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Ab initio simulation of permanent densification in silica glass

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To clarify the microscopic structure of densified SiO_2 glass, we have conducted *ab initio* molecular-dynamics simulations on the decompression process of SiO_2 glass in its relaxed state from high pressures up to 40 GPa. When decompressed from high pressures above at least 15 GPa, the density and structure always converge to those of densified glass, while the coordination number of silicon decreases to four rapidly. This is in good agreement with previous experimental studies and strongly suggests that densified glass behaves as a high-pressure polymorph of SiO_2 glass. In comparison to ordinary glass, although the coordination number of densified glass is almost the same, the size of an intermediate-range network consisting of SiO_4 tetrahedra is smaller. Detailed analyses clarify that SiO_4 tetrahedra in densified glass are deformed and the Si-O bonds are less covalent.

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I. INTRODUCTION

SiO_2 glass has been well known to be an archetypal three-dimensional network-forming glass and a material of great interest in various research fields, such as condensed-matter physics, materials science, and earth science. In particular, numerous experimental and theoretical studies on permanent densification have been carried out since its discovery in the 1950s [1]. In experimental studies, various SiO_2 glasses having a density up to about 20% larger than ordinary glass have so far been reported to be synthesized as a function of synthesis pressure, temperature, and other parameters [2]. X-ray and neutron diffraction and Raman scattering measurements have suggested that permanent densification is caused by the rearrangement of network consisting of SiO_4 tetrahedra [3–5], and the phenomenon can be interpreted as the transformation to the densified glass phase. However, these measurements can provide only the information of average structures and thus it is difficult to clarify the microscopic structure of densified glass phase.

Classical molecular-dynamics (MD) simulations on the permanent densification have long been carried out [6–12]. They could reproduce the phenomenon qualitatively and have suggested the change in the intermediate-range order similar to experimental studies, but the density values and synthesis conditions differ considerably among papers and from the experimental results because of the insufficiency of potentials. In particular, there have been contradictory reports on whether the network size of densified glass is smaller or larger than that of ordinary glass [6,8–10]. On the other hand, *ab initio* simulations have been conducted only on the compression process [13,14], and there have been no studies on the permanent densification. *Ab initio* simulations on the system with a large number of atoms are not easy and thus previous simulations have focused on the short-range structure such as the coordination number. In this study, focusing on the permanent densification, we have conducted *ab initio* simulations on the decompression process of SiO_2 glass in its relaxed state. The simulated system is confirmed to be large enough to reproduce the intermediate-range structure by comparing the results with previous experimental data. We prove the validity of the simulations and discuss the microscopic structure of densified SiO_2 glass.

II. COMPUTATIONAL METHODS

Ab initio MD simulations were mainly carried out with a system of 144 (48Si + 96O) atoms under periodic boundary conditions. In order to check the finite size effect, the simulations with a system of 288 (96Si+192O) atoms were also made at a specific condition, and the results were confirmed to be sufficiently the same as those of calculations with a system of 144 atoms [15]. The atomic forces were obtained from the electronic states calculated by the projector-augmented-wave method [16]. The details of electronic-structure calculations are summarized in a previous study [17]. The generalized gradient approximation was used for the exchange-correlation energy [18]. The plane-wave cutoff energies are 30 and 250 Ry for the electronic pseudowave functions and the pseudocharge density, respectively. Projector functions were generated for the $3s$ and $3p$ states of Si and the $2s$ and $2p$ states of O. All MD simulations were performed under isothermal-isobaric conditions. The equations of motion for atoms were solved with a time step of 1.2 fs.

The starting configurations of SiO_2 glass in its relaxed state at pressures of 10, 15, 20, and 40 GPa were prepared by heating the system to high temperatures above 3000 K and melting it for more than 6 ps and then cooling it to 300 K at each pressure. The diffusion coefficient of two atoms was above 4 $\text{Å}^2/\text{ps}$ and a number of atomic-diffusion events were observed except at 40 GPa (~ 1 $\text{Å}^2/\text{ps}$). The cooling rate was confirmed to have little effect on the discussion in this study [15]. Similarly, the configuration of ordinary glass was prepared by melting and then cooling the system at ambient pressure. The decompression process was simulated with the slow speed of pressure decrease of less than 0.25 GPa/ps on average. For comparison, the simulations were performed under the high-speed conditions where the pressure suddenly decreases from the maximum to zero.

