Silicon Self-Diffusion in Quartz

O. Jaoul, F. Béjina, and F. Élie
Laboratoire de Géophysique et Géodynamique Interne, Centre National de la Recherche Scientifique URA 1369, Université Paris-Sud, Bâtiment 510, 91405 Orsay Cedex, France

F. Abel
Groupe de Physique des Solides, Centre National de la Recherche Scientifique URA 17, Université Paris VII, Tour 23, 2 place Jussieu, 75251 Paris Cedex 05, France
(Received 1 August 1994)

^{30}Si diffusion was measured in quartz along **c** axis in the β-phase field, at $T = 1400-1600\,^{\circ}$C by Rutherford backscattering spectrometry and the ^{30}Si$(p,\gamma)^{31}$P resonant nuclear reaction. The diffusion coefficient $D(\mathrm{cm^2\,s^{-1}}) = 10^{(6.1\pm2.7)}\exp[(-7.6 \pm 1\ \mathrm{eV})/kT]$, comparable to D of silicon in vitreous SiO_2. We suggest Frenkel pairs as majority defects with diffusion occurring by interstitial mechanism.

PACS numbers: 66.30.Hs, 25.40.Ny, 61.72.Ji, 61.80.Mk

We measured silicon diffusion in dry, pure, synthetic quartz, between 1400 and 1600 °C. Our result can serve as a reference for further diffusion studies in doped quartz and help one understand two important questions: (1) Is $D_{Si} \ll D_{Ox}$ in dry quartz as it is over a wide domain of T inother silicates, such as olivines $(Fe,Mg)_2SiO_4$ [1]? For these systems high temperature creep is governed by multicomponent diffusion [2], and thus principally by the slowest diffusing species. (2) Does diffusion transport in vitreous v-SiO_2 occur through point defects? Because of the high similariy between the structure of quartz and v-SiO_2, the comparison between the activation energies of D_{Si} in quartz and in v-SiO_2 will help in the debate.

Information concerning D_{Si} is available for silica [3]. It indicates $D_{Si} \ll D_{Ox}$, even if one takes the lowest values published for D_{Ox} [4]. Brébec *et al.* [3] find a relatively high activation energy $Q = 6$ eV for D_{Si}, in the range 1100–1400 °C. This value is very close to Q for viscous flow, so they suggest that viscous flow is controlled by silicon diffusion for $T > T_g$. This is in agreement with Schaeffer [5] who already mentioned a mismatch between Q for viscous flow of 5–7 eV, and Q for D_{Ox}, and suggested that a species other than oxygen should be rate controlling viscous flow. Other data for D_{Ox} in v-SiO_2 can be found in [5]. They also include data on the molecular permeation of O_2 in fused silica, as opposed to other data on "network oxygen diffusion" [4].

The quartz single crystals (premium Q) were bought from the SICN company (Annecy, France). They are very pure, containing less than 3 ppm impurities, and are believed to contain less than 0.1 ppm H/Si (after [6]), with a quality factor $Q = 2.7 \times 10^6$. Cylinders of 2.2 mm diameter were cored from Z zones (zones with the minimum of impurities and with a dislocation density $\rho \leq 10^7\ \mathrm{m^{-2}}$ [7,8]) with their axis parallel to **c**. The faces were polished by cerium oxide, and slightly etched with diluted HF acid in order to remove the coldworked layer. 96.5% isotopic enriched $^{30}SiO_2$ was deposited on the surface by RF sputtering, and this formed a layer of thickness $h = 400-800$ Å.

