The Trapping and Release of Injected Hydrogen Isotopes in Vitreous Silica

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The behavior in vitreous silica of hydrogen isotopes, which had been introduced by 80-keV D^+-ion implantation, thermal D_2 doping, or recoil tritium implantation (2.7 MeV), was studied by means of FT-IR spectroscopy, ESR spectroscopy, and radioassay with a liquid scintillation counter. The hydrogen isotopes are trapped by forming hydroxyl bonds (OD, OT). In the D^+-ion implantation, OD bonds are formed mainly by the rupture of the $\equiv$Si–O–Si$\equiv$ bonds. In the thermal D_2 doping, however, OD bonds are formed mainly by the isotope-exchange reaction between the preexisting OH bonds and D_2 molecules. When vitreous silica implanted by recoil tritium is heated to about 1150 K, HTO and HT are released. The OD bonds produced by D^+ implantation decrease upon annealing at 1150 K. The OD bond-rupture is controlled by the diffusion of hydrogen isotopes trapped as OD(OT) bonds to the surface of vitreous silica. The mechanism of the diffusion of the hydrogen isotopes through vitreous silica was explained in terms of a repetition of the chemical reaction of $\equiv\text{SiOD(OT)}+\equiv\text{SiOSi}\equiv \longrightarrow \equiv\text{SiOSi}\equiv+\equiv\text{SiOD(OT)}$. The diffusion coefficient (D_T(HTO)) of tritium according to the above mechanism was obtained as:

$$D_T(\text{HTO}) = 2.3\times10^{-4}\exp[-1.7\times10^2(\text{kJ mol}^{-1})/RT]\ \text{cm}^2\,\text{s}^{-1}$$

Nonmetallic materials are used in fusion reactors as tritium diffusion barriers, first-wall coatings, or diagnostic window materials for the reactors. Hydrogen generally diffuses much more slowly in oxides than in metals. The first-wall materials are irradiated with high-energy tritium, neutrons, and high levels of γ-rays. The high energy tritium, injected into the material, is trapped there or diffuses through the material. In order to prevent tritium fuel from permeating through the fusion material, it is very important to elucidate the interactions between the high-energy hydrogen and the material.

Previous studies of the interaction, however, have been concerned mainly with the physical interaction, such as the sputtering of the solid surface, the production of radiation damage, and a depth-profile of the injected hydrogen. Since hydrogen isotopes are reactive species, the chemical interactions between injected hydrogen and the materials also play a significant role. The chemical interactions consist of several microscopic processes, such as hydrogen trapping, detrapping, diffusion, and desorption. The role of chemical reactions in these processes is shown in Fig. 1. Though physical interactions are not neglected in these processes, they are omitted from Fig. 1. When hydrogen isotopes with a high energy are injected into a material, they are trapped by the formation of chemical bonds. Since the first-wall material is held at a high temperature or under the high radiation field, the hydrogen isotopes are detrapped by the rupture of the chemical bonds and diffuse through the material to its surface, where the diffusion involves a chemical reaction in some cases. The hydrogen isotopes are released from the surface by surface reactions. Since the chemical interactions have been studied in only a few cases, the chemical

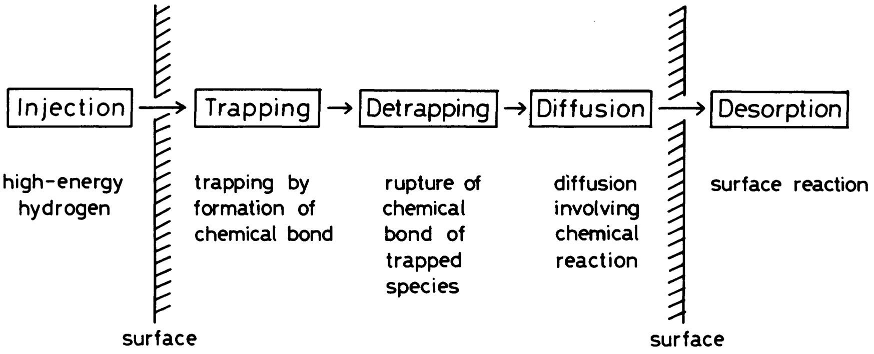

Fig. 1. The role of chemical interactions between high-energy hydrogen and materials.

interactions between hydrogen isotopes and vitreous silica (silica) will be reported here.

