Characteristics of ArF Excimer Laser Induced Absorptin and Emission Bands in Wet Fused Silica(Type III) Synthesised in Reducing and Oxydizing Atmosphare

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ArF excimer laser induced luminescence and absorption bands of type III fused silicas synthesyzed in a reducing and an oxydizing conditions are investigated. A fused silica synthesized in reducing condition shows 4.4 eV emission and 5.8 eV absorption bands. From annealing effects on the characteristics of the luminescence and the absorption bands in various atmosphare, we proposed a model that the precursor of these bands is $\equiv$Si-H H-O-Si$\equiv$ structure. The fused silica synthesized in oxydizing atmosphare show absorption band at 4.8 eV and a luminescence band at 1.9 eV which are considered to be created by oxygen molecules trapped in the glass. The solarization is enhanced strongly by annealing in He atmosphare. We proposed a model that the H2O molecules bounded to $\equiv$Si-OH create oxygen molecules dissolved in the glass which are the precursors of the 4.8 and the 1.9 eV bands. This model can also explain the characteristics of solarization induced by X-ray exporsure by which the 5.8 eV absorption band is induced in addition to the 4.8 eV band.

1. Introduction

Type III fused silica is synthesized by flame hydrolys of silicon tetrachloride in hydrogen-oxygen flame (type III)[1] and is widely used in UV lithography because we can get a material with good optical homogeneity over large size and radiation resistivity. Some material, however, show solarization by the irradiation of γ-ray[2], X-ray[3,4], RF plasma[5], and excimer laser beam[6-11].

The nature of the solarization is strongly reflected on the history of the reaction conditions, such as temperature, and ratio of chemical species in the flame, etc.

Therefore, in this paper, we studied the characteristics of the ArF excimer laser induced solarization and luminescence of type III fused silica synthesized in reducing and oxydizing atmosphare.

2. Experimental

Two kinds of type III fused silica were synthesized in reducing and oxydizing condition[12]: Sample I is synthesized in hydrogen rich atmosphare ($[H_2]/[O_2] > 2$), and Sample II is synthesized in oxygen rich atmosphare ($[H_2]/[O_2] < 2$). These samples contain about 800 and 1200 p.p.m. of OH in weight. The samples were cutted into size of 10x10x30 mm3, and polished on every surface.

The system of luminescece measurement is shown in Fig. 1a. The emission spectra were measured shot by shot monochrometally using diod array image sensor with image intensifier.

Transmission of ArF excimer laser beam was measured by a system shown in Fig. 1b.

The X-ray exposure was utilized by the beam of Rigaku 3080 fluorescent X-ray spectro photometer: a rhodium target tube was operated at 50 kV in accelerating voltage and at 30 mA in current in vacuum of about 10-2 Torr.

Samples were annealed at 900 °C for 2 hours in a tube furnace with fused quartz inner tube flowing each gases during all period of annealing.

3. Results and Discussion

3-1 Luminescence bands induced by ArF leaser irradiation

Fig. 2 shows luminescence spectra of fused silica synthesized in a reducing (I) and an oxydizing (II) condition. Sample I show a strong luminescence band at 4.4 eV, and Sample II shows luminescence bands at 1.9 and 4.1 eV. The 1.9 eV band of sample II is known to be corresponded to the 4.8 eV absorption band[3,9,11]. The photon energy of the 4.1 eV band in sample II and the 4.4 eV band in sample I are proximated each other, but they are derived from quite different origin since the the shot number dependencies are quite different: The 4.4 eV bands increases as increasing the shot numbers of the laser pulse, whereas the 4.1 eV band decreases[10]. We could not clarified the origin of the 4.1 eV band in this paper.

3-2 Fused Silica Synthesized in Reducing Condition

As shown in Fig. 3, the sample synthesized in reducing condition (I) shows an absorption band at 5.8 eV which is ascribed to be the E' center[13,14].

To clarify the characteristics of the solarization and the luminescence induced by the ArF excimer laser irradiation, we studied the effect of annealing on the sample I in various atmosphares.

Fig. 4 shows the effects of annealing in oxygen, air, nitrogen, and herium at 900 °C on the characteristics of the 4.4 eV emission band. By the annealing, the 4.4 eV band diminish and an emmision band is created at 4.1 eV. The 4.1 eV band is considered to be the same band as in sample II, because of its similarity in these shapes and the shot number dependencies.

Before annealing, the intensity of the 4.4 eV luminescence increases as increasing the shot number. After annealing, the intensities of the ArF laser induced 4.4 eV bands are supressed.

Annealing in oxygen, the 4.4 eV band is almost extingished. After annealing in air and nitregen the 4.4 eV bands appear, but the intensities of the 4.4 eV bands are supressed compared to that of before annealing. The supression effect on the creation of the 4.4 eV bands are in the order of the partial pressure of oxygen in the gas. By annealing in herium, which can be considered to be a innert gas as nitrogen, the supression effect on the creation of the

4.4 eV band is as eminent as in oxygen.

From these results, we consider that the precursor of the 4.4 eV band relates hydrogen which are bounded weakly to the glass network[11]: Oxygen molecule can pull out the hydrogen from the glass by reacting in the glass surface, and herium atom can permiate into the glass network and pushing out the hydrogen.

As shown in Fig. 3, the 5.8 eV band does not appeare again after annealing in herium. The effect of the annealing on the solarization can be seen clearly by the excimer laser tranamission as shown in Fig. 5a: Before annealing, the transmission decreases as increasing the shot number. After annealing in herium, on the other hand, the transmission remains constant as increasing the shot number.

