PHYSICAL REVIEW B VOLUME 47, NUMBER 6 1 FEBRUARY 1993-II

Energy-density and repetition-rate dependences of the KrF-excimer-laser-induced 1.9-eV emission band in type-III fused silicas

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(Received 27 July 1992)

The energy-density and repetition-rate dependences of the intensity of KrF-excimer-laser (5.0 eV) -induced 1.9-eV emission band in type-III fused silicas synthesized under different conditions were investigated. The intensity of the 1.9-eV band is proportional to the 1.7-th power of the energy density and the 0.6-th power of the repetition rate of the laser pulse. The origin of these dependencies was discussed based on the trapped-oxygen-molecule model proposed by Awazu and Kawazoe; by irradiating with the excimer laser, ozone molecules are formed from dissolved oxygen molecules and 1.9-eV photons are emitted in the course of the photodecomposition of the ozone molecules. Therefore, a two-step photon-absorption process is needed to emit the 1.9-eV photon. To form the ozone molecule, diffusion of the oxygen atoms produced by the photodecomposition of the trapped oxygen molecules are needed. This model suggests that the intensity of the 1.9-eV band is proportional to the square of the energy density and the square root of the repetition rate; this dependency is nearly the same as that of our experimental result.

I. INTRODUCTION

Synthetic fused silicas are widely used in optical materials in the uv region because these materials have high optical transmission in the uv region.[1] Recently KrF excimer lasers (5.0 eV) have often been used as a light source in lithography in semiconductor processes;[1] in the KrF-laser-lithography process, synthetic fused silicas are used as reticles and lenses in a repeat-and-step projector (a stepper).[2]

Several processes are used to produce synthetic fused silica.[3,4] In optical materials for KrF excimer lasers, type-III fused silicas synthesized by flame hydrolysis of silicon tetrachloride in hydrogen-oxygen flames are mainly used because we can obtain a material with good homogeneity over a large area.

Type-III fused silica is highly radiation resistive, but color centers may sometimes be created by γ rays, x rays, rf plasmas, and excimer lasers.[5]

We showed, in previous papers,[6-8] that characteristics of the ArF-laser (6.4 eV) -induced luminescence in type-III fused silica are strongly affected by the $[H_2]/[O_2]$ ratio in the flame.

Fused silica synthesized under a reducing condition ($[H_2]/[O_2]>2.0$) shows a strong emission band at 4.4 eV.[7] Fused silica synthesized under an oxidizing condition ($[H_2]/[O_2]<2.0$), on the other hand, shows emission bands induced at 1.9 and 4.1 eV.[8]

Upon irradiation with KrF laser on these samples, only the emission band at 1.9 eV is induced. A number of models are proposed for the origin of the 1.9-eV band:[5] Some authors suggest that the precursor of the 1.9-eV band is a nonbridgening oxygen hole center (NBOHC; $\equiv$Si-O$\cdot$).[9-12] Awazu and Kawazoe[13] proposed a model in which O_2 molecules trapped in the glass network is the precursor of the 1.9-eV band. They also observed NBOHC's and explained their formation mechanism. At any rate, the 1.9-eV emission band is related to the stoichiometrically excess amount of oxygen in the SiO_2.

The intensity of the 1.9-eV band depends strongly on the repetition rate and the energy density of the laser pulse. We studied in this paper the irradiation-condition dependence of the KrF-laser-induced 1.9-eV emission band in fused silicas synthesized under different conditions. We also discuss this dependency in relation to the trapped-oxygen-molecule model of Awazu and Kawazoe.[13]

II. EXPERIMENT

A. Samples

Fused silica samples were synthesized directly by flame hydrolysis in hydrogen-oxygen flames with three different conditions: sample DR, $[H_2]/[O_2]>2.0$; sample DS $[H_2]/[O_2]\simeq 2.0$; sample DO, $[H_2]/[O_2]<2.0$. These samples contain about 800, 1200, and 1200 ppm of OH, respectively; the OH concentrations were calculated by ir absorption at 3650 cm^{-1} whose extinction coefficient is 77.5 l/mol cm.[14] The samples were cut into pieces of size $10\times 10\times 30$ mm^3, and their surfaces polished.