Silica, one of the most popular oxides, has the following characteristic properties: a relatively simple structure, a high softening point, transparent properties, a low cross-section for neutron-capture reactions, and a high activation energy for tritium diffusion.[1] In addition, the impurity content of silica can be controlled. Since the presence of OH bonds may affect the chemical interactions of hydrogen isotopes, the concentration of the OH bonds in silica was varied from 5 to 4000 ppm in this study. Several studies of silica have been reported previously. The compaction effects on silica by irradiation were reviewed by Primak.[2] The diffusion of hydrogen isotopes in silica have also been studied,[3,4] as has the hydrogen-ion implantation in SiO_2.[5,6] The presence of the radiation damage produced by the ion-implantation protects the radiation-induced detrapping of D atoms.[6] Moreover, the kinetic behavior of H and D atoms in silica has been investigated by means of ESR spectroscopy.[7]

In this study, hydrogen is introduced into silica by 80-keV D^+-ion implantation, 2.7 MeV-recoil tritium implantation, and D_2 gas-doping at high temperatures. The interaction between the hydrogen isotopes and silica was studied here by means of infrared Fourier transform spectroscopy (FT-IR), electron spin resonance spectroscopy (ESR), and tritium analysis using a liquid scintillation counter. Since it is difficult to elucidate the microscopic processes in Fig. 1 by using only one method, we have here studied these processes by a combination of the several methods mentioned above. The elucidation of the following problems is the main purpose of this study: (1) It was reported previously[8,9] that D_2 gas is trapped thermally in silica to form OD bonds by an isotope-exchange reaction between preexisting OH bonds (as inherent impurities) and D_2. Is the efficiency of the trapping of deuterium or tritium, injected with a high energy, affected by the preexisting OH bonds? If deuterium with a high energy is trapped to form OD bonds,[6] what is the mechanism of the formation of the OD bonds? (2) The deuterium and tritium trapped as OD (OT) bonds are released by thermal heating above 700 K. What is the mechanism of the release of hydrogen isotopes from the trapping sites? (3) How much is the value of the diffusion coefficient of tritium in silica?

Experimental

The four types of vitreous silica used here are Spectrosil, obtained from the Thermal American Fused Quartz Co.; Fused silica glass, obtained from the Asahi Glass Co., and Silica T1030 and Silica T2230, obtained from the Toshiba Ceramic Co. The concentrations of preexisting hydroxyl bonds in the four kinds of silica range from 5 to 4000 ppm.[10] The OH-bond concentration of the sample was measured by means of an infrared Fourier transform spectrometer (FT-IR)[11] at room temperature. It was estimated from the O–H stretching band at 3670 cm^{-1} [8,9] taking the extinction coefficient at the wavenumber as 77.5 l/mol cm.[12] The amounts of the OH bond and metal impurities[13] contained in the samples are summarized in Table 1. The samples which contain the OH bonds at 5, 610, 960, and 4000 ppm will be denoted hereafter as silica A, B, C, and D respectively. The samples for deuterium implantation were cut in the form of plates measuring 3.3×9×0.3 mm, while those for tritium implantation were cut in the form of plates measuring 5×10×1 mm.

The deuterium implantation was performed with a low-energy ion accelerator which has previously been described in detail.[14] Deuterium ions accelerated to 80-keV were injected into the target at an ion-beam flux of 2.5×10^{14} ions $s^{-1}cm^{-2}$. The compositions of the deuterium ions were D^+(78%), D_2^+(13%), and D_3^+(9%). The total deuteron fluence was 2.7×10^{18} D/sample. The sample chamber was evacuated to 10^{-5} Pa during irradiation.

The tritium implantation was performed by the use of recoil tritium atoms from the reaction of ^6Li (n, α) T, where ^6Li-enriched lithium chloride was used as the tritium source. It was prepared from lithium metal obtained from Oak Ridge National Laboratory; the ^6Li content was 95%. An aliquot of lithium chloride solution was dried on a 7×12×1 mm polyethylene plate. Then it was wrapped with a mylar sheet. The wrapped plate was tightly attached to the sample. The assembly was put into a quartz ampoule which was sealed in vacuo. The ampoules were irradiated by neutrons in the JRR-4 reactor in JAERI for 10 min at the ambient temperature. The thermal neutron flux was 8×10^{13} n_{th} cm^{-2} s^{-1} at the irradiation port. The amount of tritium activity doped in the sample was about 37 kBq (1 μCi).

