If these bands were derived from the excitation of the B_2 α band, emission bands would appear at 4.4 and 2.7 eV. The 2.7-eV shoulder is weaker with KrF- than with ArF-laser irradiation.

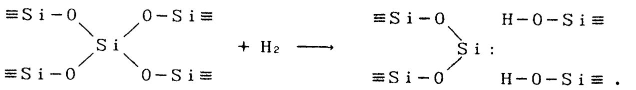
Under irradiation with the ArF laser, on the other hand, shape of the emission bands are almost the same as those before annealing. The only feature different is that the relative intensity of the 4.4-eV band compared to the 3.2-eV band is smaller than that before annealing. This fact suggests that the emission bands at 3.3 eV and the shoulder at 2.7 eV are not derived from the B_2 β band but instead are derived from the strong absorption of photons with energy higher than 6 eV [see Fig. 1(a)]. Such absorption could be due to metallic impurities because sample I contains a considerable amount of metallic impurities. The 3.2-eV peak before annealing is mainly derived from the B_2 β band. By the annealing, the B_2 β band would be annealed out and the 3.1-eV band, being derived from the tail of the absorption of impurities, would remain.

Guzzi *et al.*[22] reported that intensity of the 2.7-eV emission band is induced by exciting the B_2 α band with light monochromatized deuterium lamp is weaker than that of the 4.4-eV band. The energy density of this light is considerably weaker than that of the excimer lasers. Therefore, the 2.7-eV band would be hidden by the tail of the strong 3.1-eV band which is caused by the absorption of photons with energy higher than 6 eV.

In the annealed sample II irradiated with the KrF laser, the luminescence is strongly suppressed accompanied by the elimination of the B_2 band by the annealing. Under irradiation with the ArF laser, on the other hand, emission bands at 4.2 and 1.9 eV are induced. They also show luminescence in a region 4–2.5 eV. It is noted that the sensitivity of the luminescence measurement in the annealed sample II is about 25 times higher than that before annealing sample I because the luminescence intensity are considerably weaker than the other case. The 1.9-eV band is derived from a stoichiometrically excess amount of oxygen.[2] Whether this center originally existed in the glass or was produced by the annealing is not known because the luminescence intensity before annealing is so strong that the 1.9-eV band could be hidden by the tail of the 3.2-eV band. The feature of the KrF and ArF laser induced luminescence spectra of sample II annealed in air is similar to that of type-III silica synthesized under a reducing condition.[11]

D. B_2 band in type-II silica

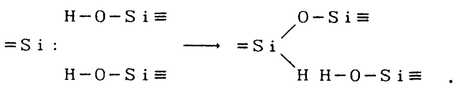
Awazu, Kawazoe, and Muta[30] studied soot remelted silica sintered in a mixture of hydrogen and helium ambient, and proposed a model for the structure responsible for the B_2 β band and its formation mechanism; the structure is a silicon lone-pair center (SLPC; $=\!\mathrm{Si}^{\cdot\cdot}$) formed by



(1)

The type-II silica is produced by melting natural quartz powder in a hydrogen-oxygen flame. The SLPC in type-II silica could be formed during quartz powder fusing at temperatures near 2000 °C. In this process, the crystalline structure of the quartz powder is destroyed but a trace of the grain-boundary interface remains. The thermal-expansion coefficient of the grain boundary and the inner domain part would be a little different. Part of an ingot of fused quartz will be cooling during the fusing process and the stress will be induced on the grain boundary. As a result, many strained bonds are created on the grain boundary. The fusing flame contains a considerable amount of hydrogen; it can diffuse easily into the glass network. This hydrogen will react with the strained bonds in the grain boundary to form the SLPC according to the reaction of Eq. (1). It is reported that similar reactions occur in the grain boundary of GeO_2 and SiO_2 clusters in SiO_2-GeO_2 glass.[31]

Now we will discuss the annealing effect. A possible annealing mechanism of the B_2 β band is to proceed as the inverse reaction of Eq. (1). However, the inverse reaction of Eq. (1) does not necessarily occur at a lower temperature (1150 °C) than the glass forming temperature (1800–2000 °C). Another probable mechanism of the annealing of the B_2 β band is as



(2)

The authors studied in a previous paper[11] the annealing effect on the ArF laser-induced absorption and emission bands in a type-III fused silica synthesized under a reducing condition. We proposed that $\equiv$Si-HH-O-Si$\equiv$ structures exist in the as-manufactured material. In this sample, an emission band at 4.4 eV is induced by irradiating with the ArF laser. Under irradiation with the KrF laser, the 4.4-eV band is not observed. These spectra are very similar to those of the type-II sample annealed in air; an absorption band at 4.2 eV is induced by irradiating with the ArF laser but this band does not appear when irradiating with the KrF laser. It is noted that in the annealed sample II the emission peak at 4.2 eV is slightly different from the emission peak 4.4 eV in type-III fused silica. However, a shoulder at 4.4 eV is observed in sample II. This shoulder could correspond to the 4.4-eV emission peak in the type-III sample. In addition to the 4.2-eV peak, weak luminescence in the region 4–2.5 eV is observed. This luminescence is considered to be derived from metallic impurities because the metallic impurity of the fused quartz is at least an order of magnitude higher than that of synthetic fused silicas. The similarity between these luminescence spectra suggests the existence of the $\equiv$Si-HH-O-Si$\equiv$ structure and supports the annealing mechanism described in Eq. (2).