B. Luminescence and absorption measurement

Luminescence spectra were measured with use of the same apparatus as in previous papers.[7,8] A Questek SQL

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2240-type excimer laser was used. The energy density was controlled by using a fused silica lens ($f=500$ mm) and the diameter of the beam was adjusted to 5 mm by using an iris. The energy density was calibrated by a joulemeter (a Gentek type ED-500).

Luminescence was detected from a direction perpendicular to the excitation beam. Emission spectra were measured shot by shot monochromatically (using a Jasco CT-10) by diode array with an image intensifier (a Hamamatsu Photonics C280-03). Spectra bandwidth of each measurement was about 100 nm. The data obtained were processed by a microcomputer (an NEC PC-9801RX). Absorption spectra were measured by use of a spectrophotometer (a Shimadzu UV-250).

III. RESULTS

A. KrF and ArF laser-induced emission spectra

Emission spectra in three samples irradiated with KrF and ArF excimer lasers are compared in Fig. 1. Under irradiation with the ArF laser, strong emission bands in the uv region are induced. Under irradiation with the KrF laser, on the other hand, only an emission band at 1.9 eV is apparent. In the following, we will only deal with the 1.9-eV band in the samples irradiated with the KrF laser.

B. Energy-density dependence of the intensity of the 1.9-eV band

Figure 2 shows an example of the laser-shot-number dependence of the intensity of the KrF laser induced 1.9 eV band. The intensity initially grows with increasing shot number and eventually reaches a steady-state value. The energy-density dependence of the steady-state value of the intensity per pulse of the 1.9-eV emission band are shown in Fig. 3. Hereafter, we mean by the "intensity" the intensity of the steady-state value per pulse. The intensity of the 1.9-eV emission band is found to vary approximately as the 1.7-th power of the energy density of the KrF laser pulse. In sample DO, the intensity tends to saturate in the high-energy-density region, i.e., greater than about 1000 mJ/cm^2.

C. Repetition-rate dependence of the intensity of the 1.9-eV band

The repetition-rate dependence of the intensity of the 1.9-eV band are shown in Fig. 4. The energy density in this measurement is 500 mJ/cm^2. In all samples, the intensity is found to vary approximately as the 0.6-th power of the repetition rate.

D. Effect of the repeats of the irradiation

Now we will examine the effect of repeated irradiations of the same position on a sample. In the following, we will only deal with sample DO, because the intensity of the 1.9-eV band is strongest among the present samples. Figure 5(a) shows the shot-number dependence of the intensity of the 1.9-eV band under irradiation with the KrF

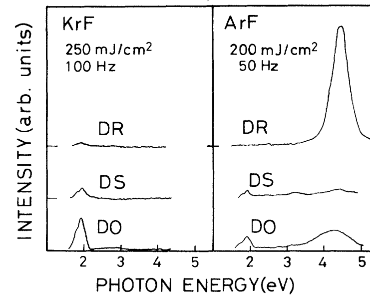

FIG. 1. Comparison of emission spectra of three samples irradiated with KrF (250 mJ/cm^2, 100 Hz) and ArF (200 mJ/cm^2, 50 Hz) excimer lasers.

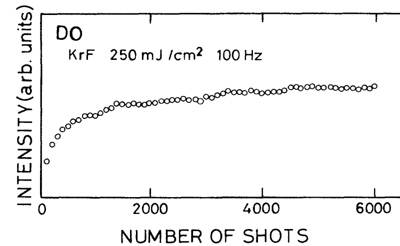

FIG. 2. An example of the shot-number dependence of the intensity of the 1.9-eV emission band. Sample DO, KrF 250 mJ/cm^2, 100 Hz.