Thermal-deuterium doping was performed by the

Table 1. Impurity Content (ppm) of Vitreous Silica

Impurity	Sample (vitreous silica)[a)]			
	Silica A (T2230)	Silica B (Silica glass)	Silica C T1030	Silica D (Spectrosil)
B	nd	nd	nd	nd
Mg	11	13	8.7	10
Al	nd	27	nd	nd
Ti	2.3	0.9	2.7	nd
Cr	1.6	nd	1.7	nd
Mn	0.2	0.4	0.1	nd
Fe	3.5	4.6	3.2	2.1
Ni	nd	nd	nd	nd
Cu	nd	nd	nd	nd
Zn	4.7	9.7	6.1	2.4
Zr	nd	6.1	0.7	nd
Sn	nd	nd	nd	nd
Na	15	9.2	nd	nd
K	nd	7.4	nd	nd
Ca	9.4	6.7	3.7	5.9
Ba	0.2	nd	nd	nd
O-H	5	610	960	4000

a) nd: undetected.

following method. The sample was saturated with D_2 gas of 7.5×10^5 Pa for 280 h at 723 K or for 1—5 h at 923—1173 K.

After deuterium-implantation or thermal-D_2 doping, the infrared absorption spectra of the sample were measured at room temperature with an infrared Fourier transform spectrometer.[11] The ESR spectra of the sample were also measured at 77 K with an ESR spectrometer.[15] In the study of the thermal desorption of trapped deuterium, the samples were held for 6 h at 1173 K in vacuo.

After tritium implantation, the sample was heated at a constant rate (5 K min^{-1}) from room temperature to 1373 K and was then held for 180 s at the maximum temperature. The HTO and HT released during the annealing were measured.[16] Then the release rate of the HTO and HT components were calculated as a function of the heating temperature. The device for the isochronal annealing of the tritium-implanted sample has previously been described in detail.[17] The tritium component, which remained in the sample even after the thermal treatment, was measured by means of a liquid scintillation counter after the sample has been chemically etched by using a hydrofluoric acid solution.

In order to measure the initial distribution of tritium contained in a tritium-implanted specimen, the samples were gradually etched from the surface by 2% hydrofluoric acid to release the trapped tritium. The distribution of tritium in the sample was determined by measuring both the released tritium and the thickness of the sample. In this measurement, the amount of tritium was radioassayed by the use of a liquid scintillation counter.

Results

When hydrogen isotope was injected into silica, the spatial distribution and the range of the trapped hydrogen depend on both the injection energy and the injection method. Figure 2 shows the results of chemical-etching experiments on tritium-implanted silica. The experimentally measured range of recoil tritium with 2.7 MeV is about 39 μm, which coincides with the calculated value (39 μm) for recoil tritium in SiO_2.[18] The distribution of the recoil-injected tritium into the silica shows a linearly decreasing distribution with the distance from the surface.

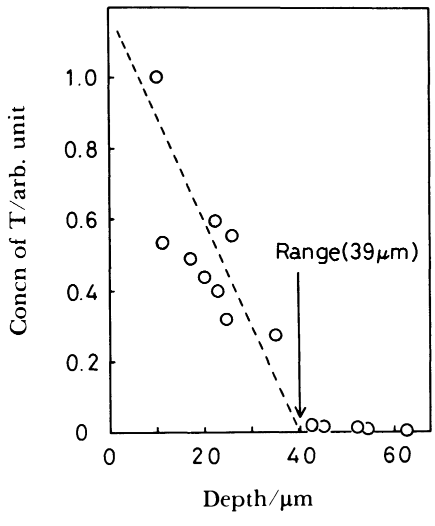

Fig. 2. Depth profile of tritium-implanted silica by ^6Li (n, α)T (2.7 MeV) reaction.

In the 80-keV D^+-ion implantation, we did not measure the distribution of the trapped deuterium. The trapped depth of the deuterium was calculated, using the TRIM code,[19] as about 0.5 μm from the surface. According to the study of 20-keV D^+ implantation in vitreous silica by Arnold et al.,[5] the deuterium is trapped between 0.2 and 0.5 μm from the surface.

