Atomic-scale disproportionation in amorphous silicon monoxide

Silicon monoxide (SiO) was first reported by Charles Mabery in 1887 [1] and has been widely used as surface coatings, insulating layers in integrated circuits, dielectric material in capacitors, and anode materials for Li-ion batteries. However, the atomic structure of SiO has been debated for nearly a century despite numerous experimental and theoretical efforts devoted to this problem. Although a random bonding Si-($Si_{4-x}O_x$) tetrahedral configuration can satisfy the stoichiometry of SiO, experiments and theoretical calculations have suggested that it is inherently unstable and undergoes an unusual disproportionation by forming amorphous Si- and SiO_2-like clusters [2]. However, it has been long known that the heat of combustion of amorphous SiO is significantly higher than that of an equilibrium mixture of amorphous Si and SiO_2 and, importantly, the X-ray diffraction (XRD) patterns of amorphous SiO cannot be interpreted by the summation of amorphous Si and SiO_2 spectra. The unique and well-defined local atomic configurations of SiO have not been directly realized by experiments mainly because of the limitation in spatial resolution of conventional diffraction methods. In this study [3] we employ our recently developed angstrom beam electron diffraction (ABED) method to investigate the local structure of amorphous SiO, which is supplemented by synchrotron high-energy XRD (HEXRD) and computational simulations based on molecular dynamics (MD) and reverse Monte Carlo (RMC) calculations.

Figure 1 shows the X-ray structure factor $S(Q)$ of amorphous SiO measured at SPring-8 **BL04B2**, together with those of amorphous Si and SiO_2 reported in the literatures [4,5]. The $S(Q)$ of amorphous SiO appears to be intermediate between those of amorphous Si and SiO_2. However, the summation curve of amorphous Si and SiO_2 is not fully consistent with that of SiO, agreeing with previous observations. In particular, the first sharp diffraction peak of the summation data splits into two sub-peaks, which cannot reproduce the first peak at $Q \sim 1.8$ Å^{-1} of amorphous SiO. The good agreement between the summation curve and SiO at the high Q portion indicates that the short-range structure of amorphous SiO could be similar to those of Si-4Si and Si-4O tetrahedra in amorphous Si and SiO_2.

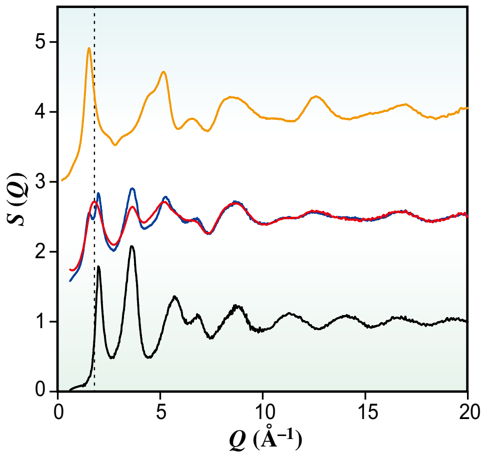

Fig. 1. X-ray total structure factors $S(Q)$ of amorphous SiO, Si and SiO_2. The X-ray $S(Q)$ of amorphous SiO obtained from HEXRD (red) is shown together with the $S(Q)$ data of amorphous Si (black) and SiO_2 (orange) reported in the references [4] and [5], respectively· The $S(Q)$ profile for the summation of amorphous Si and SiO_2 is shown as a blue curve. [3]

The local atomic structure of amorphous SiO was investigated by ABED as illustrated in Fig. 2(a). Figure 2(c)-(e) show three typical ABED patterns obtained from dark, bright and interface regions in a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of Fig. 2(b). The diffraction patterns in Figs. 2(c) and 2(e) are akin to those of amorphous Si and SiO_2 with the smallest Q values ($Q \sim 2.0$ and 1.5 Å^{-1}) in HEXRD. Meanwhile, the simulated ABED patterns based on suboxide-type tetrahedra match well with the experimental one (Fig. 2(d)). The simulated ABED patterns of amorphous Si, SiO_2 and SiO_x clusters are shown in Fig. 2(c')-(e'), together with the corresponding atomic models (Fig. 2(c")-(e")).

On the basis of the ABED and HEXRD results, we constructed an atomic model of amorphous SiO by the combination of MD simulations and RMC modeling. The final structure model is shown in Fig. 3(a), in which the coordinates of Si-4Si and Si-4O tetrahedral from the amorphous Si and SiO_2 regions are still visible. The $S(Q)$ profile of the model is well consistent with that of HEXRD (Fig. 3(b)). Additionally, the suboxide-type tetrahedral coordinates (Si-(3Si, O), Si-(2Si, 2O) and Si-(Si, 3O)) revealed by ABED are formed at the Si/SiO_2 interface regions during the structure relaxation. The density functional theory calculations confirm the presence of the suboxide-type tetrahedra in the interface regions. These suboxide-type tetrahedra keep the random networks in amorphous Si and SiO_2 continuously across the interface regions. The number fractions of the five typical atomic coordinates are shown in Fig. 3(c). There are considerable amounts of suboxide-type tetrahedra of Si-(3Si, O), Si-(2Si, 2O) and Si-(Si, 3O) from interface regions. These suboxide-type tetrahedra as the transition layers bridge amorphous Si and amorphous SiO_2 by preserving the continuity of the random networks of Si and SiO_2.