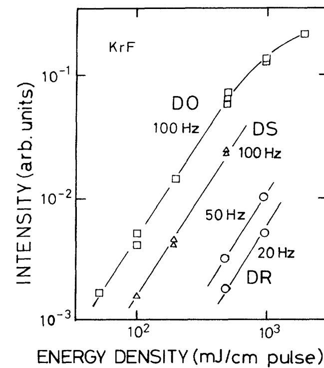

FIG. 3. Energy density dependence of the intensity of the KrF laser-induced 1.9-eV band per pulse.

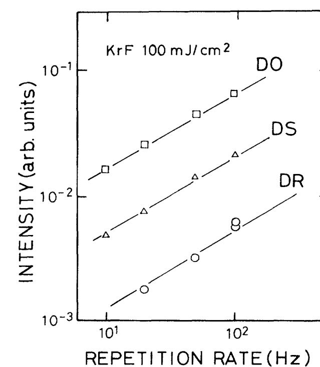

FIG. 4. Repetition rate dependence of the intensity of the KrF laser induced 1.9-eV band; the energy density is 500 mJ/cm^2 pulses.

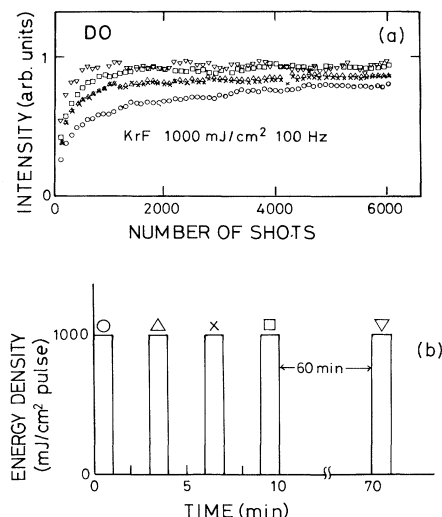

FIG. 5. Effect of repeated irradiation by the KrF laser beam of the same position on sample DO with 100-Hz, 1000-mJ/cm^2 pulses. (a) Shot-number dependence of the intensity of the 1.9-eV band irradiated according to the time schedule shown in (b).

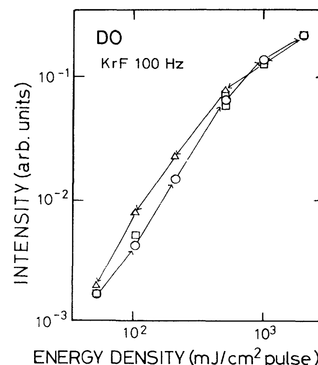

FIG. 6. Hysteresis of the irradiation on the intensity of the KrF laser induced 1.9 eV of sample DO with repetition rate 100 Hz. Square, irradiation of positions not previously irradiated; circle, increasing energy density; and triangle, decreasing energy density.

laser in the same position of sample DO repeatedly following the schedule shown in Fig. 5(b). After the second period of this irradiation, the intensity grows steeper than that of the first period. However, the steady-state value is almost the same value. It is noted that the energy density of the pulse contains about a 10% error because we use the power control function in the excimer laser system. The excimer laser was operated at about 50–70 mJ/cm^2 pulse and the laser system can control the energy density within the range of 5 mJ/cm^2. Therefore, the difference of the steady-state value in Fig. 5(a) can be mainly derived from the difference of the laser power.

E. Hysteresis of the irradiation

Next, we will show hysteresis of the irradiation on the same point. An excimer-laser beam was directed to irradiate the same point with 6000 shots with a repetition rate of 100 Hz with various energy densities. In the first, the energy density was increased successively as 50, 100, 200, 500, 1000, and 2000 mJ/cm^2 pulses (circles in Fig. 6). Then the energy density was decreased as 2000, 500, 200, 100, and 50 mJ/cm^2 (triangles in Fig. 6). These values are pairwise almost the same. These intensities are also the same as in the case when the KrF laser was used to irradiate points that had not been irradiated previously (squares in Fig. 6).