Some of the experiments were performed under pressure, and others were done at room pressure, both at temperatures between 1600 and 1400 °C, and for durations ranging from 15 min to several days. All experiments were done in the β phase, even those at room pressure. In the experiments at room pressure, we took advantage of the very high grade of our quartz specimens to avoid a transition to the high temperature phases. It probably contains impurities and dislocations in such small amounts that there are not enough seeds for phase transformations. Hence, these runs were performed in the β field, in metastable conditions [9]. In the high pressure experiments, at 2 GPa in a solid confining medium (piston-cylinder), samples were annealed by pairs with the isotopic reservoir in between, and were separated by a thin disk of graphite in order to avoid sticking. They were embedded in a graphite jacket. This assemblage and the very slow decompression procedure prevented samples from any fracturing perpendicular to the diffusion interface. Recovered samples kept their optical transparency. With this symmetrical experimental array, the diffusion sandwich provides two specimens which should give identical diffusion profiles. We use these to estimate our experimental error. From both profiles, one deduces diffusion characteristic lengths $2\sqrt{Dt}$ (D, diffusion coefficient; t, annealing duration) which could differ at maximum by a factor of 3 at 1400 °C, and by a factor 1.2 at 1600 °C. The above boundary conditions correspond to the solution

$$c(x,t) = \frac{c_0 - c_\infty}{2}\left[\mathrm{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right)\right] + c_\infty,$$

where c_∞ is the natural abundance of ^{30}Si, x the distance from the surface of the isotopic layer of concentration c_0, and h its thickness.

Two ion beam analysis techniques, appropriate to the measurements of short diffusion profiles (characteristic

 0031-9007/95/74(11)/2038(4)$06.00

length $2\sqrt{Dt} \simeq 200-1000$ Å) were used, carefully avoiding channeling effects [10]. Rutherford backscattering spectrometry (RBS) of 2 MeV α-particles was first used to make a rapid estimate of the quality of the diffusion profiles, and their approximate length. The advantage of the RBS technique is its rapidity and ease. But, in our case, the disadvantage of RBS is that ^{28}Si and ^{30}Si are not perfectly separated, because of their very close masses. The diffusion profile of the ^{30}Si must be extracted from the experimental complex spectrum, by numerical methods: we used the program RUMP [11] to fit the RBS spectra, using D as a parameter. The method has a resolution in depth of about 300 Å in our case, and is therefore well adapted for diffusion profiles ranging from $2\sqrt{Dt} \sim 0.5h$ to $5h$. The second method is the use of the nuclear reaction narrow resonance by the energy scanning technique [12] around the 68 eV FWHM resonance of the $^{30}\mathrm{Si}(p,\gamma)^{31}\mathrm{P}$ reaction at 620.4 keV by counting the 7.9 MeV emitted γ. The proton energy was automatically increased by steps of 400 eV from below 620 keV, this corresponding to depth intervals of 66 Å. Figure 1 shows typical excitation curves which are images of concentration profiles. It illustrates a diffusion profile of ^{30}Si in quartz with $2\sqrt{Dt} \sim 1150$ Å. The comparison of the integrals of the spectra before and after annealing shows that there was no loss of ^{30}Si during the experiments, probably because we made $^{30}SiO_2$ sandwiches. The depth resolution of this method is limited in a weak proportion by the width of the resonance, and by the stability of the energy of the beam (at best 100 eV), this corresponding theoretically to a depth resolution of about 16 Å at the surface. The resolution is spoiled for greater depth by energy straggling of the beam. Actually, this surface value is never reached and stands around 50 Å, because of straggling through the ~50 Å thick carbon layer deposited to avoid electrical charging under the beam. The excitation curve is the result of convolution between the concentration profile, energy fluctuation of the beam, and straggling increasing with depth. The program SPACES [13] allows the simulation of excitation curves and is particularly adapted to very narrow nuclear resonances. Unfortunately it does not contain the concentration profile adapted to our problem. We have therefore developed our own convolution program including the needed solution to Fick's equation $c(x,t)$. And we have checked that this program and SPACES are fully compatible in the case of unannealed layers.