III. RESULTS AND DISCUSSION

The pressure dependence of density and average coordination number of silicon on decompression is shown in Fig. 1. The densities in the paths from above 15 GPa converge to almost the same point, about 2.65 g/cm^3 at ambient pressure. In addition, an abrupt density change is observed in the

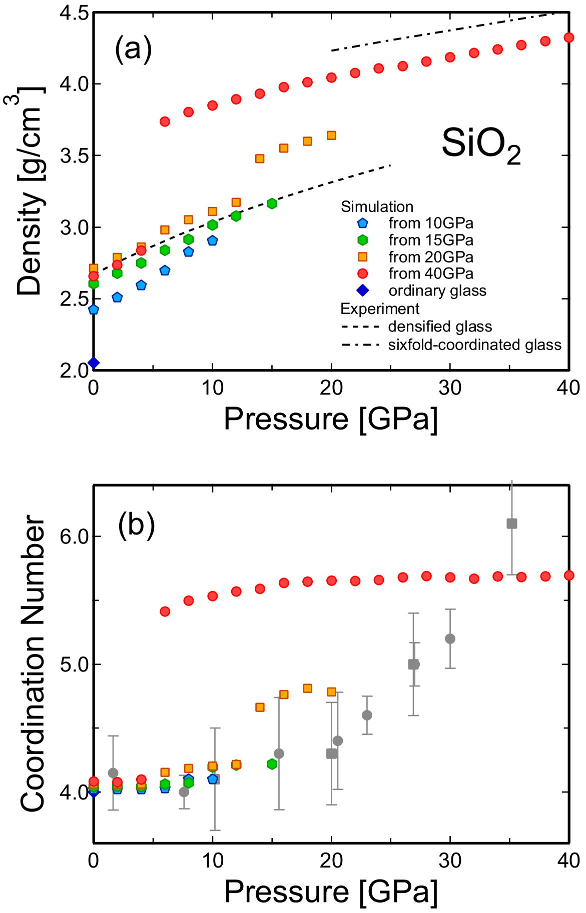

FIG. 1. The pressure dependence of density and average coordination number of silicon of SiO$_2$ glass. Colored symbols represent the data on decompression and the data of ordinary glass obtained by *ab initio* simulations. The equations of state of densified and sixfold-coordinated glasses measured in previous experiments are also shown for comparison [4,33]. Gray symbols represent the data of coordination number obtained by x-ray diffraction measurements on compression [22,23].

path from the pressure range above 20 GPa and seems to be ascribed to the change in coordination number. These observations reveal the phase transformation to a densified four-coordinated structure. The abrupt change in structure on decompression has also been observed in experiments [19]. The densities after the change in coordination number can be well explained by the equation of state of densified glass obtained by density measurements [4]. Experimental studies have suggested that the density of densified glass reflects the intermediate-range structure [4,20], and therefore it is expected that our calculations can simulate the change in intermediate-range order. The comparison of structure factor of ordinary and densified glasses between our simulations and previous x-ray diffraction measurements [5,21] is shown in Fig. 2. The structure factor of densified glass recovered from the pressure range above 15 GPa was almost consistent with each other. Our simulations can reproduce the experimental results very well. The validity of the model in which densified glass is an amorphous polymorph of SiO$_2$ was confirmed by the theoretical calculations.

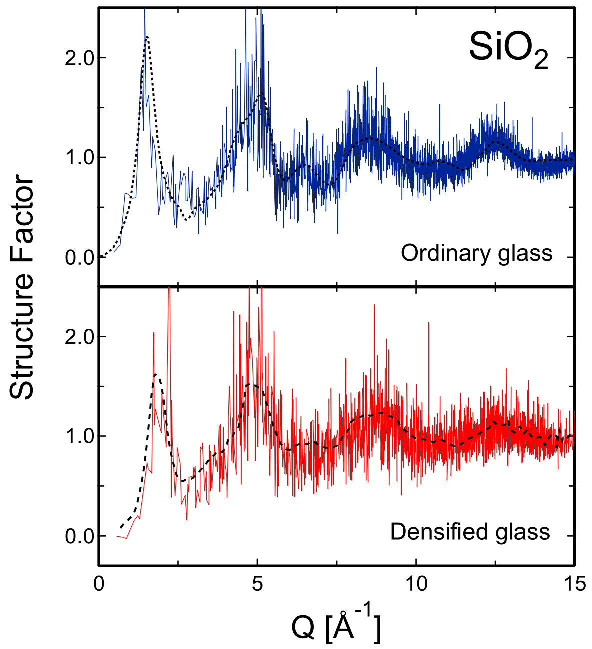

FIG. 2. The structure factor of ordinary and densified SiO$_2$ glasses. The structure factor measured with an x-ray diffraction method is also shown for comparison [5,21].