As discussed above, the 4.4 eV emmision band and the 5.8 eV absorption band is considered to be related to hydrogen which is weakly bounded to the glass network.

We assume a candidate of the precursor of the center is

$$\equiv \mathrm{Si{-}H}\ \ \mathrm{H{-}O{-}Si}\equiv\ . \qquad (1)$$

This model can explain the annealing and solarization phenomena. Irradiating the ArF excimer laser, the E' center is created as follows:

$$\equiv \mathrm{Si{-}H}\ \ \mathrm{H{-}O{-}Si}\equiv\ \xrightarrow{h\nu}\ \equiv \mathrm{Si}\cdot\ \ \mathrm{H{-}O{-}Si}\equiv\ +\ \mathrm{H}, \qquad (2)$$

and the annealing effect can be explained as

$$\equiv \mathrm{Si{-}H}\ \mathrm{H{-}O{-}Si}\equiv \xrightarrow{\text{Annealing}} \equiv \mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2}. \qquad (3)$$

Some of hydrogen in the right hand side of eq.(2) will be react with the E' center to form the ≡ Si-H structure. Therefore, the concentration of the E' center will be decay after cessation of the irradiation. In fact, as shown in Fig. 6, absorbance at 5.8 eV decays after cessation of the irradiation. Similar phenomena have been reported by Imai et. al.[7].

Next, we discuss the annealing effect on the luminescence characteristics. We assme that the 4.4 eV band is caused by the E' center[4]. The reaction of eq.(3) is promoted by removing hydrogen molecules: If the sample is annealed in oxygen, hydrogen molecules in the glass will react with oxygen in the glass surface and promote the diffusing out of the hydrogen molecules from the glass. If the sample is annealed in herium, the herium atmos will permiate into glass and will mix with the hydrogen molecules in the glass. By the mixing, entropy of the system is increased and the reaction of eq.(3) will be promoted.

3-3 Fused Silica Synthesized in Oxydizing Condition

It is reported that type III fused silica which shows 1.9 eV emmision band have an absorption band at 4.8 eV. However, in the present sample, the absorption band cannot be measured within the experimental sensitivity. But the 4.8 eV absorption band can be measured directly ArF excimer laser irradiation after annealing in herium.

In a fused silica synthesized in oxydizing condition (sample II), as shown in subsection 3-1, an absorption band at 4.8 eV is induced by ArF excimer laser irradiation. The solarization is strongly enhanced by the annealing in herium as shown in Fig. 3. The annealing effects can be seen by the shot number dependence of the ArF excimer laser transmission: After annealing in herium, the transmission markedly decreases as increasing the shot number, and the decrement of the excimer laser transmission is prevented by the annealing in hydrogen.

Since the intensity of the 4.8 eV band of as-prepared sample is very weak, as shown in Fig. 3, it is beter to compare by the effect of annealing in herium on the 1.9 eV emission band. The 1.9 eV emission band is extinguished by annealing in hydrogen as shown in fig. 7. However, the band is created again by annealing the same sample subsequently in air, and the intensity of the band became stronger than that of before annealing.

Very recently, Awazu and Kawazoe proposed a model of the solarization[11] that the precursor of the 4.8 and the 1.9 eV bands are oxygen molecules dissolved in the glass.

The effect of annealing in herium cannot be explained by the model. Therefore, there must be the other mechanism to create the precursor of the 4.8 eV band. To examine these mechanism more clearly, we studied the X-ray induced solarization.

An absorption band at 5.8 eV is induced by X-ray irradiation in addition to the 4.8 eV band as shown in Fig. 8. Although the 5.8 eV band does not be appeared by the ArF excimer laser irradiation as shown in Fig. 5. In addition to these bands, an absorption band at 2.0 eV is appeared as shown in Fig. 8. This band is ascribed to be the NBOHC[15].

Now, we discuss the absorption band and emission band induced by the ArF excimer laser irradiation of fused silica synthesided in oxydizing atmosphare and the effect of annealing based on the model of Awazu and Kawazoe[11].

Although their model can successfly explain the solarization and the luminescence characteristics of as-prepared materials, the effect of the annealing cannot explain. Therefore, it should be some mechanism to produce the oxygen molecules by the annealing.

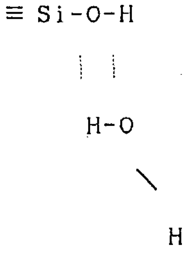
If a fused silica containing oxygen molecules annealed in hydrogen, H2O molecules would be formed by reaction between the hydrogen and the dissolved oxygen

$$2H_2 + O_2 \rightarrow 2H_2O, \qquad (4)$$

and the creation of the 4.8 and therefore 1.9 eV bands would be prevented. In fact, as shown in Fig. 7, the creation of these bands are prevented by the annealing in hydrogen.

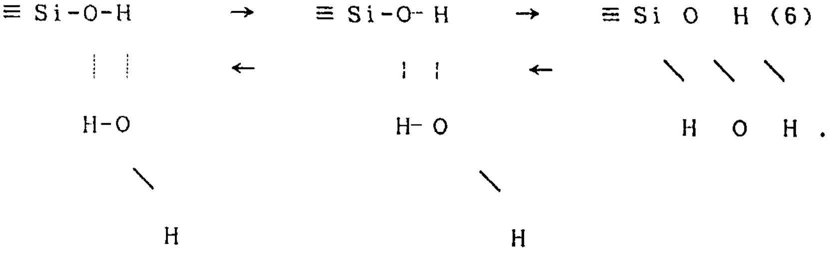
However, these bands appeared again by annealing in air. The inverse reaction of eq.(4) would not be occured in usual condition. There must be some catalytic reaction to proceed the inverse reaction of eq.(4) since hydrogen molecuse is stable even in the sufficiently high temperature.