In summary, we systematically investigated the atomic structure of amorphous SiO by utilizing the ABED, complemented with synchrotron HEXRD and MD-RMC simulations. The ABED experiment provides direct evidence on the atomic-scale disproportionation in amorphous SiO, predicted by theoretical calculations. The distinctive interfacial structure between amorphous Si and SiO_2 clusters, revealed by the sub-nanoscale electron diffraction, uncovers the structural origins of amorphous SiO different from the simple mixture of Si and SiO_2.

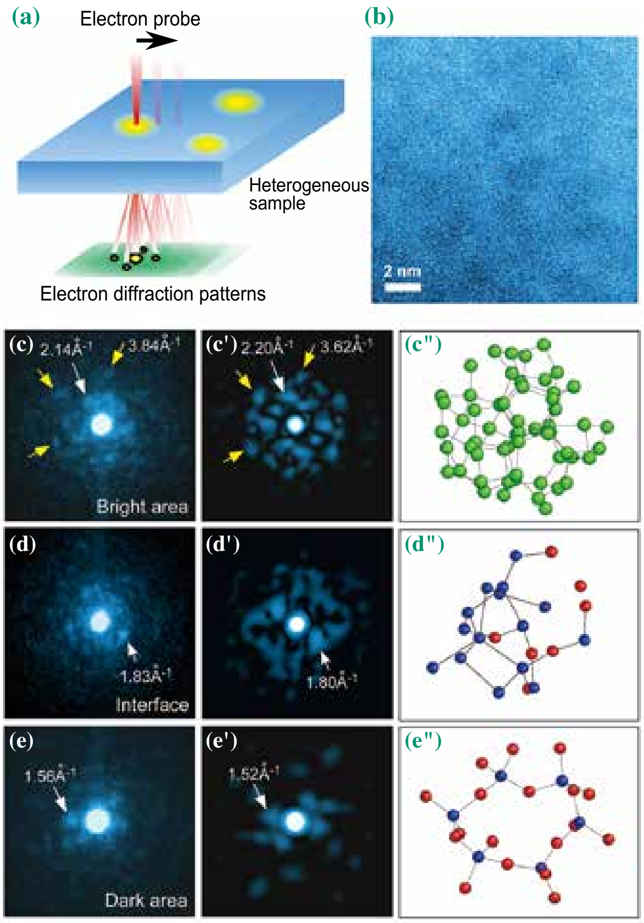

Fig. 2. **(a)** The schematic diagram of the ABED measurements of amorphous SiO with nanoscale structural heterogeneity. **(b)** HAADF-STEM image of the amorphous SiO. **(c)-(e)**, Typical ABED patterns taken from bright, interface and dark regions in the HAADF-STEM image shown in (b). **(c')-(e')** Simulated ABED patterns based on the atomic models of amorphous Si, interfacial suboxide-type tetrahedra and amorphous SiO_2 in **(c")-(e")**. [3]

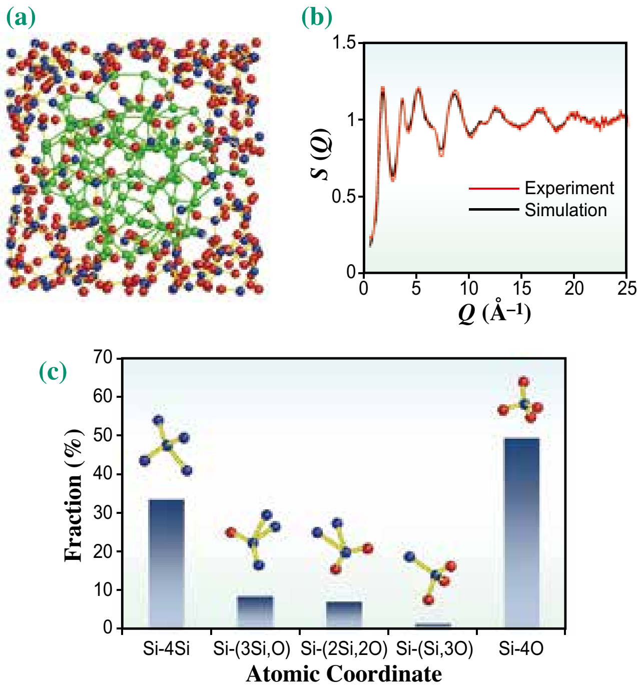

Fig. 3. **(a)** Reconstructed heterostructure model of amorphous SiO. The inner part corresponds to an amorphous Si cluster and the outer part is amorphous SiO_2 matrix. The blue, red and green circles denote Si and O in amorphous SiO_2 and Si in the Si cluster, respectively. **(b)** Experimental and simulated X-ray total structure factor $S(Q)$ curves. **(c)** Fractions of the five atomic coordinates found in amorphous SiO. Si-4Si and Si-4O are from the Si cluster and SiO_2 matrix while Si-(3Si, O) Si-(2Si, 2O) and Si-(Si, 3O) appear at the interfacial regions between the Si cluster and amorphous SiO_2 matrix. [3]

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References

[1] C.F. Mabery: Amer. Chem. J. **9** (1887) 11.
[2] A. Hohl *et al.*: J. Non-Cryst. Solids **320** (2003) 255.
[3] *A. Hirata, S. Kohara, T. Asada, M. Arao, C. Yogi, H. Imai, Y. W. Tan, T. Fujita and M. W. Chen: Nat. Commun. 7 (2016) 11591.*
[4] K. Laaziri *et al.*: Phys. Rev. Lett. **82** (1999) 3460.
[5] S. Kohara and K. Suzuya: J. Phys.: Condens. Matter **17** (2005) S77.