Figure 1 shows that SiO$_2$ glass is fully densified by applying the pressure of at least 15 GPa and the coordination number of relaxed glass is higher than 4 above 20 GPa. The pressure dependence of abundance of fourfold-, fivefold-, and sixfold-coordinated silicon is shown in Fig. 3. Sixfold-coordinated silicon appears in relaxed glasses at about 20 GPa and seems dominant at higher pressures. In experiments, densification is known to be completed at around 10 GPa at high temperatures [4,20]. In addition, the phase transformation from fourfold- to sixfold-coordinated structures is known to occur between 20 and 35 GPa on compression, as shown in Fig. 1(b) [22,23]. Our simulations are basically consistent

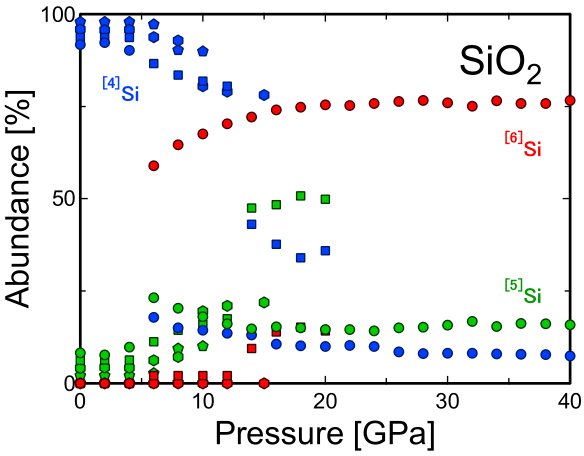

FIG. 3. The pressure dependence of abundance of fourfold-, fivefold-, and sixfold-coordinated silicon in SiO$_2$ glass ($^{[4]}$Si, $^{[5]}$Si, and $^{[6]}$Si in the figure). Pentagons, hexagons, squares, and circles represent the data on decompression from 10, 15, 20, and 40 GPa obtained by *ab initio* simulations, respectively.

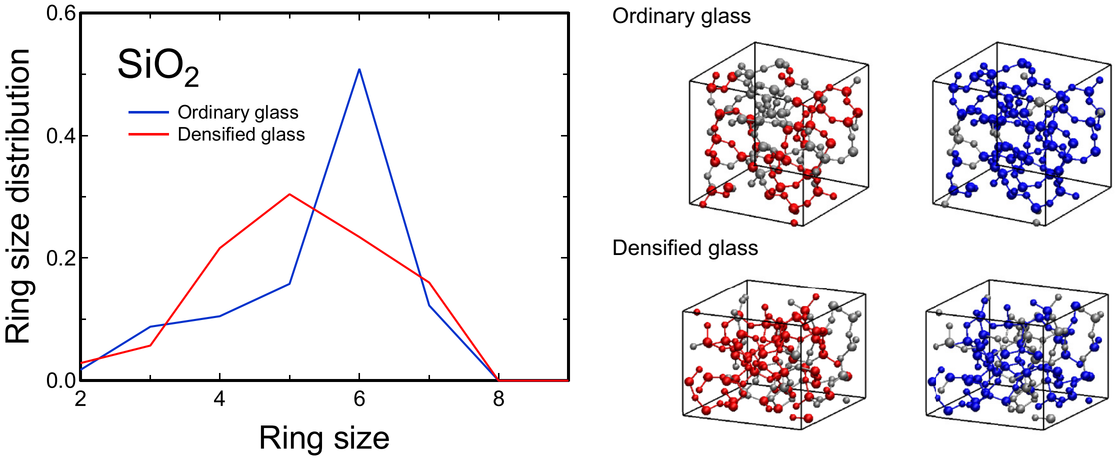

FIG. 4. The ring distribution of ordinary and densified SiO_2 glasses. In the right side of the figure, constituent atoms of five- and six-membered rings are shown in red and blue, respectively.