It is well known that H_2O molecules form clusters in water. Since the concentration of the dissolved molecules is sufficiently low, c.a. 10^{18} cm^{-3}[11] it is natural to assume that the dissolved H_2O molecules does not form large clusters each other. Some of the H_2O molecules will be bounded to ≡ Si-OH base as



(5)

This structure can be recombined as follow:



(6)

The structure of the third part of eq. (6) is unstable compared to the other parts. But the probability of the existance of the structure of the third part will be increased in sufficiently high temperature. In sufficiently high temperature, some part of the hydrogen molecules will be diffuse out from the vicinity of the structure, and the concentration of dissolved oxygen molecules will increase. Therefore the intensity of the irradiation induced absorptions are enhanced by annealing as reported by Nakamura et. al.[3]. Annealing in herium, the removal of the hydrogen is promoted by the "mixing entropy effect" as discussed before in the case of the sample synthesized in the reducing condition. As result, oxygen molecule are remained in the glass and the creation of the 4.8 and 1.9 eV bands are promoted.

The creation of the NBOHC which is reported by several authous[9,11] can be explained as

$$\equiv \mathrm{Si{-}H} + \mathrm{O} \xrightarrow{h\nu} \equiv \mathrm{Si}\cdot + \mathrm{H} + \mathrm{O} \longrightarrow \equiv \mathrm{Si{-}O}\cdot + \mathrm{H} \quad (7)$$

The oxygen in the first part of eq. (7) is created by ArF excimer laser induced photolysys[11]. Since the hydrogen atom will exist in the vicinity of the E' center, as described in eq. (7), the E' center will be disapeared immediatly after cessation of the ArF excimer laser irradiation.

By the X-ray irradiation, on the other hand, the probability to rupture the ≡Si-H bond is considarably higher than that of ArF excimer laser since the photon energy of X-ray is two orders higher than that of the excimer laser.

Therefore the mean lifetime of the E' center is considarably longer then in the case of the ArF excimer laser, and the some part of the hydrogen could be diffuse out from the glass. Therefore the 5.8 eV band is observed.

5. Summary and Conclusion

Solarization and luminescence characteristics of type III fused silica synthesized in reducing and oxydizing condition are investigated. In fused silica synthesized in reducing condition, the 5.8 eV absorption band ascribed to be the E' center and the 4.4 eV emission band is induced by the irradiation of the ArF excimer laser. The creation of these band can be prevented by annealing in herium. We proposed that the precursor of these band is the ≡ Si-H H-O-Si≡ structure.

In the fused silica synthesized in oxydizing condition, the 4.8 eV and the 1.9 eV emission bands are induced by the ArF excimer laser irradiation. Creation of these bands are enhanced by annealing in herium. By annealing this material in hydrogen, the creation of these bands can be prevented by annealing in hydrogen, but these bands will be created again by annealing in air. These phenomena cannot be explained solely by the dissolved oxygen molecule model of Awazu and Kawazoe. We proposed that the precursor to create the oxygen molecules in the glass by annealing is H2O molecules bounded to the silanol base in the glass network. The present model can also explain the characteristics of the X-ray induced solarization.

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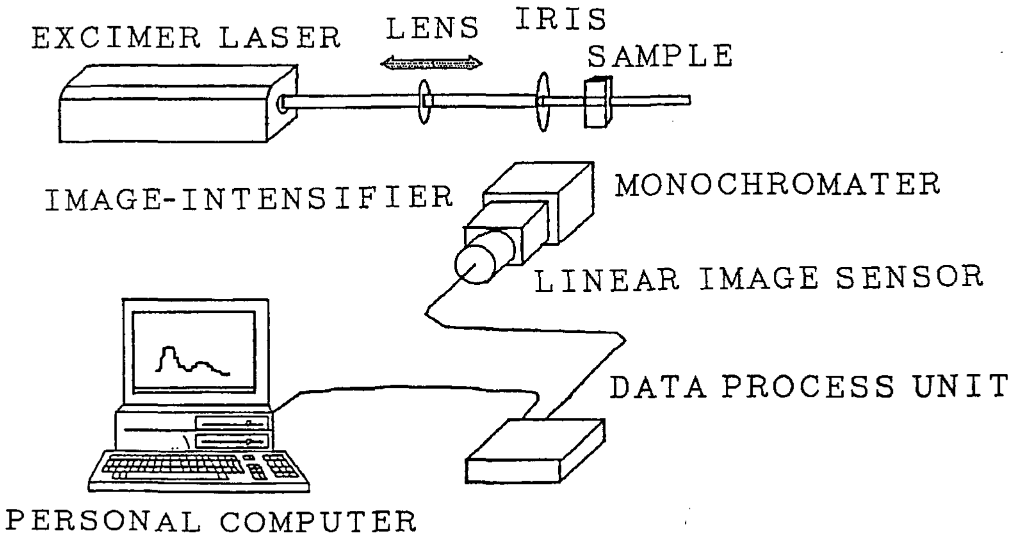