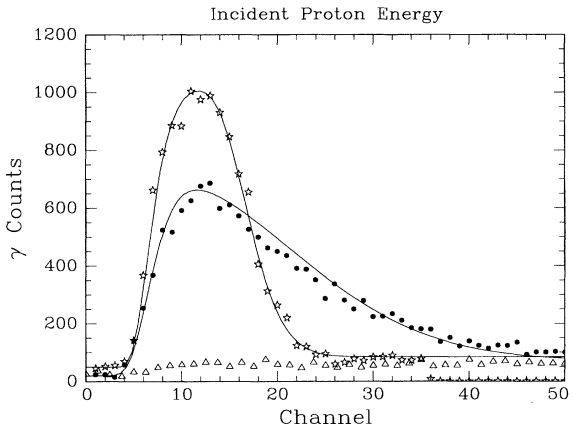

FIG. 1. Excitation curves using the $^{30}\mathrm{Si}(p,\gamma)^{31}\mathrm{P}$ narrow resonance at 620.4 keV. Stars: 720 Å thick $^{30}SiO_2$ layer on top of a quartz specimen and its fit (full line). Triangles represent the natural abundance in quartz without the layer on top. Dots represent the diffusion profile after anneal at 1400 °C for 30 hr 39 s. Energy 620.4 keV is between channels 6 and 7 (this corresponds to the surface of the layer, or of the uncovered quartz). Channel width is 400 eV (= 66 Å in depth). Note the conservation of the integrals. From these spectra, one deduces $D = 3 \times 10^{-16}$ cm^2 s^{-1}, corresponding to the full line fitting the excitation curve.

Table I gives the results. The error bars come from the sensitivity to the simulation of the fit of the data, and the comparison between the two profiles obtained on both sides of the diffusion sandwiches. Figure 2 is the corresponding Arrhenius plot, with an activation energy of 7.6 ± 1 eV, and a preexponential factor D_0 (cm^2 s^{-1}) such that $\log_{10} D_0 = 6.1 \pm 2.7$. The silicon diffusion coefficient is much lower in this temperature range than the lowest data found in the literature for oxygen diffusion [4]. The activation energy of 7.6 eV will be compared in the discussion to that of the Si-O bond (4.5 eV as deduced from the formation of the β quartz from its elements [14], an updated value compared to 3.8 eV given by Pauling [15]) and compares well with that of viscous flow, 7.4 eV in vitreous silica v-SiO_2 [16] (6 eV in [17]) below 1400 °C but which is only 5.2 eV above 1200 °C [17,18], and is somewhat superior to that silicon diffusion in v-SiO_2 (6 eV) in the range 1100–1400 °C [3]. But a lone piece of information, an activation energy, is not sufficient to make a choice for a diffusional mechanism. However, it may add constraints and help to rule out some mechanisms. A first remark concerns the similarity of activation energies in crystalline and vitreous SiO_2. This suggests (but does not demonstrate) that point defects in v-SiO_2 could be preferred to the free volume model. A second remark deals with the absence of any observable effect of pressure on D between 0 and 2 GPa: this puts an upper limit on the value of the activation volume $V = -RT\partial \ln D/\partial P \leq 1.7$ cm^3 mol^{-1} around 1500 °C with a maximum uncertainty of 0.1 $\log_{10}$ unit on D.

We use Fig. 3 to support the following discussion. The first case which can be precluded is diffusion by simple thermally activated vacancies. A vacancy costs two Si-O broken bonds (2 × 4.5 eV) minus one or two O-O reconstructions (2 × 1.4 eV) for its formation (see discussion and review in [19]). To that must be added a migration energy roughly consisting of breaking one more Si-O bond, and pushing Si across an oxygen triangle: the latter strong distortion of the Si-O-Si angle could cost an energy of the order of 1 eV [20]. This first case gives a diffusion energy much too high compared to data (7.6 eV).

TABLE I. ^{30}Si diffusion data in β-quartz along **c**. t is the annealing duration, h the $^{30}SiO_2$ layer thickness, $x_c = 2(Dt)^{0.5}$ the characteristic diffusion length, and D (cm^2/s) the diffusion coefficient with its estimated error bars $\Delta \log D$ as extracted from the spectra. The uncertainty on D contains only that of the fit using various sets of C_0h values, and different spectra taken from different places of a same sample.