with these experimental results, although the glass recovered from 10 GPa is not fully densified and the coordination number at 40 GPa is slightly lower than six. These slight discrepancies may be due to the difference between theoretical and experimental time scales. In fact, the atomic diffusion may not be enough at 40 GPa as pointed out above. Densified glass after decompression contains up to 10% fivefold-coordinated silicons (defects). These defects may reflect the fact that the speed of pressure decrease is higher in simulations than that in experiments. An abrupt density change occurs between 5 and 15 GPa on decompression [Fig. 1(a)], indicating that there is hysteresis in the transformation between fourfold- and sixfold-coordinated structures. Indeed, the hysteresis was pointed out by experiments [19,23]. The pressure conditions where an abrupt density change occurs differ among the paths in our simulations. The pressure conditions may be affected not only by the maximum pressure and speed of pressure decrease but also by the amount and state of defects, which may be related to the cooling rate at the maximum pressure [15].

The ring size distribution in ordinary and densified glasses is shown in Fig. 4. The number of rings was counted with Guttman's definition [24]. The cutoff distance of the Si-O bond was determined from the first minimum of pair distribution function. The figure shows that the network of densified glass consists of rings in a smaller size than that of ordinary glass. In the right side of figure, constituent atoms of five- and six-membered rings are shown in red and blue, respectively. Densified glass has more five-membered and less six-membered rings than ordinary glass. Density measurements also suggested that densified glass is an amorphous polymorph like coesite having a number of four-membered rings (cf. ordinary glass is considered to be an amorphous polymorph like quartz or cristobalite consisting mainly of six-membered rings) [4]. Our results clarify that permanent densification is caused by the reconstruction of the network structure to a smaller one.

Zeidler *et al.* [11] considered that the network is divided by the appearance of a fivefold- and/or sixfold-coordinated silicon at high pressures. The number of fivefold- and sixfold-coordinated silicons in recovered glass is below 10% in this study (Fig. 3). As discussed in Tsuneyuki and Matsui [25], the densification may be caused by the rearrangement of network through fivefold- and/or sixfold-coordinated transient states. On the other hand, some classical MD simulations pointed out that the ring size in densified glass is larger than ordinary glass [9,10]. The rebonding may be less likely to occur during the rearrangement of network due to the insufficiency of their potentials, causing the increase of defects and thus the increase in ring size. As for SiO_2 melt, *ab initio* simulations suggested that the ring size increases with pressure at low pressures [26]. The probability of rebonding is very high in melt, and therefore SiO_2 melt can be densified even at around 0 GPa. In fact, the characteristic ring size of SiO_2 melt was reported to be about five at low pressures, which is close to that of densified glass (Fig. 4). As discussed in the next paragraph, the bonds in densified glass (melt) are weak. In SiO_2 melt, the densification takes place at around 0 GPa and the weakening of bonds may cause the increase in ring size with increasing pressure.

The difference in the bonding properties between densified and ordinary glasses was estimated with a population-analysis method [27]. By expanding the electronic wave functions in an atomic-orbital basis set, the overlap population $\bar{O}$ between silicon and oxygen was obtained. The $\bar{O}$ distribution of densified and ordinary glasses is shown in Fig. 5(a). $\bar{O}$ indicates the strength of the covalentlike bonding between silicon and oxygen. In densified glass, a peak shifts to lower $\bar{O}$, suggesting that the Si-O bond becomes less covalent. This observation is in remarkable agreement with previous experiments and classical simulations which reported high plasticity of densified glass [12,28,29]. The O-Si-O angle distribution of ordinary and densified glasses is shown in Fig. 5(b). Densified glass shows a broad distribution compared to ordinary glass, suggesting that SiO_4 tetrahedra of densified glass are deformed. The deformation should be related to the change in the Si-O bond covalency.