IV. DISCUSSION

A. Excimer-laser-induced 4.8-eV band

In a previous paper,[8] we studied effects of annealing in a He ambient on the ArF laser-induced absorption band at 4.8 eV. Under irradiation with ArF laser, an absorption band at 4.8 eV is induced in sample DO. The creation of the ArF laser-induced 4.8-eV band is strongly enhanced by annealing in the helium ambient.

We tried to measure the KrF laser-induced 4.8-eV band in the present study. However, we could not detect this band within experimental accuracy. The effect of the creation of the 4.8-eV absorption band can be monitored by the shot-number dependence of the KrF laser beam transmission because the photon energy of the KrF laser 5.0 eV is very close to the peak position of this band. However, we could not detect a decrease of the transmission of KrF laser beam (500 mJ/cm^2, 50 Hz, up to 12 000 shots) even in sample DO.[15]

B. A model to describe the origin of the 4.8- and 1.9-eV bands

Awazu and Kawazoe[13] proposed a model to describe the origin of the 1.9- and 4.8-eV bands. In their model, precursor of these bands are oxygen molecules trapped in the glass network. These bands are induced by the following mechanism:

$$O_2\ (\text{trapped}) \xrightarrow{h\nu} 2O\ , \qquad (1)$$

$$O + O_2 \rightarrow O_3(\text{trapped})\ , \qquad (2)$$

$$O_3 \xrightarrow{h\nu} O(^1D) + O_2\ , \qquad (3)$$

$$O(^1D) \rightarrow O(^3P) + 1.9\ \text{eV}\ . \qquad (4)$$

The 4.8-eV absorption band is caused by the Hartley band of O_3 molecules in Eq. (2). The 4.8-eV band is very stable at room temperature after irradiation. We could observe the 4.8-eV band in the fused silica even a year after the irradiation. The stability of the O_3 molecule can be explained as follows: Atomic radii (van der Waals' radii)[16] of hydrogen and the oxygen atoms are 1.2 and 1.40 Å, respectively. These radii are smaller than that of helium (1.50 Å) which can easily diffuse into the glass network. The radius of argon atom, which cannot diffuse into the glass network is 1.90 Å. Therefore, at room tem-

perature, only atomic oxygen can diffuse into the glass network but not O_2 or O_3 molecules. The O_3 molecules can recombine with other molecules under collision. Because atomic oxygen is created only by the excimer laser irradiation at room temperature, the O_3 molecules trapped in the glass network are stable.

Since the photon energy of the KrF laser (5.0 eV) is near 4.8 eV, the reaction of Eq. (3) proceeds easily and most ozone molecules will not exist for a long period. Therefore the KrF laser-induced 4.8-eV band is not apparent. Under irradiation with the ArF laser, on the other hand, the 4.8-eV band can be induced easily because the photon energy of the ArF laser (6.4 eV) is much higher than the threshold energy (5.1 eV) of the reaction of Eq. (1) and apart from the absorption energy of the ozone molecule (4.8 eV).

The 1.7-th power dependence of the intensity on the energy density per pulse is nearly a square dependence; one may consider that this dependency suggests a two-photon process.[17] However, in the present case, the process is not a two-photon process but rather a two-step photon-excitation process as shown in Eqs. (1)–(4); in the first step, ozone molecule is formed by the process in Eqs. (1) and (2), and in the second step, a 1.9-eV photon is emitted in the processes of Eqs. (3) and (4).

C. The 0.6-th power dependence of the repetition rate

The 0.6-th power dependence on the repetition rate can be interpreted as follows:

To understand the 0.6-th power dependence of the repetition rate, the process to create the 1.9-eV band is shown schematically in Fig. 7. Oxygen molecules are trapped in the glass network and find it hard to diffuse into the glass network at room temperature. Under irradiation with the excimer laser, oxygen atoms are produced by Eq. (1) and can diffuse into the glass network to form ozone molecules by reacting with oxygen molecules. In the following discussion, we only deal with the steady-state value. Therefore, we can assume that concentrations [O], $[O_2]$, and $[O_3]$ are constant.

