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Physical property changes of crystalline and non-crystalline SiO_2 due to neutron irradiation and recovery by subsequent annealing

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Abstract

Physical property changes of quartz and vitreous silica due to neutron irradiation and recovery by subsequent annealing were examined. Specimens were fast-neutron-irradiated up to a fluence of 3.0×10^{23} n/m^2 at 140 °C, and 6.9×10^{23} n/m^2 at 300 °C. Vitreous silica shrunk ~0.8% in length after both irradiations. On annealing, the length started to increase above 200 and 500 °C for the lower and higher fluence specimens, respectively, and gradually increased with increasing annealing temperature. Quartz expanded in an anisotropic manner, with larger expansion along the *a*-axis as compared to the *c*-axis, due to the irradiation. Length and lattice parameter of quartz started to reduce for annealing over 300–500 °C, and were almost fully recovered at 800 °C in the lower fluence case, and 1000 °C in the higher fluence case. Thermal diffusivity reduced ~10% in vitreous silica and 60–70% in quartz by the irradiation. Recovery of thermal diffusivity of vitreous silica and quartz by annealing resembled the corresponding length change.

1. Introduction

Silicon dioxide (SiO_2) materials are expected to be used in fusion reactors as functional materials such as optical fibers for plasma diagnostics in non-crystalline form, and can be applied as insulators, windows in crystalline form. Many aspects on optical property change of fibers were recently mentioned, but less attention was paid for physical property change due to neutron irradiation.

Based on the early but extensive studies mainly by Primak et al. [1–3], by Wittels [4] and reviewed by Crawford and Wittels [5], Lell et al. [6] and Bruckner [7], it is known that both crystalline (quartz) and non-crystalline (vitreous/fused silica) SiO_2 suffer large change in volume, contraction (maximum ~3% increase in density) in the case of vitreous silica and swelling (maximum ~14% decrease in density) in the case of quartz, and both saturated densities are the same ~2.26 g/cm^3. In the case of quartz, atomic displacement due to neutron irradiation induces crystalline imperfection in the lattice rendering it into a partially disordered state. For the case of vitreous silica, the original

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disordered state (glassy structure) rearranged upon irradiation to a partial crystalline form, which should be more dense compared with that of amorphous, glassy structure [1–3]. Whereas the irradiation response of these materials are very complex, after the work carried out in the 1950′–1960′, there are few experimental data on dimensional and thermal property changes [8–11]. Furthermore, precise thermal property measurement for crystalline and non-crystalline SiO_2 following post-irradiation annealed material was very limited [12,13].

In this study, dimensional, thermal and XRD studies of quartz and vitreous silica due to neutron irradiation and recovery by subsequent annealing were conducted to clarify the irradiation response, particularly using the same materials and the same irradiation conditions to compare the length/lattice parameter and thermal diffusivity changes.

2. Experimental procedures

A set of rectangular specimens ($2 \times 4 \times 25$ mm, *X*-cut and *c* was a long edge; and *Z*-cut and $[1\,1\,\bar{2}\,0]$ was a long edge in the case of crystal) and discs (10 mm in diameter and 2 mm in thickness, *Z*-cut in the case of crystal) were neutron-irradiated in the Japan Materials Testing Reactor up to a fluence of 3.0×10^{23} n/m^2 ($E_n > 0.1$ MeV) at 140 °C, and 6.9×10^{23} n/m^2 at 300 °C. Specimens were high purity single crystal α-quartz (SEIKO Denshi. Ltd.) and vitreous silica (synthetic silica glass, T4040, OH 800 ppm, Toshiba Ceramics Co.). After irradiation, these specimens were isochronally annealed for 1 h in vacuum from 100 to 1000 °C. Macroscopic length, thermal diffusivity, lattice parameter of the specimens following neutron irradiation and under subsequent annealing were measured at room temperature.

