Effects of charge transfer on a-SiO$_2$ surface structure: A molecular dynamics study

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The effects of charge transfer between atoms on an amorphous SiO$_2$ surface were studied by comparing a model with fixed charge ($FQ$) and a model that takes into consideration charge transfer by the charge equilibration ($QEq$) method. The $QEq$ surface has more oxygen atoms and denser structures compared to the $FQ$ sample. We found, on the surface of the $QEq$ sample, three-coordinated Si with an O–Si–O bond angle in the range of 109–115°. This structure is similar to that of the experimentally observed E’ center (=Si ·). We also found a structure similar to the nonbridging oxygen hole center (=Si–O ·), which has been observed experimentally on a silica glass surface. These structures were not observed in the $FQ$ model. The results suggest that consideration of the charge transfer is essential to reproduce the defect structure of the silica glass surface. © 2002 American Institute of Physics. [DOI: 10.1063/1.1506392]

I. INTRODUCTION

Amorphous silica (a-SiO$_2$) is an important material in information technology for its significant role in semiconductor devices. However, due to the disordered nature of a-SiO$_2$, our knowledge of the structure and properties obtained through experiments is still limited. Therefore, computer simulation is a complementary tool for clarification of the structure of a-SiO$_2$. Since the first work using the Born–Mayer–Huggins-type potential by Woodcock et al.$^1$ a number of potentials$^{2-5}$ have been used to simulate a-SiO$_2$.

Feuston and Garofalini$^6$ and Trioni et al.$^7$ studied the surface structure by molecular dynamics simulation. These studies showed that the surface structure of a-SiO$_2$ is quite different from that of the bulk. The dangling bonds exist on the surface$^{6,7}$ and formed during initial generation of the surface and the surface structure was modified by the migration of atoms in subsequent heat treatment. All of the results indicated that the degree of structural variation at the surface is large. In those studies, screened Coulomb interaction was used to avoid the long-range effect; the standard Ewald method$^8$ cannot be applied straightforwardly on the surface. In addition to the usage of the screened potential, the ionic charges were assumed to be fixed. Consideration of electrostatic interaction between atoms is essential in determining the surface structure.

The charge equilibration ($QEq$) method$^9$ can be used to treat the charge of each atom as a variable; charge in an atom is determined by the system environment based on the principle of electronegativity equilibration. The $QEq$ method has been successfully applied for bulk a-SiO$_2$.$^3$ Since the $QEq$ method has not yet been applied on an a-SiO$_2$ surface, the charge transfer effects on that surface, for instance (1) the effects of instantaneous charge on the surface structure, and (2) the difference in the surface structures simulated by the fixed charge ($FQ$) model and by the $QEq$ model, remain unclear. To clarify the effects, the difference between the surface structures simulated by the $FQ$ and $QEq$ models was investigated in this study.

Another problem in the simulation of the silica surface is the simulation conditions. In previous studies$^6$, the characteristic time scale of computer simulation was $\leq 50$ ps, whereas that in a real experiment is at least several seconds. In this study, we performed a longer time scale simulation (100 ps) than those in the previous studies.

In another study,$^{10}$ we compared two kinds of surfaces which have different thermal histories, i.e., the sample had been held at temperatures greater than [the high temperature (HT) sample] and less than [the low temperature (LT) sample] the glass transition temperature. The former sample had more defect structures than the latter sample. In that study, however, the effects of taking into account the $QEq$ method have not been verified. Therefore, in this work, we analyzed the effects of electrostatic interaction on the a-SiO$_2$ surface structure, and the effects of charge variation by comparing the results of $QEq$ and $FQ$ models.

II. MOLECULAR DYNAMICS SIMULATION

Electrostatic interaction is one of the key factors in determining the structure of a-SiO$_2$. We determined the charge of each atom by the $QEq$ method. A more accurate Coulomb interaction can be obtained by this approach. As proposed by Rick et al.$^{11}$ charges are determined by the electronegativity equilibration (EE) principle; the chemical potential $\chi_A$ is the same for all atoms, and $\chi_A$ can be expressed as

$$\chi_A = \frac{\partial E}{\partial Q_A} = \chi_A^0 + \sum_B J_{AB}(R_{AB})\xi_B,$$

(1)