In the thermal-D_2 doping, the distribution of the trapped deuterium can be expressed by a model of a tarnishing reaction,[20,21] in which the range (d) of trapped deuterium from the surface in the partially deuterated silica is estimated by the use of Eq. 1:

$$d = L\cdot C/(2C_f) \qquad (1)$$

where L, C, and C_f are the thickness of silica, the concentration of OD bonds of partially deuterated silica, and the OD concentration of completely deuterated silica respectively. The ranges of the trapped deuterium in this study were varied from 7 to 125 μm from the surface by controlling the amount of deuteration at 923 K, where a model of the tarnishing reaction can be applied.[21]

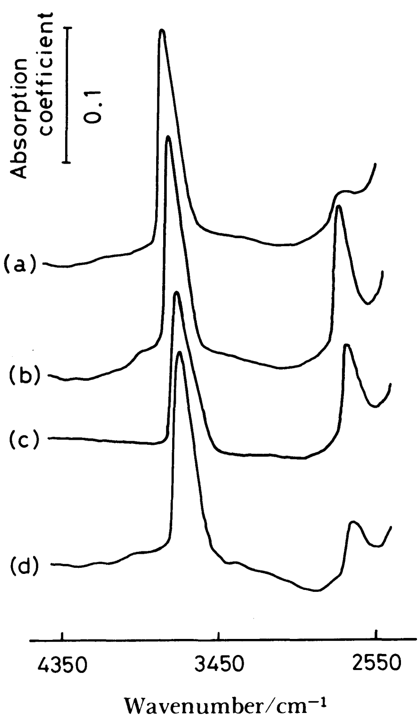

Fig. 3. Infrared absorption spectra of fused silica B (OH 610 ppm). (a) Before deuterium treatment, (b) after 80-keV D^+ ion implantation, (c) after thermal D_2 doping in which silica was stored in 7.5×10^5 Pa gas at 723 K, and (d) after annealing the sample of Fig. 3(b) at 1173 K for 6 h.

Figure 3(a) shows the infrared absorption (IR) spectrum of silica B before deuterium treatment. The absorption band at 3670 cm^{-1} in the figure is the O–H stretching band, which agrees with the previously reported values (3690,[8] 3640[9] cm^{-1}) of the O–H stretching band. When the silica is implanted with 80-keV D$^+$ ions or doped by D$_2$ gas at a high temperature, OD bonds are formed.[6] In a previous study,[6] however, the amount of deuteration was very small. In order to examine the effect of deuteration on the preexisting OH bonds, the OD bonds were produced in very high yields in this study. Figure 3(b) shows an IR spectrum of silica B after 80-keV D$^+$-ion implantation. The appearance at 2670 cm^{-1} of the absorption band, which is identified as the O–D stretching band in silica on the basis of previous studies,[6,8,9] indicates the formation of OD bonds in the sample by the ion-implantation, while the amounts of the preexisting OH bonds are not changed by the OD-bond formation. Figure 3(c) shows an IR spectrum of silica B after thermal-D$_2$ doping at 723 K for 280 h. The absorption band at 2670 cm^{-1} indicates the formation of OD bonds by such treatment in silica B, where the amounts of the OH bonds decrease. The amount of OD bonds in the silica was estimated from the intensity of the O–D stretching band at 2670 cm^{-1}, where the extinction coefficient (ε_{OD}) of the OD band was taken as $0.53\times\varepsilon_{OH}$.[22] Figure 3(d) shows the spectrum of the sample of Fig. 3(b) after annealing at 1173 K for 6 h. The amounts of OD bonds decrease drastically upon the thermal annealing.

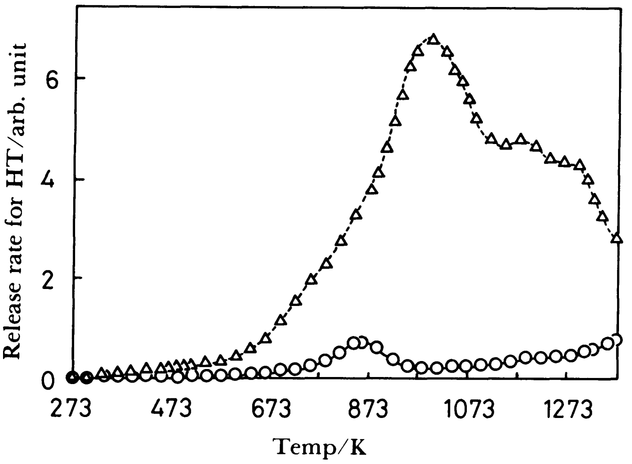

Fig. 4. Release spectra of HT in annealing at the same heating rate (5 K min^{-1}) from T-irradiated silica A (OH 5 ppm: △----△), and from T-irradiated silica D (OH 4000 ppm: ○—○).