The comparison of low- and high-speed decompression processes is summarized in Table I. The density of densified glass synthesized in the high-speed process is equal to or lower than that of densified glass synthesized in the low-speed process. At ambient pressure, ordinary glass is more stable

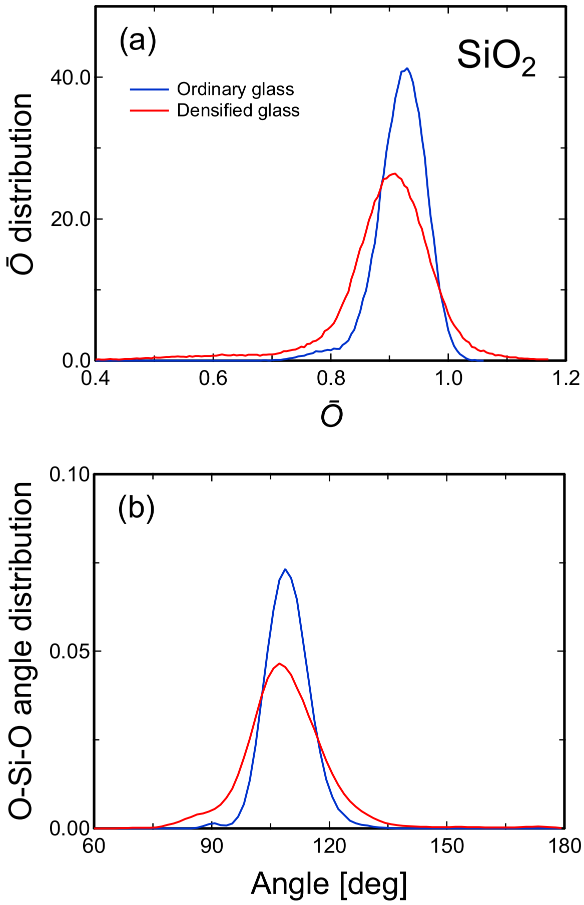

FIG. 5. The bond overlap population between silicon and oxygen and the O-Si-O bond angle distribution of ordinary and densified SiO_2 glasses. The bond overlap population indicates the strength of the covalentlike bonding.

TABLE I. Density of densified glass at ambient conditions obtained by *ab initio* simulations. Densities are in g/cm^3.

	Synthetic pressure			
	10 GPa	15 GPa	20 GPa	40 GPa
Gradual decompression[a]	2.42	2.61	2.71	2.66
Sudden decompression[b]	2.43	2.59	2.56	2.45

[a] The speed of pressure decrease is less than 0.25 GPa/ps on average.

[b] The pressure suddenly decreases from the maximum to zero.

than densified glass. A sudden change in pressure (and density) makes a number of atoms move, which may relax the structure. The speed of pressure decrease generally affects the amount and state of defects, and the high-speed process is expected to cause the persistence of five- and six-coordinated silicons and the resultant increase in density of densified glass at ambient conditions. However, the coordination number was almost completely recovered to four and the density was not larger even with decreasing from the maximum to ambient pressures suddenly. It could be concluded that SiO_2 glass in its higher-coordinated state is unquenchable to ambient pressure, consistent with previous experimental studies [30]. In fact, the coordination number of silicon decreases very rapidly on decompression within a time scale of *ab initio* calculations (a few picoseconds). Also, classical simulations pointed out the discontinuous change in coordination number and suggested that higher-coordinated glass is unquenchable [8]. Our simulations clarified that the discontinuity is more abrupt and that SiO_2 glass pressurized up to above 10–15 GPa is always recovered in its four-coordinated densified state. *Ab initio* simulations on $MgSiO_3$ glass have suggested the presence of a significant amount of higher-coordinated silicons in its densified state [31]. The network-modifying cations such as Mg^{2+} are considered to affect the densification process of silicate glass.

This study clarified that fully densified glass has a small network structure consisting of deformed SiO_4 tetrahedra and its Si-O bond is less covalent. On the other hand, intermediately densified glass recovered from 10 GPa has a structure between ordinary and fully densified glasses [15]. Some previous studies by experiments and classical simulations suggested that intermediately densified glass behaves in an elastic manner at low pressures [4,10,32], but it still remains unclear whether it is in a single state or in a mixed state of ordinary and fully densified structure. To answer this question, however, it is necessary to conduct simulations with a larger number of atoms, but the simulations are not easy at present. To deepen the understanding of permanent densification, further technical improvements and detailed studies in both experiments and theoretical calculations will be required.

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