Awazu, Kawazoe, and Muta[30] estimated the absorption cross section of the SLPC to be 5×10^{-15} cm^2. In the present case, this difference of the optical density at the B_2 band is 0.044 cm^{-1}, which corresponds to a concentration of the SLPC of 9×10^{15} cm^{-3}. If the SLPC exists in the structure shown in Eq. (2), this structure corresponds to about 0.5 ppm of OH by weight. Such a small change in the OH concentration is hard to detect with the usual optical measurement using an absorption band of OH at 2.7 μm whose extinction coefficient is 77.5 1/mol cm.[32]

E. B_2 band in type-I silica

As described in Sec. C, the main component in the B_2 band in sample I is the B_2 α band and there also exists a small amount of the B_2 β band. The B_2 β band in this sample would be related to the small amount of OH base (<5 ppm). The B_2 α is caused by unrelaxed oxygen vacancy $\equiv\mathrm{Si}\cdots\mathrm{Si}\equiv$. The $\equiv\mathrm{Si}\cdots\mathrm{Si}\equiv$ bond in this structure is elongated and contains an absorption band at 5.0 eV. If the elongated Si-Si bond is relaxed to the usual

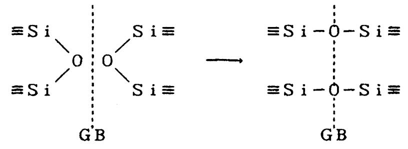
$\equiv$Si-Si$\equiv$ bond, the 5.0-eV band will change to an absorption band at 7.6 eV.[27] Imai *et al.*[27] named the $\equiv$Si-Si$\equiv$ structure the ODC-I and the $\equiv$Si $\cdots$ Si$\equiv$ structure the ODC-II in which ODC stands for "oxygen-deficient center."

In the present case, the elongated $\equiv$Si $\cdots$ Si$\equiv$ bond is stable in the annealing temperature because the intensity of the B_2 α did not change by the annealing. The ODC-II in type-I silica must have existed on the grain boundary. The origin of the ODC-II is not clear at present. However, a similar structure appears in a soot remelted silica dehydrated by chlorine.[27] Therefore, it may be related to silica to silica particle contact. In soot remelted silica, dehydration is performed by replacing the $\equiv$Si-OH by $\equiv$Si-Cl. A possible mechanism of the formation of the ODC in the soot remelted silica is

$$\equiv\text{Si-ClCl-Si}\equiv \rightarrow \equiv\text{Si}\cdots\text{Si}\equiv + \text{Cl}_2 \, . \qquad (3)$$

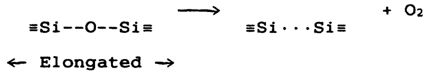
If the Cl_2 molecule remains in the glass, an absorption band at 3.8 eV will be observed.[33] However, the 3.8-eV band is not observed in the soot remelted silica.[23,27] Therefore the Cl_2 molecules diffuse out from the silica during the sintering process or recombine with the ODC by the inverse reaction of Eq. (3).

In type-I silica, the $\equiv$Si-Cl structure is not found. Therefore the model described in Eq. (3) is ruled out. A candidate of the precursor of the ODC is normal $\equiv$Si-O-Si$\equiv$ bond in the surface of quartz powder. In the fusing adhesion process, some bonds will be recombined as



, (4)

where "GB" stands for the grain boundary. Similar to the case of type-I silica, stress will be induced in the grain boundary during the cooling process. By this stress, some amount of the Si-O-Si band on the right-hand side of Eq. (4) will be elongated to form the ODC-II by



$$\begin{matrix}\equiv\text{Si--O--Si}\equiv \\ \equiv\text{Si--O--Si}\equiv \\ \leftarrow \text{Elongated} \rightarrow\end{matrix} \longrightarrow \begin{matrix}\equiv\text{Si}\cdots\text{Si}\equiv \\ \equiv\text{Si}\cdots\text{Si}\equiv\end{matrix} + \text{O}_2 \qquad (5)$$

The O_2 molecules on the right-hand side of Eq. (5) might be confirmed by a emission band at 1.9 eV.[12,15] However, in the present sample, the tail of a strong luminescence band hides the 1.9-eV band.

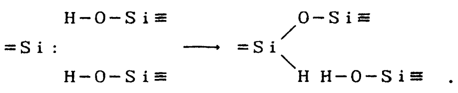
IV. SUMMARY AND CONCLUSION

We have studied the effect of annealing on the absorption spectra and excimer-laser-induced luminescence spectra in type-I and type-II fused quartz, and obtained the following results:

(1) Both types of fused quartz possess absorption bands near 5 eV called the B_2 band. By comparing the peak position, the FWHM and excimer-laser-induced emission band, these B_2 bands are found to have been derived from different origins.

(2) The B_2 band in type-II silica is the B_2 β band caused by the silicon- lone-pair center. This band can be annealed out with air at 1150 °C.

(3) By comparing the luminescence spectra between the type-II fused silica annealed in air and a type-III fused silica synthesized under a reducing condition, we proposed a model to describe the annealing mechanism of the B_2 β band as



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(4) The B_2 band of type-I silica is mainly the B_2 α band derived from the oxygen-deficient center $\equiv$Si $\cdots$ Si$\equiv$. It also contains a small amount of the B_2 β band. The B_2 α band cannot annealed out, unlike the case of the B_2 β band.

(5) Other luminescence bands that are observed may be derived from absorption near 200 nm due to metallic impurities.

(6) Defect structures responsible for both types of the B_2 bands should exist in the grain boundary which is a remnant of the adhesion of the quartz powder.

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