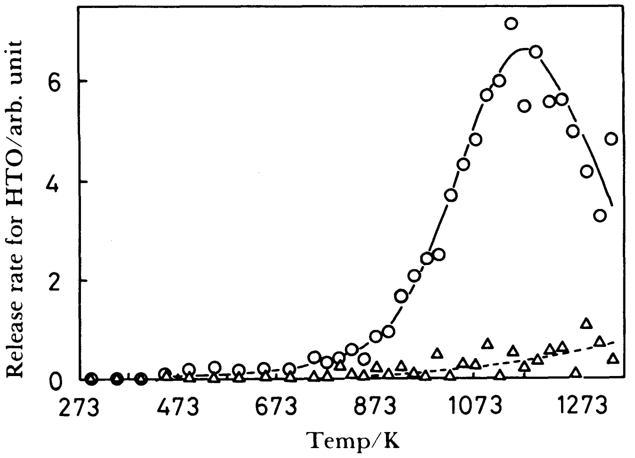

Fig. 5. Release spectra of HTO in annealing at the same heating rate (5 K min^{-1}) from T-irradiated silica A (OH 5 ppm: △----△), and from T-irradiated silica D (OH 4000 ppm: ○—○).

When the recoil tritium-implanted silica is heated at a high temperature, the trapped tritium is released from the silica as HT and HTO. Figure 4 shows the releasing behavior of HT from tritium-implanted silica A and D at a heating rate of 5 K min^{-1}. The evolution of HT begins around 700 K and reaches a peak at 970 K.

Figure 5 shows the releasing behavior of HTO from tritium-implanted silica A and D at the same heating rate as that in Fig. 4. HTO is released gradually around 900 K and reaches a peak around 1150 K. It can be seen from the results in Figs. 4 and 5 that tritium from silica A, which contains OH bonds at 5 ppm, is released almost entirely as HT, whereas tritium from silica D, which contains 4000-ppm OH bonds, is released as HTO.

Discussion

Trapping of Hydrogen Isotopes in 80-keV D$^+$-Ion Implantation, Thermal D$_2$ Doping, and Recoil T Implantation.

1. Trapping Efficiency and Preexisting Hydroxyl Bonds. When deuterium is injected into silica by 80-keV D$^+$ implantation or thermal D$_2$ doping deuterium is trapped by the formation of OD bonds (cf. Figs. 3(b) and 3(c)). The hydroxyl-bond formation by ion implantation and hydrogen gas-doping was reported previously.[5,6] The OD-bond formation may be the main trapping process in the D$^+$-ion implantation for the following reasons. First, since trapped D atoms were not observed in the D$^+$ ion-implanted silica by ESR spectroscopy, deuterium must be trapped in silica by the formation of a chemical bond. Second, the SiD-bond formation is another possible process of trapping. The IR absorption spectrum of SiD bonds is expected to appear around 1600 cm^{-1},[23] but the spectrum of the SiD bonds could not be observed in D$^+$-implanted silica (silica B), not even by the subtraction of the spectrum of silica before the implantation from that after the implantation. Third, the total amount of OD bonds in D^+-implanted silica is about 2.4×10^{21} bonds cm^{-3}, which is approximately the same as the saturation value (2.1×10^{21} D atoms cm^{-3})[5] of the total trapped deuterium in D^+-implanted silica. Fourth, when T-implanted silica is heated, HT is released at a high temperature such as 970 K. If HT molecules are trapped physically in the implanted silica, HT is released, probably at a much lower temperature. Thus, tritium is not trapped as hydrogen molecules after T-implantation. HT is produced by some chemical reaction upon thermal annealing.