The probability of producing oxygen atoms on the right-hand side of Eq. (1) is proportional to $[O_2]$ and the net irradiation time, i.e., the product of the repetition rate R and pulse energy density E:

$$[O] \propto RE[O_2] . \tag{5}$$

Creation of the O_3 molecules is related to a diffusion-controlled reaction; diffusion of the O atom into the glass network is needed to form the O_3 molecules. The concentration of a species produced by a diffusion controlled reaction, such as the O_3-molecule concentration in the glass network, is proportional to the square root of time. The reaction can proceed only between pulses, because O_3 will be destroyed by the photon pulse. Therefore, in the steady state, the population will be proportional to [O], $[O_2]$, and the square root of the period of the laser pulses $1/R$,

$$[O_3] \propto [O][O_2]R^{-1/2} . \tag{6}$$

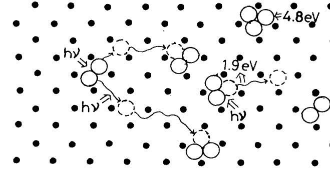

FIG. 7. Schematic drawing of the creation mechanism of the 1.9-eV emission band: Small full circles represent the glass network and larger open circles represent oxygen atoms.

From Eqs. (3) and (4), intensity I per pulse of the 1.9-eV band is proportional to $[O_3]$ and E.

$$I \propto [O_3]E . \tag{7}$$

From Eqs. (5), (6), and (7) we obtain

$$I \propto R^{1/2}E^2[O_2]^2 . \tag{8}$$

If $[O] \ll [O_2]$ and $[O_3] \ll [O_2]$, we can assume $[O_2]$ to be constant. Therefore we obtain

$$I \propto R^{0.5}E^2 , \tag{9}$$

which is very close to our experimental result, $I \propto R^{0.6}E^{1.7}$.

The slight difference could be derived from the assumption that $[O_2]$ is constant. The tendency to saturation in sample DO in high-energy densities in Fig. 3 is derived from the E dependence of $[O_2]$. The growth of the intensity in Fig. 2 corresponds to the process to form ozone molecules. Although the concentration of ozone molecules is small, the ozone molecule will be stable as mentioned above. Therefore if the KrF laser is used to irradiate the same point on a sample, the intensity of the 1.9-eV band grows more steeply than the first time as in Fig. 5, but the saturated value will be the same as the first irradiation.

The independence of the steady-state value to the history of irradiation (Figs. 5 and 6) is due to the existence a steady-state value in Eqs. (1)–(4).

V. SUMMARY AND CONCLUSION

We have studied the pulse-energy-density and -repetition-rate dependence of the 1.9-eV band in type-III fused silicas irradiated with a KrF excimer laser. We also discussed these results based on the dissolved-oxygen-molecule model of Awazu and Kawazoe.

(1) The intensity of the 1.9-eV emission band is found to be proportional to the 1.7-th power of the energy density per pulse and to the 0.6-th power of the repetition rate of the KrF laser.

(2) We interpreted this result by use of the dissolved-oxygen model of Awazu and Kawazoe: In the first step, O atoms are formed by absorbing the photon of the KrF laser and O_3 molecules are formed by reacting these O atoms with dissolved O_2 molecules. In the second step, O_3 molecules are dissociated by absorbing the photon of the KrF laser, and in the course of the dissociation 1.9-eV photons are emitted.

(3) The 1.7-th power dependence is nearly the square dependence derived from a two-step excitation process in the dissolved-oxygen model: formation of ozone molecules and decomposition of the ozone molecule.

(4) The 0.6-th power dependency of the repetition rate of the excimer laser pulse is very close to a square-root dependence; the square-root dependence suggests a diffusion-controlled process, i.e., the diffusion of the oxygen atom is produced by the photodecomposition and it diffuses to form an ozone molecule.

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