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# Structural Study of SiOx Amorphous Thin Films by the Grazing Incidence X-ray Scattering (GIXS) Method*

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Atomic structures of $SiO_x$ amorphous thin films of 200 nm thick were analyzed by the grazing incident x-ray scattering (GIXS) method. The radial distribution functions (RDFs) were experimentally determined in two $SiO_x$ amorphous thin films grown in the atmosphere with and without $N_2$ gas. The $SiO_x$ amorphous film grown with $N_2$ gas forms the network structure consisting of $SiO_4$ tetrahedra which are connected each other by oxygen atoms at their vertices. This network structure is similar to the one observed in $SiO_2$ glass. On the other hand, in the $SiO_x$ amorphous film grown without $N_2$ gas, the atomic distance of Si-O pairs is a few percent longer and the coordination number of O-O pairs is smaller than the other. This suggests that some of oxygen atoms in a $SiO_4$ tetrahedron are not connected to a next neighboring tetrahedron. Namely, some part of the network structure is disconnected in the $SiO_x$ amorphous film grown without $N_2$ gas. Due to this imperfection of the network structure, it is expected that the $SiO_x$ film grown without $N_2$ gas would be inferior to the other one grown with $N_2$ gas in some electrical properties as an insulator.

KEYWORDS: $SiO_x$ amorphous film, grazing incident x-ray scattering, structural analysis, $SiO_2$ glass

## 1. Introduction

$SiO_x$ amorphous thin films are widely used such as insulators for silicon devices, protection films for magneto-optical recording media, etc. The thickness of $SiO_x$ amorphous films is currently of the order of a few hundred nano meters. In a very near future, their thickness will be 20 to 30 nm or less. Many workers is making a great effort to establish a method to produce such a thin $SiO_x$ amorphous films with maintaining good electric properties equal to those in the thicker $SiO_x$ films. In these studies, the information on an atomic structure as well as chemical properties are extremely important. The chemical properties are investigated by some surface analytical techniques such as x-ray photoelectron spectroscopy (XPS)[1], infrared spectroscopy[2], etc., few studies on the atomic structure of these amorphous thin films are present.

X-ray diffraction technique is a valuable method for studying the quantitative structural analyses of amorphous materials. Since the penetration depth of x-rays with the ordinary diffraction geometry is about of the order of a few hundred micron meters, the ordinary diffraction method is not appropriate for structural studies of a thin amorphous film grown on a substrate. The Seemann-Bohlin geometry with a small angle of incidence is often used for the structural characterization of thin crystalline films. This method has also been successfully applied to the structural analysis of the amorphous film whose thickness is of the order of a few micron thick[3]. In the thin amorphous films of a few hundred nm or less, however, quite a large scattering from the substrate is always observed and this becomes serious especially at a higher scattering angle. The large scattering intensity from the substrate is often hardly corrected, which disables to obtain the precise scattering from the amorphous film itself for a further quantitative structural analysis. Thus, in the present study, the grazing incident x-ray scattering technique was used for the structural analysis of $SiO_x$ amorphous films of a few hundred nano meters thick.

X-rays are totally reflected on the surface of thin films and strongly attenuated at small incident angle less than a critical angle. Marra et al.[4] utilized the x-ray total external-reflection phenomena and developed a new technique for surface structural studies by x-rays in Fig.1. This method is often called the grazing incidence x-ray scattering method (hereafter referred to as GIXS method). This GIXS method has been applied to many surface structural studies. The x-ray penetration depth changes from several hundred nm to a few nm by varying the incident angle from below to above the critical angle. When the incident angle is set to neighbor of the critical angle, the x-ray penetration depth is limited to a few nm to a few hundred nm. In this way, we can determine even the scattering from an amorphous film of a few 100 nm or less without any contribution from the substrate. The quantitative structural analysis of the amorphous thin films by the GIXS method has been firstly carried out by Fuoss et al.[5] in the $GeSe_2$ amorphous film.

In the present study, this GIXS method has been applied to measure the scattering intensity from the $SiO_x$ amorphous films of 200 nm thick grown in different conditions. One $SiO_x$ amorphous film was grown in $SiH_4$, $N_2O$ and He atmosphere and another in $SiH_4$, $N_2O$, He and $N_2$ atmosphere. By analyzing the observed intensities

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from these two films, the difference of atomic structures depending on the presence of $N_2$ gas during the growth of the film will be revealed and the difference of the electric properties in these films will be discussed.