The effect of preexisting OH bonds on the deuterium-trapping has been studied here by the use of silica containing the OH bonds at different concentrations. The relative yields of OD bonds produced by D^+ implantation and D_2 doping are summarized in Table 2, where the yields in silica A is taken as 1.0. A radiation-damage center produced by 80-keV D^+-implantation can be observed clearly by means of ESR spectroscopy.[6] The relative yields of the radiation-damage center, also shown in Table 2, do not depend on the OH-bond concentration. In the recoil tritium-implantation, the total amount of tritium trapped in silica can be measured by the use of a liquid scintillation counter after the irradiated sample has been etched. The relative yields of the total trapped tritium are also shown in Table 2. The total amounts of trapped tritium are almost independent of the concentration of preexisting OH bonds. The yields of the OD bonds produced by D^+-implantation also do not depend on the concentration of preexisting OH bonds. In the thermal D_2-gas doping, however, the yields of OD bonds increase with an increase in the preexisting OH bonds, though the OD-bond yields are not linearly proportional to the concentration of the OH bonds.

2. Mechanism of Trapping Reaction. The production of OD bonds is an important process for the trapping of deuterium in the D^+-ion implantation or the D_2-gas doping. The injected D^+ ions are neutralized in the silica and change into D atoms. Thus, the production mechanisms of the OD bonds in the D^+-implantation and the D_2-doping may be given as follows:

$$\equiv\text{Si-O-Si}\equiv + \text{D}(\text{D}_2) \longrightarrow \equiv\text{Si-OD} + \text{P} \tag{2}$$

$$\equiv\text{Si-OH} + \text{D}(\text{D}_2) \longrightarrow \equiv\text{Si-OD} + \text{Q} \tag{3}$$

where P and Q are some other products in these reactions. Reaction 2 represents the OD-bond formation by the insertion reaction accompanying the scission of the ≡Si–O–Si≡ bonds. Reaction 3 represents the substitutional reaction between H in preexisting hydroxyl bonds and $D(D_2)$, where the formation of OD bonds accompanies the decrease in the amount of the OH bonds.[24]

Figures 3(a) and 3(b) show that the amounts of preexisting OH bonds are not affected by the formation of OD bonds in the D^+-implantation, but Figs. 3(a) and 3(c) show that those of the OH bonds decrease in the D_2-gas doping. In order to analyze the results in Figs. 3(a), (b), and (c) quantitatively, the relation between the increase in the OD bonds and the decrease in the OH bonds is shown in Table 3. The values of $-\Delta OH/\Delta OD$ in silica represent the fraction of Reaction 3 to the total OD-bond formation in the deuterium treatment. The formation of OD bonds in the D^+-implantation is not accompanied by a drastic decrease in the preexisting OH bonds. Therefore, in the ion-implantation, hydroxyl bonds are formed mainly by the insertion reaction (cf. Reaction 2). D^+ ions, implanted into silica, are neutralized in silica and so become hot D atoms. The hot atoms may react with ≡Si–O–Si≡ bonds to form ≡Si–OD bonds. A part of the hot D atoms are thermalized and may react with ≡Si–O radicals, which are produced along the trajectory of hot D atoms by the radiolysis of the ≡Si–O–Si≡ bond, to form ≡Si–OD bonds. Both possibilities are represented by Reaction 2.

In the D_2-doping, however, about 60% of the OD-bond yields correspond to the decrement of the preexisting OH bonds. Thus, the OD bonds in the thermal doping are produced mainly by the substitu-

Table 2. Trapping of D (T) in Silica

Silica	Impurity		Method of injection[a]			
			80-keV D^+-implantation		Thermal D_2-doping	Recoil T-implantation
	OH ppm	Metal ppm	Yield of radiation damage	Yield of OD bond	Yield of OD bond	Total T yield
Silica A	5	23	1.0	1.0[b]	1.0	1.0[c]
Silica B	610	62	2.1	0.8	3.3	0.9
Silica C	960	23	1.5	0.9	2.5	1.1
Silica D	4000	15	1.2	1.1	5.6	1.4

a) Yields are expressed by relative values. The yield in silica A is taken as 1.0. b) The amount of OD bonds is 1.2×10^{-7} mol/sample. c) The amount of tritium is 1.1 μCi, that is, 3.8×10^{-11} mol/sample.

tional reaction (cf. Reaction 3). Since some metal ions may exist near OH bonds as impurities, D_2 gas may react with the OH bonds by some catalytic effect of the metal ions to form OD bonds.