Here, $\chi_A^0$ is referred to as electronegativity and $J_{AB}$ is the Coulomb overlap integral calculated from a normalized s-wave-like Slater orbital, $\phi_{n_s}$, $\xi = N_\ast n_s^{\alpha_s - 1} e^{-\xi_{ss}}$. The $J_{AB}(R)$ for Si–Si, Si–O and O–O tends toward finite values when $R$
is equal to zero \((J_{\text{Si-Si}}^0 = 4.738 \text{ eV}, J_{\text{Si-O}}^0 = 5.811 \text{ eV}, \text{ and } J_{\text{O-O}}^0 = 7.822 \text{ eV})\) and behaves like ordinary Coulomb interactions when \(R\) tends toward infinity.\(^3\)\(^9\)\(^10\)

The Morse-Stretch (MS) potential\(^3\)

\[
U(R_{ij}) = D_0 [\alpha (1 - R_{ij}/R_0) - 2 \alpha \gamma (1 - R_{ij}/R_0)],
\]

is used to take into account the nonelectrostatic interactions. The parameters used in the \(Q\text{Eq}\) method and the MS potential are given in Table I. It has been confirmed that the MS potential combined with the \(Q\text{Eq}\) method describes all fourfold- and sixfold-coordinated polymorphs of silica well.\(^3\)\(^9\)\(^10\) Coulomb interaction was treated by the Ewald method\(^6\) to account for the long-range interaction.

Bulk \(\alpha\)-Si\(_2\)O\(_5\) with 648 particles (216 Si and 432 O) was first generated using the MS potential combined with the \(Q\text{Eq}\) method. The Gear predictor-corrector algorithm\(^12\) is used to integrate the motion of the equation with a time step of 0.5 fs. Another bulk \(\alpha\)-Si\(_2\)O\(_5\) sample was also generated using the same force field without using \(Q\text{Eq}\). In the \(Q\text{Eq}\) sample, the charge of all silicon atoms is 1.318 \(\text{e}\), and that of all oxygen atoms is \(-0.659 \text{e}\) according to Demiralp \textit{et al.}\(^3\)

The charge distributions in both samples are given in Fig. 1. In both cases, the annealed \(\alpha\)-Si\(_2\)O\(_5\) bulk materials were initiated from \(\beta\)-crystobalite with density of 2.2 g/cm\(^3\). The sample was held at 8000 K for 10 ps and then cooled to 2000 K at a cooling rate of 100 K/ps stepwise. The temperature was controlled by the Nosé NVT method.\(^13\)

At 2000 K, we generated an “initial surface” of \(\alpha\)-Si\(_2\)O\(_5\),\(^14\) which can be used to simulate the surface at a high temperature (3500 K). A technique used by Bakaev\(^14\) was employed; a three-dimensional (3D) Ewald summation was calculated by artificially elongating a unit cell twofold, in which a slab of silica was located at the center of the extended region. The only difference between the two samples was whether or not \(Q\text{Eq}\) was applied. The 10 surface samples generated under different initial conditions at 2000 K were prepared for both cases. Then they were cooled to 1000 K stepwise at a cooling rate of 100 K/ps for 50 ps. Subsequently holding to 1000 K for 15 ps of the Nosé NVT ensemble, the samples were cooled to 300 K at a cooling rate of 100 K/ps. Then their properties were analyzed. All quantities obtained were averaged over the 10 samples with different initial conditions.

### III. RESULTS

We took the \(z\) direction as the normal direction of the surface. The surface properties were analyzed by dividing the sample into sublayers along the \(z\) direction. Here the system layer was divided into 12 sublayers in which the number of atoms in each sublayer is 54. The \(z\) coordinate of the surface was set to zero at the beginning of the surface simulation and the inner part of the silica corresponded to a negative \(z\) value. Some atoms moved beyond \(z = 0 \text{ Å}\) during the relaxation process. The number densities of \(FQ\) and \(Q\text{Eq}\) samples are shown in Fig. 2 where the range of several layers is indicated.

The radial distribution function (RDF) is one of the most important indices of the structure. The RDFs of the \(Q\text{Eq}\) and \(FQ\) samples are shown in Fig. 3. The first three peaks correspond to the distance of the nearest Si–O, O–O, and Si–Si pair. In the two types of samples, the RDFs in the innermost part are almost the same because the charges at the center of the slab of the \(Q\text{Eq}\) sample are almost the same as those of the \(FQ\) sample,\(^10\) the width of the O–O peak in the fifth layer in the \(FQ\) is wider than that in the \(Q\text{Eq}\) sample. The Si–Si peak position shifted toward that of the O–O peak in the \(FQ\) sample whereas the Si–Si peak totally disappeared in the \(Q\text{Eq}\) sample.