Sample	T (°C)	t (s)	h (Å)	$\log D$	$\Delta \log D$	x_c (Å)
QHP5a[a]	1600	3600	890	−13.65	0.03	1800
QHP5b[a]	1600	3600	890	−13.60	0.07	1905
QHP6b[a]	1500	14 400	890	−14.74	0.30	1025
QHP7a[a]	1500	7200	890	−14.38	0.08	1100
QHP7b[a]	1500	7200	890	−14.26	0.11	1260
Q01	1600	900	540	−13.75		800
Q02	1600	900	620	−13.60	0.17	960
Q05	1400	247 080	615	−16.77		410
Q06	1400	247 080	580	−16.16	0.31	825
Q07	1400	110 340	720	−15.52	0.06	1150
Q08	1400	110 340	380	−15.95	0.18	705

[a]High-pressure runs (20 kbar).

One could invoke a second mechanism which resembles the precedent for migration, but for which vacancy concentration does not depend on temperature below a given T. In v-SiO_2, this temperature, usually called T_F (for which the amorphous structure is that of the frozen liquid with its frozen defects), can be very high and depends on the quench temperature as demonstrated by v-SiO_2 viscosity studies [16]. Hydrothermally grown quartz has "growth vacancies" which could be relatively abundant compared to thermal vacancies, because the latter have a very high activation energy; we can assume that the growth vacancies dominate up to a very high temperature because of the close similarity of the microscopic structures of v-SiO_2 and quartz. In that frame, only migration contributes to the activation energy of diffusion. For this mechanism and the previous one, the motion, for instance, along **c**, of an initial vacancy in 1234 (Fig. 3) occurs by the movement of Si leaving tetrahedron 4567, becoming an interstitial inside the ten-oxygen cage which is surrounded by two vacancies. In quartz, this cage is placed between two main helicoidal axes 6_2 and could relax dynamically owing to the presence of two disturbing neighboring vacancies which provide dangling bonds at oxygen sites. The motion of Si could occur by reconstruction of SiO_4 tetrahedra 2345, then 3456, and finally 4567, "rolling" along the walls of the cage. At each intermediate step, Si passes through an oxygen triangle, with only one Si-O bond broken and rebonding at the opposite oxygen. Meantime O-O reconstruction dynamically evolves in one of the two Si vacancies in order to minimize the overall energy. This mechanism could similarly work in v-SiO_2 but in less rigid

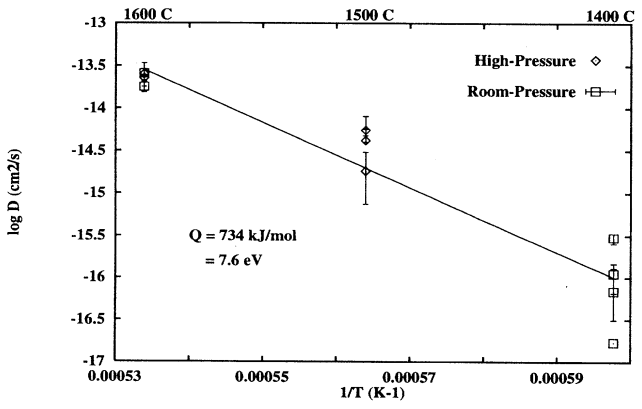

FIG. 2. Plot of $\log D$ vs $1/T(\mathrm{K}) - 1$ for ^{30}Si diffusion in quartz. Cross symbols are for runs at room pressure, diamond symbols for runs at 2 GPa. All these results fit the same line, which gives an activation energy of 7.6 eV.