Fig. 1a

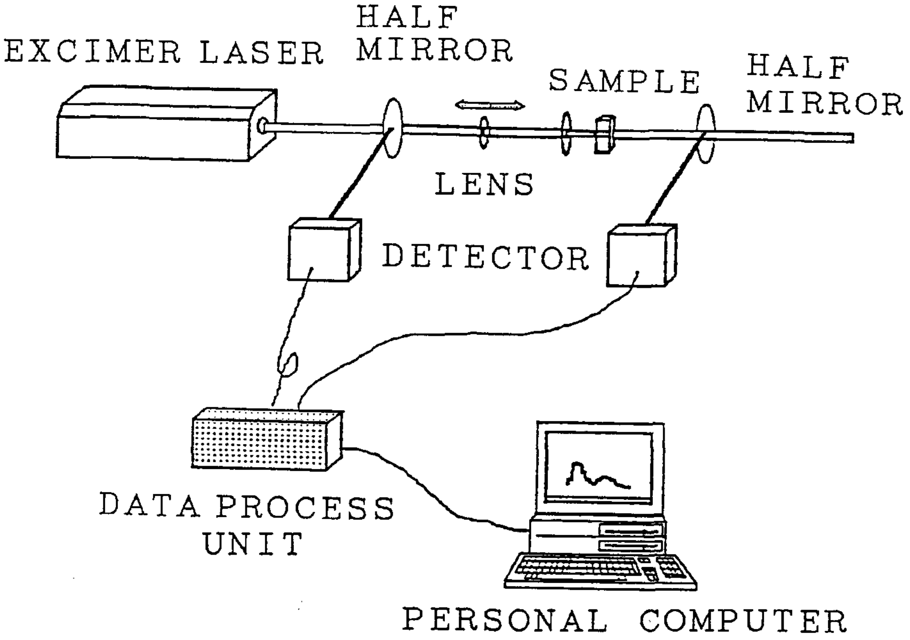

Fig. 2b

Fig. 1: Schematic drawing of the luminescence measurement system (a) and the excimer laser transmission system (b).

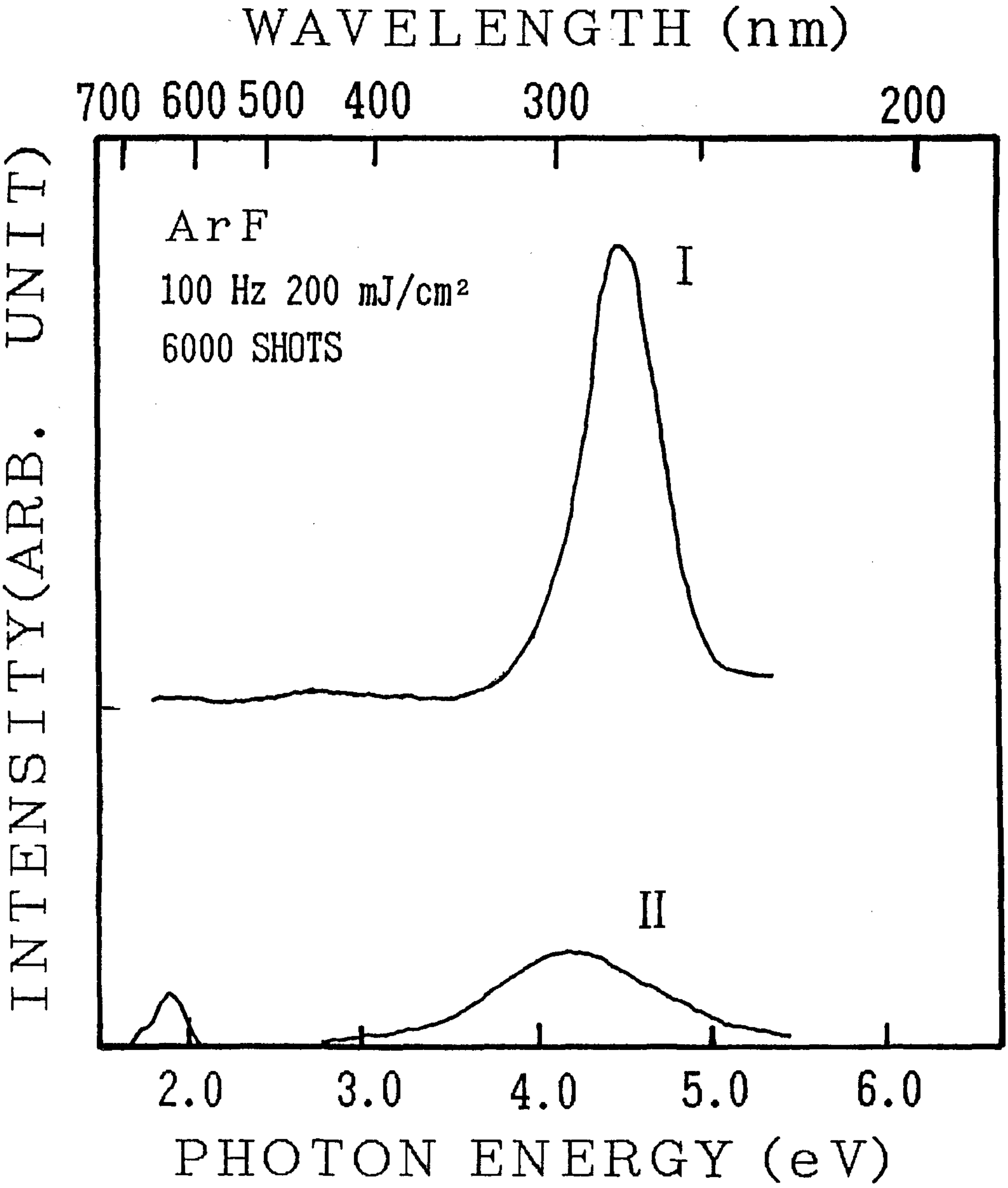

Fig. 2: Luminescence spectra of type III fused silica synthesized in reducing (I) and oxidizing condition.