The bond-angle distributions of \(Q\text{Eq}\) and \(FQ\) samples are shown in Fig. 4. At the inner portion, the O–Si–O bond angles are distributed at around 109° almost symmetrically in both samples up to the fifth layer. The width of the O–Si–O bond-angle peak of both samples becomes wider upon going from the bulk to the surface. The widths of the O–Si–O bond-angle distribution of both the samples are similar up to the fifth layer. At the outermost layer (L6), the discrepancy between the two samples is more distinct: The O–Si–O angle of the \(FQ\) sample has a peak at 109° and a shoulder at 120°, whereas that of the \(Q\text{Eq}\) sample has a unified peak between 109° and 120°. The 54 atoms in the outermost layer have a wider spatial distribution than those in the inner layers as seen from Fig. 2. Thus the contribution of bond-angle distribution of atoms in the outermost layer should be different between the part near the surface and that near the bulk. In the \(FQ\) and \(Q\text{Eq}\) sample, the 109° peak can mainly originate from the near-bulk part and the 120° peak can mainly originate from the near-surface part. The 120°...
peak should be derived from the planar Si=O₃ structure. Therefore the fraction of planar structure should be greater at the part near the surface than at that near the bulk in the outmost layer. The height of the 120° peak in the FQ sample is lower than that in the QEq sample, since the surface of the QEq sample should have a more flexible surface structure.

In order to study the surface dynamics, the mean square displacements (MSDs) were calculated layer by layer. As stated above, the number of atoms in every layer is set at 54 in order to eliminate the effect of density variation in the surface and to harmonize the accuracy of analysis. First the MSD of each atom was calculated and then the MSDs were averaged over each sublayer in which each atom initially existed. The MSD was calculated by

$$\langle r^2 \rangle = \frac{1}{N} \sum_{i} \left[ r_i(t) - r_i(0) \right]^2,$$

for Si and O atoms, respectively. The MSD increases within a short time and approaches a constant value with a sufficiently long time (~ 2 ps). The constant value is called the Debye–Waller factor (DWF). The distribution of DWFs is shown in Fig. 5. FQ and QEq samples share some common DWF features; there is no obvious difference in atomic vibration in the bulk. However, the DWF of oxygen near the surface of the QEq sample is larger than that in the FQ sample. The DWFs of O in the QEq samples increase steeply
upon nearing the surface, whereas such a steep change was not observed near the surface of FQ samples.

The coordination number distributions of Si and O are shown in Fig. 6. The horizontal coordinates of each point indicate the center position of each sublayer. Here BO stands for bonding oxygen, which is an oxygen atom bound to two silicon atoms, and NBO stands for nonbridging oxygen which is an oxygen atom bound to only one silicon atom. The number of NBOs is negligible in the bulk and the fraction of NBOs increases as it approaches the surface. Similarly, almost no three-oxygen-coordinated silicon exists in bulk and the fraction of Si defects, i.e. three-oxygen-coordinated silicon, increases upon nearing the surface. The fraction of surface three-oxygen-coordinated silicon in the QEq sample is slightly larger than that in the FQ sample; the fraction of NBOs in the QEq sample is 76% and that in the FQ sample is 47%.

IV. DISCUSSION

Most of our results can be interpreted in terms of a difference in electrostatic interaction between the two samples. Since the difference in charge between two samples in the center of a simulation cell (z ~ 9 Å) is quite small, the Si–O–Si bond-angle distribution is almost the same in the two samples. In the sixth layer, the discrepancy between the two samples becomes obvious. The absolute charge value of the oxygen atoms at the surface decreases in order to maintain the surface electronegativity equilibrium; thus the O atoms could lose electrons and generate an ion at the surface. In light of this, the discrepancy in the O–Si–O angle distribution can be explained. The charge of the FQ sample is fixed and larger than that of the QEq sample. Consequently, the repulsive force between O atoms in the FQ sample is larger than that in the QEq sample. As a result, in the FQ sample, if the Si atoms become three coordinated, the surface configurations are apt to form a planar structure. This is why a peak at 109° and a shoulder at 120° are observed in the outermost layer of the FQ sample (Fig. 4). In the QEq sample, on the other hand, the surface structure deviates from the planar structure due to the weakened repulsive force. This is why the O–Si–O bond-angle distribution has a unified peak in the range of 109°–120°. In QEq samples, the mean charge of oxygen atoms decreased from the bulk to the surface (see Fig. 1). Those oxygen atoms with charge loss should form ions because the structural variation at the surface changes the charge distribution between atoms from its original topology and bonding state.