Length of a rectangular specimen was measured using a point-type micrometer and a specimen fixture (precision ~1 μm). Thermal diffusivity was measured using laser-flash-type equipment. The thermal diffusivity measurement was repeated three times to six times at each measurement. The standard deviations were obtained as in the range of 0.0005–0.0013, in average 0.0008 cm^2/s. Lattice parameter of quartz was obtained by powder X-ray diffractometry using Cu-Kα radiation at 24 ± 1 °C and an internal standard. Reflection angles from (104), (302), (220), (311), (312), (214) and (223) planes were used for the lattice parameter determination.

3. Results and discussion

3.1. Non-crystalline SiO_2

Average length change of the irradiated vitreous silica was −0.82(0.01)% and −0.73(0.01)% for the fluence of 3.0×10^{23} n/m^2 (140 °C) and 6.9×10^{23} n/m^2 (300 °C), respectively. The standard deviation was shown in the parentheses. The change, i.e., contraction, was very uniform for each of ten specimens. Thermal diffusivity of the vitreous silica before the irradiation was 8.6×10^{-3} cm^2/s, and the values after irradiation were 7.7×10^{-3} and 7.9×10^{-3} cm^2/s for the lower and higher fluence specimens, respectively. About 8–10% reduction in thermal diffusivity was observed.

Fig. 1 indicates recovery of the length of the vitreous silica specimens due to annealing up to 1000 °C. It is obvious that length of the lower fluence specimen increased (recovered) gradually from ~300 °C and more steeply above ~500 °C. After the annealing at 1000 °C, a slight amount of irradiation-induced swelling remained. In the case of the higher fluence specimen, the length was almost unchanged up to 500 °C. Above 500 °C, it increased quickly, and recovered nearly completely after annealing at 1000 °C.

Fig. 2 shows the change in thermal diffusivity of the vitreous silica specimen due to annealing. Whereas some scatter in data during relatively low temperatures was observed, the thermal diffusivity increased with increasing annealing temperature more than 300 °C in both specimens, and recovered 80–90% after the annealing at 1000 °C.

It was reported [2,6] that density of vitreous silica increased rapidly up to $\sim 5 \times 10^{23}$ n/m^2, and showed

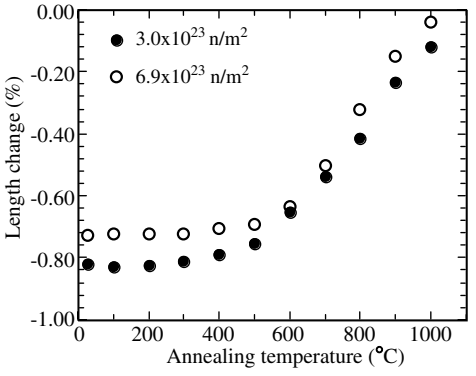

Fig. 1. Change in length of the irradiated non-crystalline SiO_2 (vitreous silica) due to isochronal annealing for 1 h.

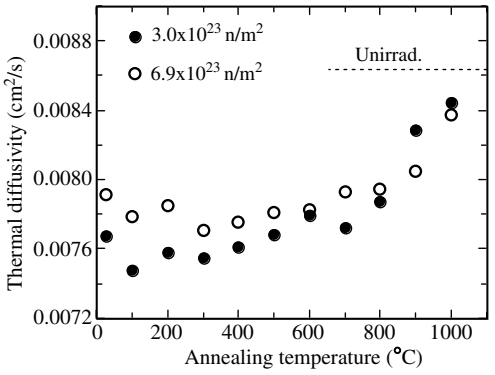

Fig. 2. Change in thermal diffusivity of the neutron-irradiated non-crystalline SiO_2 (vitreous silica) by isochronal annealing for 1 h.

a maximum (2.5–3.0%), and further increase in fluence resulted in slightly lower density. Above 1.1×10^{24} n/m^2 density change nearly saturate to ~2.26 g/cm^3. Increase in density obtained from length change was +2.44% and +2.17% for the specimens of 3.0×10^{23} n/m^2 and 6.9×10^{23} n/m^2, respectively. From the data by Primak [2], considering only the irradiation fluence the latter should be denser. However the latter specimen was irradiated ~160 °C higher than the former, therefore the difference can be attributed to the difference in irradiation temperature [9,14]. The present result for the specimen irradiated to 3.0×10^{23} n/m^2 was the same with the reported result [2], but the recovery of the higher fluence specimen was different, i.e., unchanged up to ~500 °C. The reason for the difference can be attributed to the higher irradiation temperature.