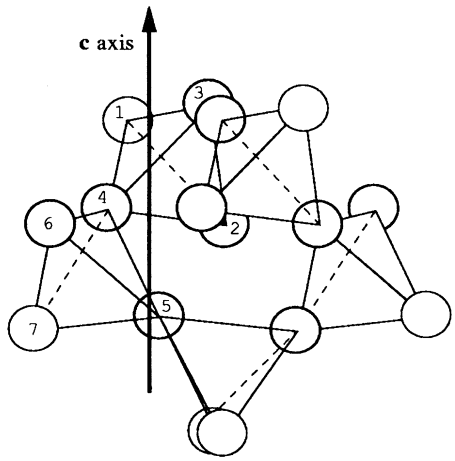

FIG. 3. A side view of five SiO_4 tetrahedra of right β-quartz. The silicon atoms are not represented. [0 0 1] = **c** is vertical; the normal to the sheet is approximately [14 3 0]. Circles indicate oxygen atoms: ten of them form a cage surrounded by four tetrahedra with one apex pointing outward from the cage. Labels 1 to 7 on some oxygens are used in text.

and more distorted cages surrounded by Si-O rings of order 3 to 7 [20], and by definition contains many dangling bonds by comparison with the perfect crystalline organization. The energetic cost is one Si-O bond (4.5 eV) to which an energy E_D must be added for the intermediate steps, $E_D \simeq 7.6 - 4.5 = 3.1$ eV, in β-quartz and is less ($E_D \simeq 6 - 4.5 = 1.5$ eV) in v-SiO_2, 7.6 and 6 eV being, respectively, the experimental activation energies of silicon diffusion in β-quartz (present work) and in v-SiO_2 [3]. Motion along **a** direction can be described by a similar process with four elementary steps instead of three. If the above mechanism has its own interest for comparing v-SiO_2 to its crystalline polymorph, it is not the most convincing solution, because one needs to have frozen-in Si vacancies in quartz. In addition, the number of congealed vacancies should decrease with the annealing duration, so that the diffusion coefficient decreases and the viscosity increases. Is that true for β-quartz? Anyway, this was observed for the metallic glass $Fe_4Ni_4B_2$ [21].

The third possibility which has our preference is to consider Si Frenkel defects. This possibility is already well documented for oxygen in v-SiO_2 (see review in [19]). These associated defects need to break four Si-O bonds (4×4.5 eV) minus two O-O reconstructions (2×1.4 eV), i.e., cost $E_F = 15.2$ eV. The Si interstitial Si_I is in the ten-oxygen cage neighboring the vacancy V_{Si} after the reaction $Si_{Si} \rightleftharpoons V_{Si} + Si_I$ (Kröger-Vink notation). These defects have equal concentrations; the mass action law gives $[Si_I] = [V_{Si}] = \exp(-Q/kT)$, with $Q = E_F/2 = 7.6$ eV as formation energy. In reality this formation energy can be lowered by rearrangement of the V_{Si}-Si_I defect: supposing V_{Si} in site 1234, the idea consists in overbonding an oxygen (site 5 in Fig. 3) as proposed by Mott [22] with the Si_I in site 2345. This defect resembles the "valence alternation pairs" (VAP) formed by two defects: $O^+(3Si)$, a threefold bonded oxygen at site 5, and the dangling bond O^- at site 1. The possibility of this defect is defended in [23] and discussed in [24]. Once in the cage, the Si_I could move more or less freely with almost zero as migration energy. On the contrary, vacancies are much less mobile because their motion would necessitate to break the extra Si-O bond. We therefore propose an interstitial mechanism for Si diffusion in SiO_2 with an activation energy corresponding to half the Frenkel pair formation energy, 7.6 eV in β-quartz and 6 eV in v-SiO_2, the difference probably being linked to different sizes of oxygen cages in quartz and in v-SiO_2. This Frenkel-controlled Si diffusion should be insensitive to oxygen partial pressure.

We acknowledge E. d'Artemare for help during the use of the Van de Graaff facilities for Ion Beam Analysis measurements and C. Noguera and Y. Limoge for fruitful discussions. We thank I. Vickridge for his help in the use of the program SPACES. This work was supported by the GDR 86 (CNRS) directed by G. Amsel and the INSU-CNRS which provided special funding to buy ^{30}Si isotope and is greatly acknowledged.