Release of Trapped Hydrogen Isotopes.

1. Diffusion-Controlled Release of OD Bonds. As is shown clearly in Figs. 3(b) and (d), the amounts of OD bonds produced by the D^+-ion implantation decrease upon the thermal annealing at 1173 K for 6 h to become about 30% of the initial amounts of the OD bonds. The question of whether the process of the detrapping of deuterium from OD-bond sites is a reaction-controlled process or a diffusion-controlled one will be discussed here. In order to solve this problem, the distributions of OD bonds in silica were varied by partial D_2-doping. The silicas with OD bonds distributed at different depths from the surface were annealed at 1173 K for 6 h in vacuo. The efficiency of the decrease in OD bonds by the annealing are shown in Table 4, together with that for the OD bonds produced by D^+-ion implantation and that for the preexisting OH bonds.

If the dissociation reaction of the OD bond is a rate-determining process, the efficiency of the decrease in OD bonds should be independent of the depth of the OD-bond distribution. The results in Table 4, however, show clearly that the efficiency of the decrease depends on the depth of the OD-bond distribution. The efficiency increases with a decrease in the depth of the OD-bond distribution. The D, as OD bonds near the surface, can easily diffuse to the surface and decompose there to form some product, such as HDO. Therefore, it may be concluded that the process of the detrapping of deuterium from OD bond sites, followed by the formation of HDO, is not a reaction-controlled (bond-rupture) process, but a diffusion-controlled one.

Table 3. Ratio of Decrement of the OH Bond to the Increment of the OD Bond in 80 keV D^+-Implantation and Thermal D_2-Doping in Silica[a]

Silica OH/ppm	$-\Delta$OH/ΔOD	
	80 keV D^+-implantation	Thermal D_2-doping
610	0.1	0.58
960	0.2	0.75

a) $-\Delta$OH represents the decrement of the amount of preexisting OH bonds on the D^+-implantation or the D_2-doping. ΔOH represents the increment of the amount of OD bonds on the same deuterium treatment.

Table 4. Efficiency of Decrease of the OD Bond and Depth of OD-Bond Distribution from the Surface[a]

Method of injection	Hydroxyl group	Depth µm	Efficiency of decrease[d]
D^+-implantation	OD	0.5[b]	≈0.7
Thermal	OD	7[c]	0.61
D_2-doping	OD	13[c]	0.42
	OD	23[c]	0.27
	OD	125[c]	0.11
Inherent impurity	OH	125	0.13

a) Silica was heated at 1173 K for 6 h. Silica D was used here. b) Estimated theoretically.[19] c) Estimated by a model of a tarnishing reaction.[21] d) 1 − [(amount of OD(OH) after heating)/(amount of OD(OH) before heating)].

2. HTO and HT Formation from Tritiated Silica. In order to detect thermally-released products from hydrogen-implanted silica, tritium analysis is the most convenient method because of its high sensitivity. When silica implanted by recoil tritium is annealed from room temperature to 1373 K, HTO and HT are released from the silica (cf. Figs. 4 and 5). Since HTO is released at a higher temperature (1150 K) than that for HT (970 K), HTO and HT must be produced by different mechanisms.

The amount of OD bonds, which are one of the main trapped species in D^+-implanted silica, decreases upon thermal annealing. Table 5 compares the release of trapped tritium in the recoil T-implanted silica with the decrease in the OD bonds in the D^+-implanted silica. Both the release of the trapped tritium and the decrease in the OD bonds take place efficiently upon heating at 1200—1300 K. If it is assumed that HTO is produced by the thermal decomposition of OT bonds, the HTO formation corresponds to the decrease in the OT bonds in the thermal annealing. Since the decrease in OD bonds is a diffusion-controlled process, the decrease in OT

Table 5. Release of Trapped Tritium from T-Implanted Silica and Decrease of OD Bonds from D^+-Implanted Silica on Thermal Annealing

Sample	D^+-implantation[a]		Recoil T-implantation[b]	
	Efficiency of decrease in OD bonds[c]	Efficiency of release of trapped tritium[d]	Composition of released tritium/%	
			HTO	HT
Silica A	0.72	0.89	4	96
Silica B	0.79	0.45	23	77
Silica C	0.55	0.34	41	59
Silica D	0.66	0.53	71	29

a) D^+-implanted silica is heated at 1173 K for 6 h. b) HTO and HT are produced when T-implanted silica is heated from room temperature to 1373 K. c) The efficiency is 1 − [(amount of OD after heating)/(amount of OD before heating)]. d) The efficiency is (amount of released tritium)/(amount of total trapped tritium before heating).

bonds and the HTO formation may also be controlled by diffusion to the surface. Therefore, the diffusion coefficient of tritium trapped in silica can be estimated from the releasing behavior of HTO.