It was reported that very low temperature (<10 K) thermal conductivity of vitreous silica was improved by neutron irradiation [6,10,15], whereas heat capacity decreased [16]. Thus, the increase in thermal conductivity should be attributed to the increase in phonon mean free path (~ thermal diffusivity) [6,13,15]. The present results indicate a slight decrease in thermal diffusivity, which is inconsistent with the previous conclusion. From Fig. 2, the thermal conductivity started to increase above 300 °C, and was mostly recovered at 1000 °C. Taking into account the relatively large possibility of data scatter compared with the changes, the decrease and trend of recovery of the thermal diffusivity of vitreous silica is still obvious. The recovery tendency of the thermal conductivities was mostly comparable to those of the length changes. Therefore, it is reasonable to assume that the origin of the irradiation effect on length and thermal diffusivity on vitreous silica should be the same. The difference in thermal diffusivity change of the present result (decrease by irradiation) and previous reports (increase by the irradiation) [10,13,15] is not clearly explained but may be attributed to the difference in temperature range (room temperature and less than 10 K, respectively) thus the contribution of kind of phonons for thermal diffusivity is different [15], or the difference in materials itself, i.e., fabrication process and impurity.

Neutron irradiation-induced defects in vitreous silica were discussed extensively [5–7], and it is believed that the irradiation-induced thermal spike is responsible for most of the effects. Some parts of the thermal spike regions are rapidly quenched, leaving it in a slightly denser state than the original glass state. Some experimental results indicate transformation to a more ordered form [17,18]. The nucleation of α-quartz structure in heavily (~1.5×10^{24} n/m^2 at <60 °C) irradiated vitreous silica was suggested. Other results indicated formation of a more disordered form [10,19,20]. Our powder XRD spectra supported the latter results, which indicated a broader main peak centered at ~22 deg./2θ-CuKα after the irradiation. The higher angle portion of the peak increased compared with that of the unirradiated specimen, indicating a wider distribution of interatomic distance for shorter direction, the same as that of Lukesh [21]. After annealing at 1000 °C, the XRD profile was restored to completely the same as the unirradiated one, indicating more dense and disordered portions were relaxed into ordinary state by the thermal annealing. The decrease in thermal diffusivity from the irradiation and recovery by annealing contradicted the formation of a denser nucleus in general, but if the nuclei are very small and uniformly distribute throughout the body, they may contribute to phonon scattering.

3.2. Crystalline SiO_2

The average length change of the irradiated quartz along the *c*-axis was 0.09(0.01)% and 0.17(0.13)% for fluences of 3.0×10^{23} n/m^2 (140 °C) and 6.9×10^{23} n/m^2(300 °C), respectively. Change along the *a*-axis was 0.31(0.11)% and 0.99(0.60)% for fluences of 3.0×10^{23} n/m^2 and 6.9×10^{23} n/m^2, respectively. The swelling was anisotropic depending on the crystal axis, larger along the *a*-axis (or perpendicular to the *c*-axis) than along the *c*-axis, as indicated previously [2,4].

Furthermore, it is noted that the standard deviation in five specimens was unexpectedly large, particularly in higher fluence specimens. Thermal diffusivity of the quartz specimen before the irradiation was 6.34×10^{-2} cm^2/s, and the values after the irradiation were 1.86×10^{-2} and 2.42×10^{-2} cm^2/s for the specimens at 3.0×10^{23} n/m^2 and 6.9×10^{23} n/m^2, respectively. About 62–70% reduction in thermal diffusivity was observed.