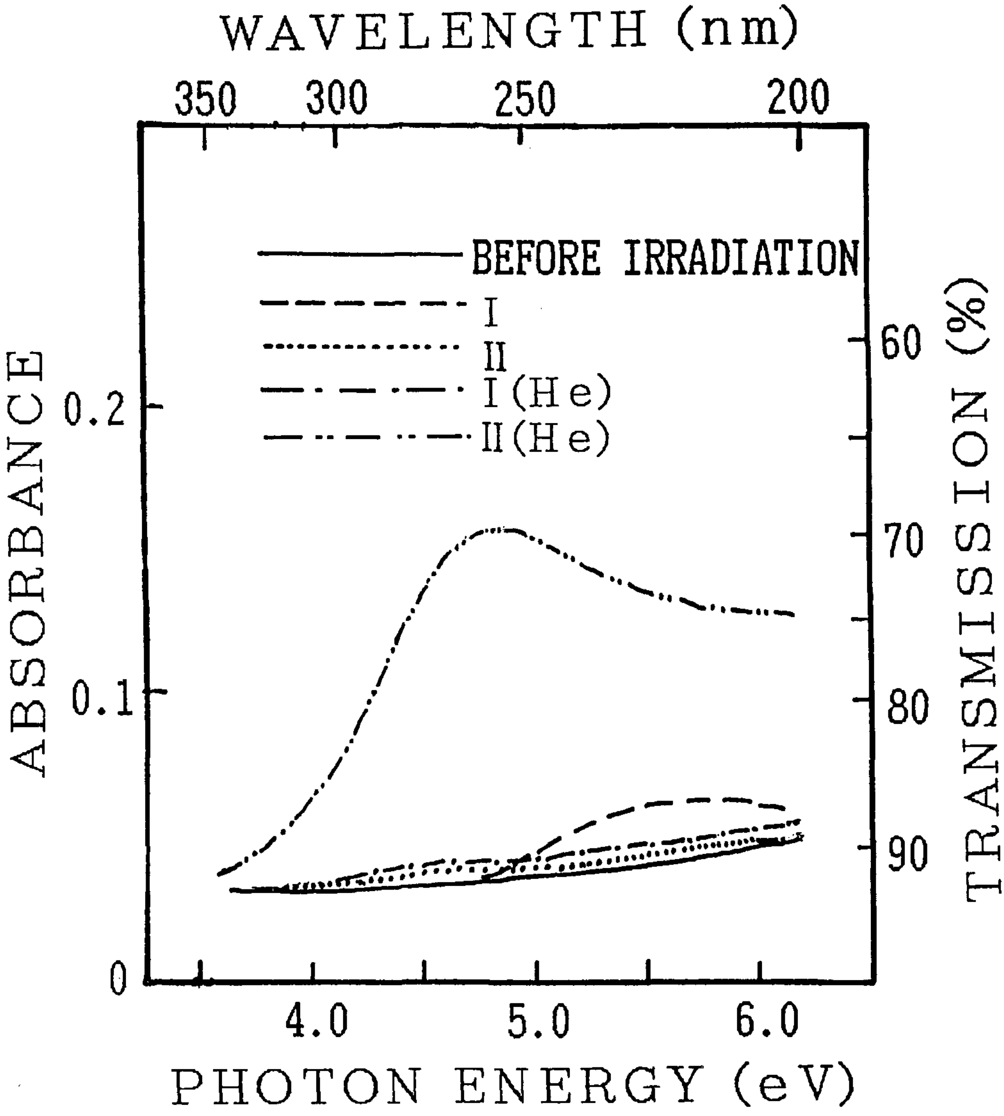

Fig. 3: Absorption spectra induced by ArF excimer laser irradiation (50 Hz, 500 mJ/cm^2, 2 minutes) before and after annealing.