From the results of the measurement of the depth profile of tritium, implanted into silica by the recoil reaction of ^{6}Li(n,α)T(2.7 MeV) (cf. Fig. 2), the distribution of the recoil-injected tritium in silica is shown to be that of tritium, implanted from a tritium source of infinite size. In this depth profile, the solution of Fick's second law can be given by the following equation:[25,26]

$$F(t) = 4[D \cdot t/(\pi \cdot R^2)]^{1/2} \tag{4}$$

where $F(t)$ is the fractional release of HTO at an annealing time of t at a constant temperature, while R represents the recoil range of tritium (39 μm) in silica. The diffusion coefficients (D_T(HTO)) can be obtained from the slope of the plot of $t^{1/2}$ vs. $F(t)$ in the isothermal annealing of tritium-implanted silica; they are shown in Fig. 6 in relation to $10^3/T$. They are expressed by the following equation:

$$D_T(\text{HTO}) = 2.3 \times 10^{-4} \exp[-1.7 \times 10^2 (\text{kJ mol}^{-1})/RT]\ \text{cm}^2\,\text{s}^{-1} \tag{5}$$

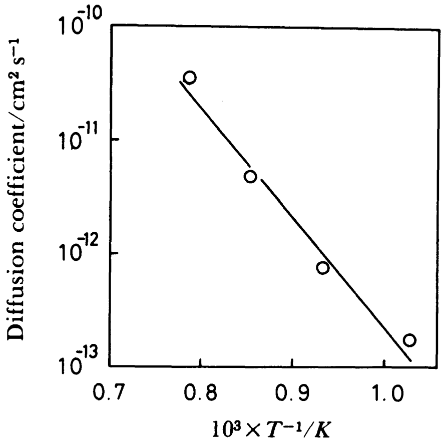

Fig. 6. Arrhenius plot for tritium diffusion in vitreous silica. (O) tritium released as HTO in isothermal annealing from T-irradiated silica C (OH 960 ppm).

Table 6. Activation Energy for the Diffusion of Hydrogen Isotopes in Vitreous Silica

Species	$\frac{E_d}{\text{kJ mol}^{-1}}$	Temperature range/K	Reference
H	15	77— 110	7
D	15	77— 110	7
H_2	37.8	573—1273	28
D_2	39.2	573—1273	28
D_2	37.0	497—1066	4
H_2O	76.7	873—1473	29
"HTO"	171	973—1273	This work

Table 6 compares an activation energy for the diffusion in this work with the reported values of hydrogen diffusion in silica. The activation energy for diffusion in Eq. 5 is much larger than the energies for the diffusions of H(D) atoms, H_2, D_2, and H_2O molecules. Thus, the diffusing species for the HTO formation in silica can not be these atoms and molecules, but must be some other species. The diffusing species has not yet been conclusively identified. As has discussed in the previous section, the decrease in OD bonds upon heating is controlled by their diffusion to the surface, where the OD bonds do not rupture during diffusion, but decompose only at the surface. Thus, one plausible mechanism is that tritium in an OT bond migrates from one oxygen site to a neighboring oxygen site as a consequence of the forllowing chemical reaction, and then repeats this reaction to the surface of silica. Then, the OT bond decomposes into HTO at the surface, and tritium is released from silica:

$$\equiv\text{Si-OT} + \equiv\text{Si-O-Si}\equiv \longrightarrow \equiv\text{Si-O-Si}\equiv + \text{TO-Si}\equiv \tag{6}$$

$$\equiv\text{Si-OT} \xrightarrow{\text{at surface}} \text{HTO} + \text{S} \tag{7}$$

where S represents some products at the surface. Tritium migration by the repetition of a chemical reaction like Reaction 6 was also suggested for the tritium migration in MgO.[27]

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