Macroscopic length along both the *a*-axis and the *c*-axis of quartz started to reduce (recover) by annealing over ~450 °C. The temperature was slightly higher for the higher fluence specimen, as shown in Figs. 3 and 4. They changed gradually and were almost completely recovered at 800 °C for the lower fluence specimen, but at ~1000 °C in higher fluence specimen. This indicates that the kind of defect induced into the two specimens were partly different. The change in lattice parameter of the quartz by annealing showed almost the same trend as that of length change, as shown in Figs. 3 and 4. Whereas the tendency of the changes due to the annealing was similar, the absolute values of the changes along the *a*-axis in the higher fluence specimens observed by length measurement and lattice parameter measurement were different greatly. As mentioned above, the standard deviation in length change within the same lot was extraordinary large.

Fig. 5 shows the recovery in thermal diffusivity of the quartz by annealing. The tendency was the same with those of length and lattice parameter for corresponding specimens. In the lower fluence specimen, thermal diffusivity gradually increased from ~400 °C, and completely recovered after annealing at 1000 °C, whereas in the higher fluence specimen

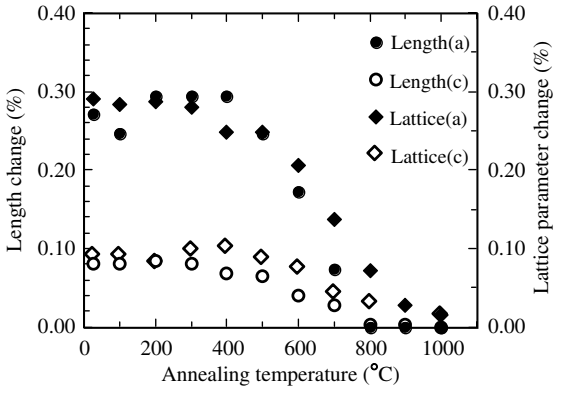

Fig. 3. Change in macroscopic length and lattice parameter of the crystalline SiO_2 (quartz) irradiated to 3.0×10^{23} n/m^2 due to isochronal annealing for 1 h.

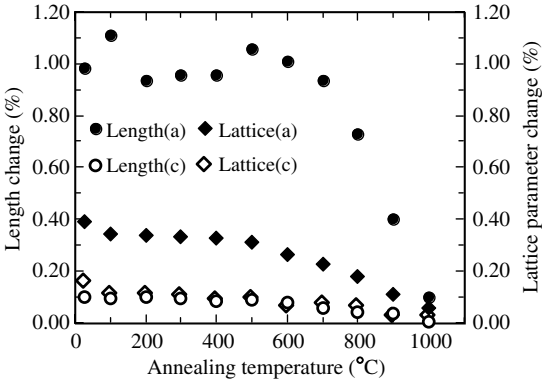

Fig. 4. Change in macroscopic length and lattice parameter of the crystalline SiO_2 (quartz) irradiated to 6.9×10^{23} n/m^2 due to isochronal annealing for 1 h.

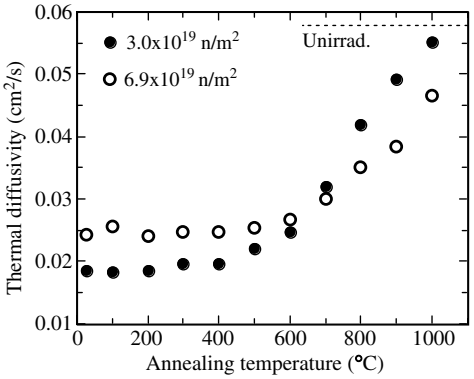

Fig. 5. Change in thermal diffusivity of the neutron-irradiated crystalline SiO_2 (quartz) by isochronal annealing for 1 h.

it started to increase above ~600 °C and not fully recovered after annealing at 1000 °C.