[1] O. Gérard and O. Jaoul, J. Geophys. Res. **94**, 4119 (1989).
[2] O. Jaoul, J. Geophys. Res. **95**, 17 631 (1990).
[3] G. Brébec, R. Seguin, C. Sella, J. Bevenot, and J. C. Martin, Acta Metall. **28**, 327 (1980).
[4] J. C. Mikkelsen, Jr., Appl. Phys. Lett. **45**, 1187 (1984).
[5] H. A. Schaeffer, J. Non-Cryst. Solids **38&39**, 545 (1980).
[6] M. S. Paterson, in *Rheology of Solids and of the Earth,* edited by S. Karato and M. Toriumi (Oxford University Press, Oxford, 1989), p. 107.
[7] R. L. Barns, P. E. Freeland, E. D. Kolb, R. A. Laudise, and J. R. Patel, J. Cryst. Growth **43**, 676 (1978).
[8] A. F. Armington and J. J. Larkin, J. Cryst. Growth **71**, 799 (1985).
[9] M. A. Moseman and K. S. Pitzer, J. Am. Chem. Soc. **63**, 2348 (1941).
[10] A. L'Hoir, D. Schmaus, J. Cawley, and O. Jaoul, Nucl. Instrum. Methods Phys. Res., Sect. B **191**, 357 (1981).
[11] L. R. Doolittle, Nucl. Instrum. Methods Phys. Res., Sect. B **9** 344 (1985); **15**, 227 (1986).
[12] B. Maurel, G. Amsel, and J. P. Nadai, Nucl. Instrum. Methods Phys. Res. **197**, 1 (1982); O. Jaoul, V. Sautter, and F. Abel, in *Diffusion, Atomic Ordering, and Mass Transport: Selected Problems in Geochemistry,* edited by J. Ganguly, Springer Series in Advances in Physical Geochemistry Vol. 8 (Springer-Verlag, Berlin, 1991), p. 198.
[13] I. Vickridge and G. Amsel, Nucl. Instrum. Methods. Phys. Res., Sec. B, **45** 6 (1990); G. Amsel and I. Vickridge, Nucl. Instrum. Methods Phys. Res., Sect. B **45**, 12 (1990).
[14] *Handbook of Physics and Chemistry* (CRC Press, Florida, 1980), 60th ed., pp. D-49, D-75, and F-224.
[15] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Oxford, 1960), 3rd ed.
[16] G. Hetherington, K. H. Jack, and J. C. Kennedy, Phys. Chem. Glasses **5**, 130 (1964).
[17] P. Donnadieu, O. Jaoul, and M. Kléman, Philos. Mag. A **52**, 5 (1985).
[18] G. Urbain, Y. Bottinga, and P. Richet, Geochim. Cosmochim. Acta **46**, 1061 (1982).
[19] Y. Limoge, in *Diffusion in Materials,* edited by A. L. Laskar *et al.,* NATO ASI Ser. E: Applied Sciences, Vol. 179 (Kluwer Academic Publishers, Dordrecht, 1990), p. 601.
[20] F. L. Galeener, Solid State Commun. **44**, 1037 (1982).
[21] A. Van den Beukel, E. Huizer, A. L. Mulder, and S. Van der Zwaag, Acta Metall. **34**, 483 (1986); J. Horvath, K. Pfahler, W. Ulfert, W. Frank, and H. Mehrer, J. Phys. C **8**, 46, 645 (1985).
[22] N. F. Mott, Adv. Phys. **26**, 4, 363 (1977).
[23] G. Lucovsky, J. Non-Cryst. Solids **35&36**, 825 (1980).
[24] J. Robertson, Phys. Chem. Glasses **23**, 1 (1982); Y. Serruys, Y. Limoge, and G. Brébec, in *Diffusion Processes in Nuclear Materials,* edited by R. P. Agarwala (Elsevier Science Publishers B.V., Amsterdam, 1992), p. 353.