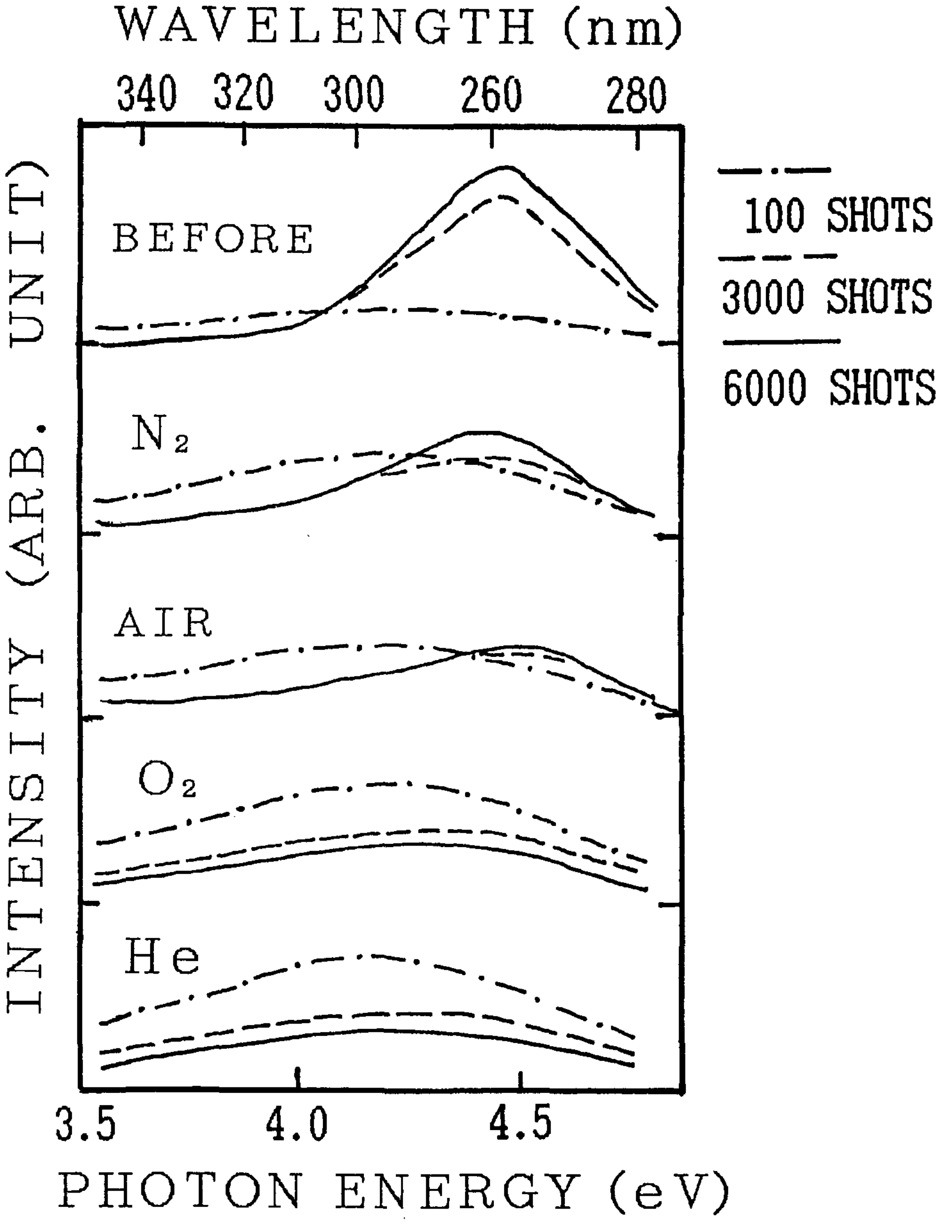

Fig. 4: Shot number dependence of luminescence spectra induced by ArF laser irradiation (100 Hz, 200 mJ/cm^2) of the fused silica synthesized in reducing condition (I) before and after annealing: Full lines, 6000 shots; dashed line, 3000 shots; chain line, 100 shots.