The calculated vitreous silica surface shown in Fig. 7 comprises the experimentally detected E’ centers (1O=Si•, the centered dot indicates an unpaired electron). Most silicon atoms at the surface are three coordinated and the fraction of four-coordinated Si is relatively small, as shown above. Some of those silicon atoms have a coordination number of three and bond angle of around 109°–115°. Such
a structure is similar to the $E'$ center structure [$_{3}O=Si\cdot$, see Fig. 7(c)]. Some of the silicon atoms are four coordinated with bonding to a NBO, which is similar in structure to the nonbridging oxygen hole center (NBOHC; $_{=Si-O\cdot}$) shown in Fig. 7(b). These defect structures have been observed by electron paramagnetic resonance (EPR). In contrast, the $FQ$ model should reproduce neither an $E'$ center-like nor NBOHC-like structure as in the case of $QEq$ because of the higher repulsive force between O atoms due to the fixed charges. The O–Si–O bond-angle distributions in the $FQ$ sample were approximately 120°, which means that the $FQ$ sample surface consisted of planar three-coordinated silicon. Thus only the $QEq$ method can reproduce structures similar to the $E'$ center and NBOHC. Elucidation of the existence of the $E'$ center and NBOHC should still be performed based on an ab initio quantum mechanical calculation.

The difference in dynamics between $QEeq$ and $FQ$ samples can also be explained in a similar manner. Because of a small charge difference between $QEeq$ and $FQ$ samples, their DWFs are almost the same in the bulk. As the charge decreases upon nearing the surface of the bulk, the electrical interaction becomes weaker and the DWFs become larger. Since all charge is constant in $FQ$ samples, electrostatic interaction between subsurface layers is uniform. The $QEeq$ sample, on the other hand, exhibits different charge transfer ratios between sublayers and has a relatively small charge value. Therefore, atoms can move more freely and the DWF in $QEeq$ at the surface becomes very large compared to in the $FQ$ sample. In particular, the DWF of O atoms in the $QEeq$ sample is very large compared to that of Si atoms. The following reasons for a larger amplitude of O atoms in the $QEeq$ sample can be considered: (i) The fraction of nonbridging oxygen in the $QEeq$ sample, which can vibrate more freely than bonding oxygen, is greater than that in the $FQ$ sample. (ii) The density of the surface layer in $QEeq$ is lower than that in $FQ$ (see Fig. 2). (iii) The electrostatic interaction of nonbridging oxygen in the surface layer of the $QEeq$ sample is weaker than that in the $FQ$ sample due to the smaller charge at the nonbridging oxygen in the $QEeq$ sample.

V. SUMMARY AND CONCLUSION

The MS potential in combination with $QEeq$ method was verified to be transferable to the surface. The difference in $\alpha$-SiO$_2$ surface structure between $QEeq$ and $FQ$ samples was examined. The effects of the electrical interaction on the surface structure and dynamics were analyzed. A single O–O RDF peak formed on the $QEeq$ sample surface while the O–O and Si–Si peaks combined to form a wide distribution in $FQ$ samples. This suggests that more oxygen atoms exist on the $QEeq$ sample surface than on the $FQ$ sample surface.

The DWF increased steeply near the surface in the $QEeq$ model, while that in the $FQ$ increased gradually from the bulk to surface. This difference in vibrational behavior suggests that the $QEeq$ sample has a more open structure near the surface.
The O–Si–O bond angle in \( QEq \) samples has a wider distribution at the surface. Similar structures to the experimentally observed \( E' \) center and NBOHC were observed in the \( QEq \) sample. Those structures have not been observed in the \( FQ \) sample. Therefore, the effect of charge transfer should be taken into account to reproduce the surface structures of silica glass.

\textit{Ab initio} simulations such as those in the scheme proposed by Car and Parrinello\textsuperscript{16} based on the same philosophy as the present model. Both of them take the instantaneous geometry of the ions into consideration. The drawbacks of the \textit{ab initio} method, at the present stage, is that the computational at burden is huge, the time scale accessible is limited to a few ps which is too short to bring the system into equilibrium and the system size is limited to few hundred particles. The present model, on the other hand, can simulate a system as large as thousands of particles over several ns. Therefore, the present approach is more efficient in treating the effect of the instantaneous geometry of ions which is essential to simulate the surface structure reasonably. Recently, an \textit{ab initio} molecular dynamics simulation was reported by Mischler \textit{et al.}\textsuperscript{17} However, due to the limited simulation conditions mentioned above, a critical comparison is difficult.

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