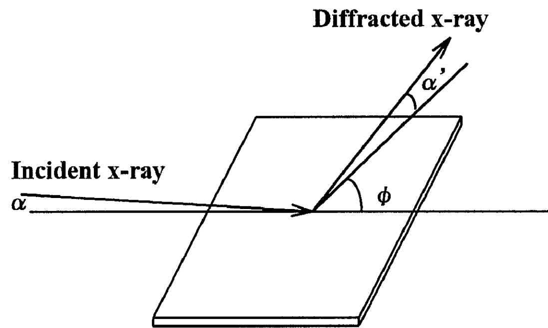
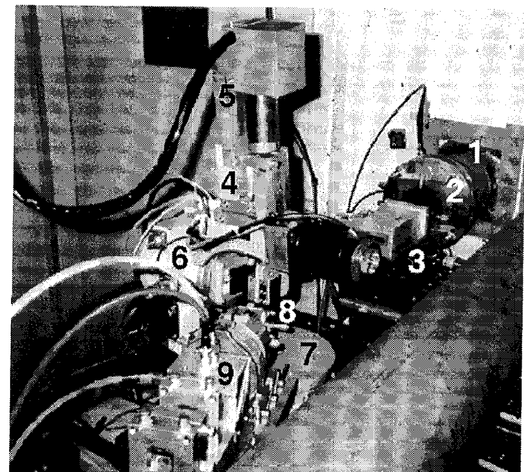



**Figure 1.** The schematic diagram of the grazing incident x-ray scattering (GIXS) geometry.

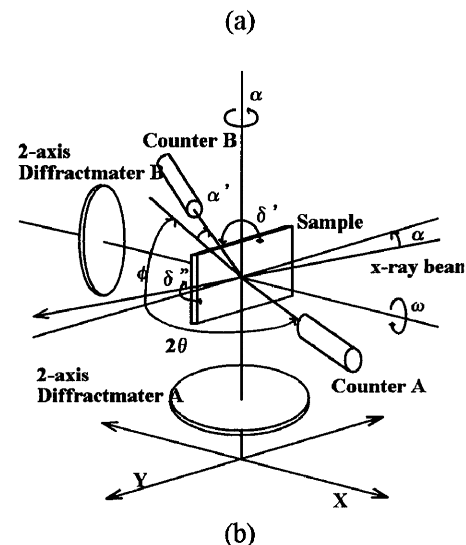
## 2. Experimental

$SiO_x$ amorphous films of 200nm thick were deposited by the plasma enhanced chemical vapor deposition on a Cr substrate grown on a glass plate of Corning 7059. Two kinds of $SiO_x$ amorphous films were prepared. One $SiO_x$ film was deposited in $SiH_4$, $N_2O$ and He atmosphere at a total gas pressure of 0.30 torr. Another film was prepared in $SiH_4$, $N_2O$, He and $N_2$ atmosphere at a total gas pressure of 0.75 torr. Namely, the difference between these two amorphous films is whether it is grown in the atmosphere containing $N_2$ or not. During the deposition, a temperature of the substrates for both films was kept at 573K.

The GIXS measurements were carried out at BL-6B in the photon factory of National Laboratory for High-Energy Physics, Tsukuba, Japan. The diffractometer[6,7] which was specially developed for the GIXS measurement was used in the present study. The experimental setting in the present measurement at the photon factory is shown in Fig.2(a). The angular motions built in this diffractometer are explained in Fig.2(b). The monochromatic x-ray with the wavelength of 0.09nm was obtained with the double Si111 crystal monochromator installed at BL-6B. As seen in Fig.1, the incident angle to the film surface was adjusted by rotating round the α axis. The reflection from the surface was observed by rotating the counter A in Fig.2(b) round the 2θ axis coupled with the rotation round the α axis so that the angle of α becomes a half of the 2θ angle. The α and α′ rotations were used to determine the grazing angles of the incident and diffracted beams, respectively. Since the film is amorphous in the present study, the scattering intensity with the GIXS geometry was observed by only rotating the counter B round the φ-axis in Fig.2(b). In this way, the absorption by the film is independent of the scattering angle. Thus, in this kind of geometry, it is not necessary to correct the absorption effect in the structural analysis of amorphous materials. Because the counter B was scanned round the φ axis with an extremely small incident angle α and the synchrotron radiation is almost completely polarized in the orbital plane, the polarization effect is ignored in the present analyses of the scattering intensity. The intensity of the incident beam was monitored with the ionization chamber which was placed just in front of the sample film.