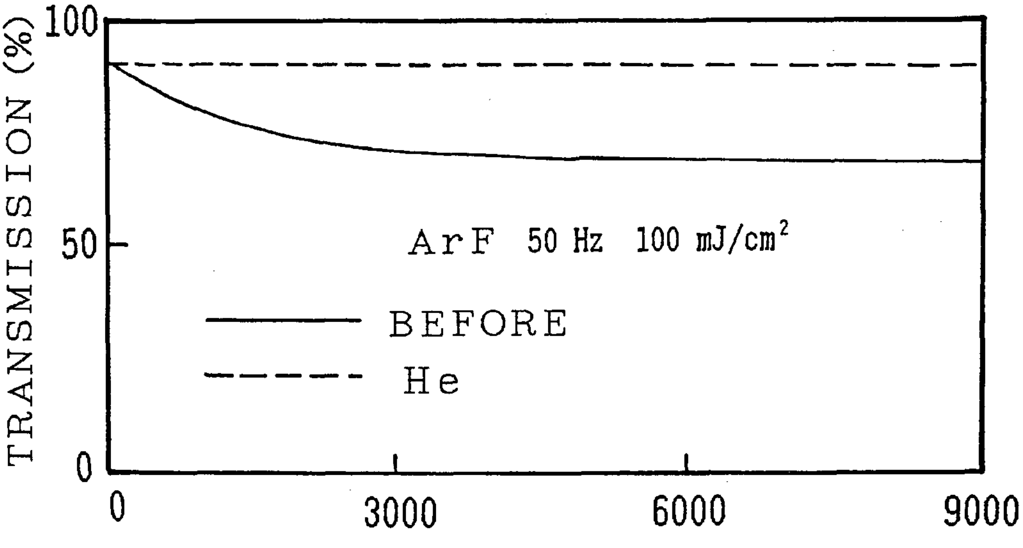

Fig. 5a

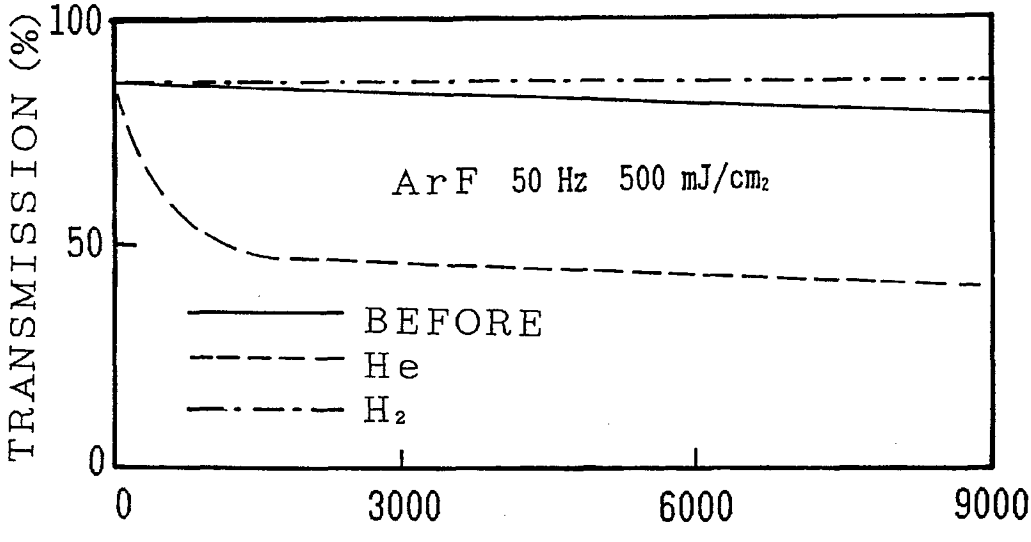

Fig. 5b

Fig. 5: Effect of annealing on the shot number dependence of the ArF excimer laser transmittance. (a) Sample I: 50 Hz, 100 mJ/cm^2 before and after annealing in herium. (b) Sample II, 50 Hz, 500 mJ/cm^2, before annealing and annealing in He and H2.

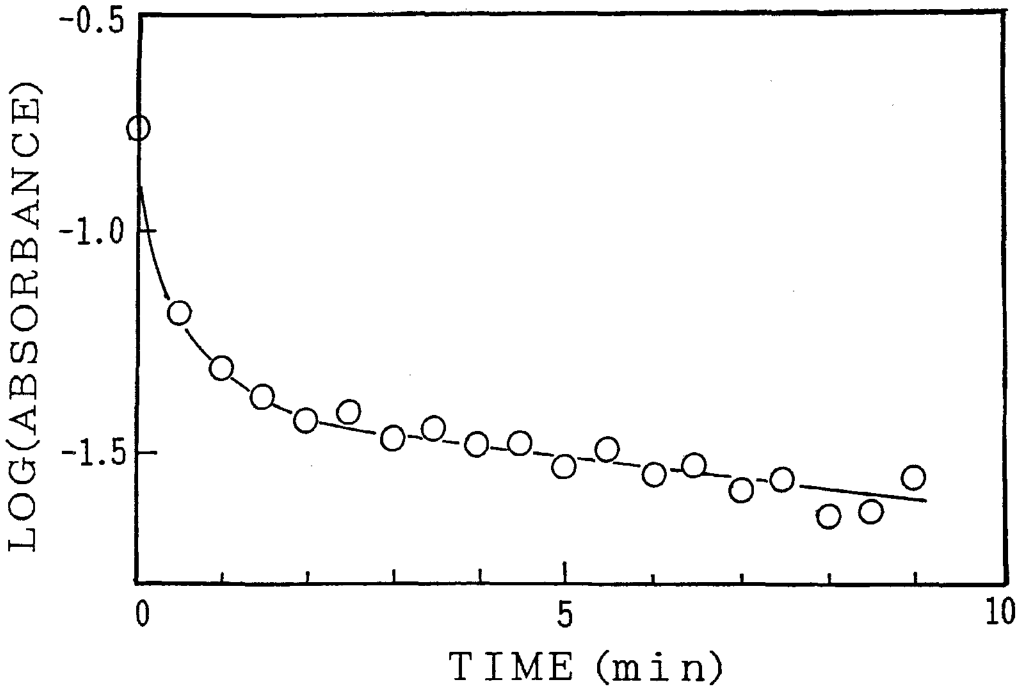

Fig. 6: Decay of the intensity of 5.8 eV absorption after cessation of the irradiation.