The change in length and other properties of neutron-irradiated quartz by the annealing was reported by Primak [2]. He divided the fluence range into three stages, such as 'early stage, or stage I' (less than 5×10^{23} n/m^2) in which the crystal maintained crystallinity, 'intermediate stage, or stage II' ($5–11 \times 10^{23}$ n/m^2), and a 'final stage, or stage III' (more than 11×10^{23} n/m^2) in which the crystal lost crystallinity. One of the present specimens belongs to the 'early stage' and the other to the 'intermediate stage'. Both cases of the present results resemble each other and nearly equal the reported results of the stage I specimen. It can be said that if the irradiation does not mostly disorder the crystalline lattice, below the neutron fluence of $\sim 1 \times 10^{24}$ n/m (irradiated at ambient temperature), the specimen can recover its crystallinity (i.e., long-range order

observed by XRD) by the annealing at 1000–1100 °C [2]. The slight difference with the present results and the early study [7] was that the recovery of the length, lattice parameter and thermal diffusivity in the present study started at a relatively lower temperature (~400 °C) than in the early study, as shown in Figs. 3–5. Furthermore, it was clarified that there is a small fluence or irradiation temperature dependence, i.e., the initial recovery temperature of the higher fluence/irradiation temperature specimens was slightly higher, and higher temperature was necessary to complete recovery.

Defects formed in the neutron-irradiated quartz were observed by Weissmann and Nakajima [22]. They reported that silicon-rich clusters were observed, and the size and density of the clusters increased with increasing fluence. Furthermore, the size and volume fraction of defect clusters was dependent on crystal orientation, indicating formation of the cluster predominantly along the open screw channel of the crystal. Above 8×10^{23} n/m^2 exposure, these clusters interact each other to form a stable hexagonal defect structure, which corresponds to an irrecoverable microstructure. On the other hand, Wittels [4] suggested the formation of simple defects such as point defects, particularly oxygen, and slightly disordered regions for doses less than 3×10^{23} n/m^2. Exceeding this fluence, not only did the difference in volume determined by the density and lattice parameter change, but also inhomogeneous shear strains were observed, which is interpreted as being due to the clustering of oxygen interstitials.

At present, by comparing recovery in length, lattice parameter and thermal diffusivity of the specimens irradiated to $3.0–6.9 \times 10^{23}$ n/m^2, the conclusion of Wittel [4] is supported, i.e., the main defects introduced into the quartz specimens may be rather simple, point or point-like defects. On the other hand, very tiny dislocation loops can cause anisotropic lattice expansion in the case of AlN [23]. Thus possibility of defect clusters or other causes still remains.

4. Conclusions

A set of high purity α-quartz and vitreous silica specimens were neutron-irradiated up to a fluence of 3.0×10^{23} n/m^2 at 140 °C, and 6.9×10^{23} n/m^2 at 300 °C. Macroscopic length, lattice parameter and thermal diffusivity of these specimens following irradiation and under subsequent isochronal annealing were measured. The results obtained mostly support previously reported results.

Vitreous silica shrank about 0.8% in length for both irradiation conditions. During annealing the length began to increase in the 300–500 °C range, and gradually increased with increasing annealing temperature. After 1000 °C annealing, the length had mostly recovered. The length of quartz expanded in an anisotropic manner due to irradiation. An unexplained statistical variation in length change for the same irradiation conditions of the higher fluence quartz was observed. The length of quartz started to reduce by the annealing over 500 °C, and was almost completely recovered at 800 °C for the lower fluence specimen, but required 1000 °C annealing for the higher fluence specimen. This indicates the defects induced were partly different. Thermal diffusivity of vitreous silica reduced ~10% and that of quartz reduced 60–70%. In both cases the thermal diffusivity increased upon annealing above ~500 °C for the higher fluence specimen and at a lower temperature for the lower fluence specimen, and was mostly recovered after annealing at 1000 °C. Recovery of thermal diffusivity of vitreous silica and quartz by annealing were correlated with the corresponding length change.

Acknowledgements

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