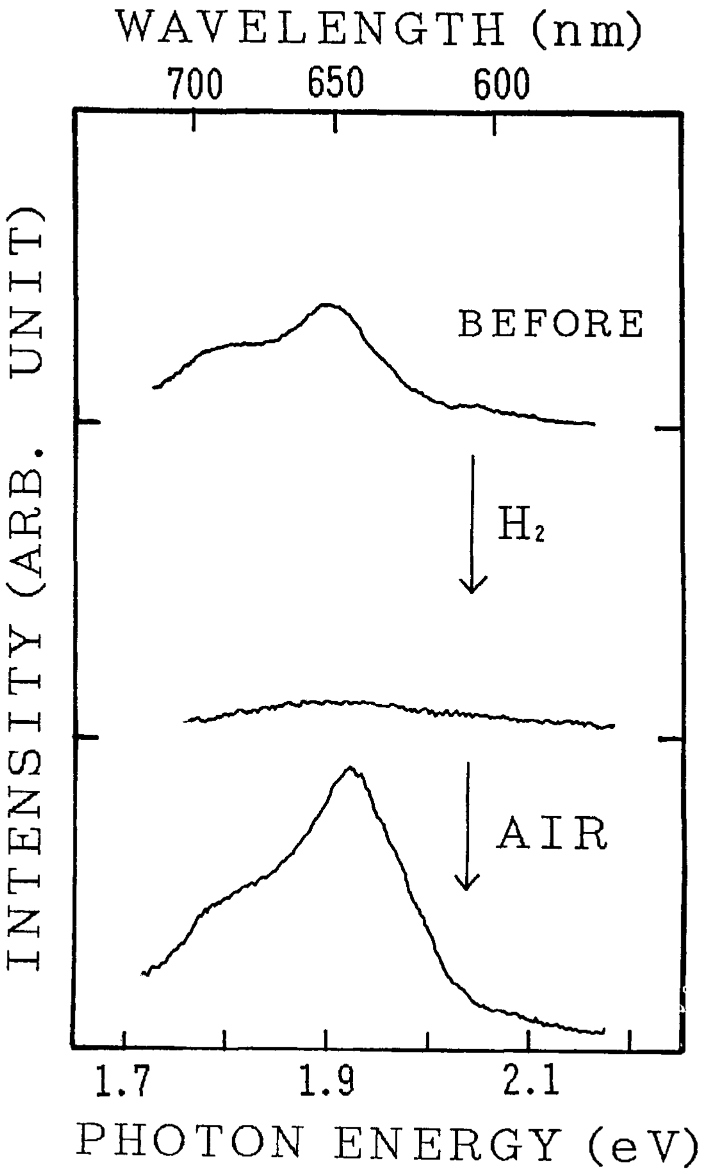

Fig. 7: Effect of annealing in hydrogen on the 1.9 eV emission band induced by ArF excimer laser irradiation (100 Hz, 200 mJ/cm^2).

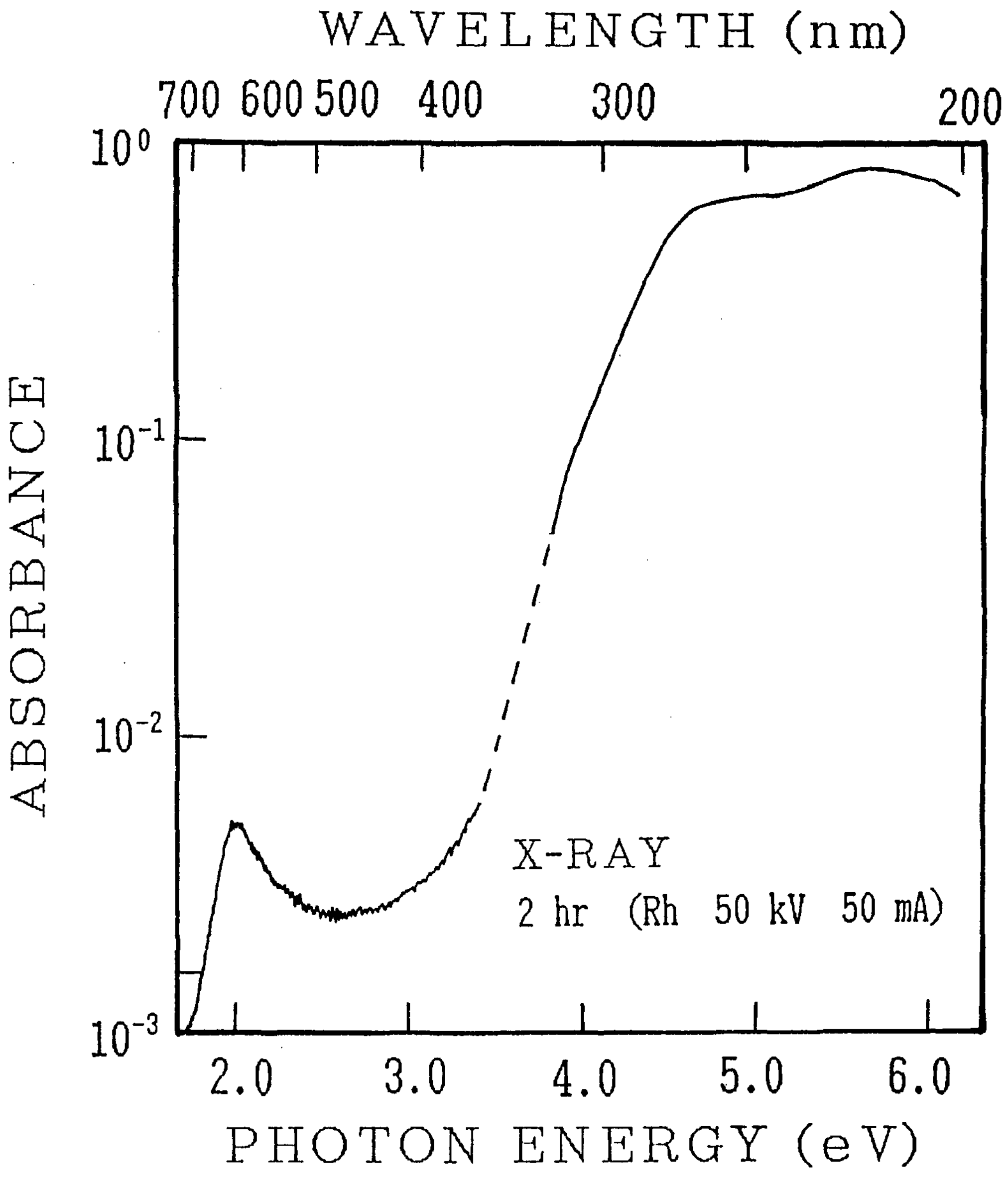

Fig. 8: X-ray induced absorption spectra of the fused silica synthesized in the oxidizing condition (sample II).