(a)




(b)

**Figure 2.** (a) Experimental setting used at BL-6B in the Photon Factory, Tsukuba Japan for the GIXS measurement. (1: the beam path for incident x-rays, 2: the incident slits, 3: the ionization chamber as a monitor, 4: the sollar slits for diffracted beams, 5: the scintillation counter (the counter B in figure (b)), 6: the double axis diffractometer (the diffractometer B in figure (b)), 7: the double axis diffractometer (the diffractometer A in (b)), 8: the SiOx amorphous film, 9: the ionization chamber for measurements of a reflection profile.) (b) Schematic diagram of the angular geometry in the GIXS diffractometer.

## 3. Results and Discussion

The reflection curves of the $SiO_x$ amorphous films grown with and without $N_2$ gas are shown in Fig.3. The refraction index of a substance for x-rays is given by

$$n = 1 - \delta - i\beta, \qquad (1)$$

where

$$\delta = \frac{N_A r_e \lambda^2 \rho}{2\pi} \frac{Z + f'}{M}, \quad (2)$$

and

$$\beta = \frac{N_A r_e \lambda^2 \rho}{2\pi} \frac{f''}{M} = \frac{\mu \lambda}{4\pi}. \quad (3)$$

In eqs. (2) and (3), $N_A$ is Avogadro's number, $r_e$ the classical electron radius, $\lambda$ the wavelength of incident x-ray, $\rho$ the density of the reflected substance, $Z$ the atomic number and $M$ the atomic mass. $f'$ and $f''$ are the real and imaginary parts of the anomalous dispersion term. The critical angle $\alpha_c$ is evaluated by

$$\alpha_c = \sqrt{2\delta}. \quad (4)$$

Thus, it is easily noted that the critical angle depends on the values of $\rho$ and $\lambda$. Three steps are observed at about 0.04°, 0.13° and 0.22° in the reflection curves of Fig.3. The step at about 0.22° corresponds to the reflection by the Cr substrate under the $SiO_x$ amorphous film and the second one at about 0.13° to that by the surface of $SiO_x$ amorphous film. The third one at the lowest angle may be attributed to the reflection of the $SiO_x$ amorphous film by the higher harmonic of $\lambda/3$ which is diffracted by Si 333 of the double crystal monochromaotor. Quite sharp oscillations observed between the critical angles of $SiO_x$ and Cr are due to interference of x-rays reflected by the $SiO_x$ surface and the Cr substrate. It is obvious from the fact that the thickness evaluated from the period of these oscillations coincides with that of the present $SiO_x$ amorphous film.

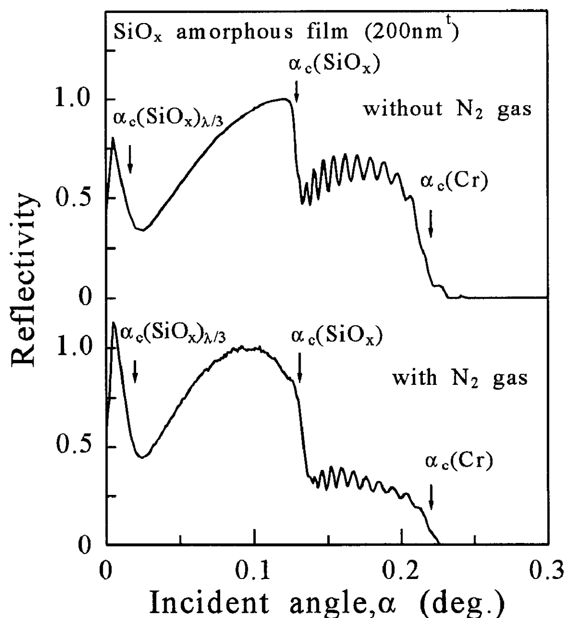



**Figure 3.** X-ray reflection curves of $SiO_x$ amorphous films of 200 nm thick grown on Cr polycrystals. These two profiles correspond to the $SiO_x$ amorphous films produced in the atmosphere without and with $N_2$ gas.

The penetration depth of x-rays by the GIXS geometry is evaluated by the 1/e penetration depth, i.e.

$$D(\alpha) = \frac{\lambda}{4\pi q}, \quad (5)$$

where

$$2q^2 = \sqrt{\left(\alpha^2 - \alpha_c^2\right)^2 + 4\beta^2} + \alpha^2 - \alpha_c^2. \quad (6)$$

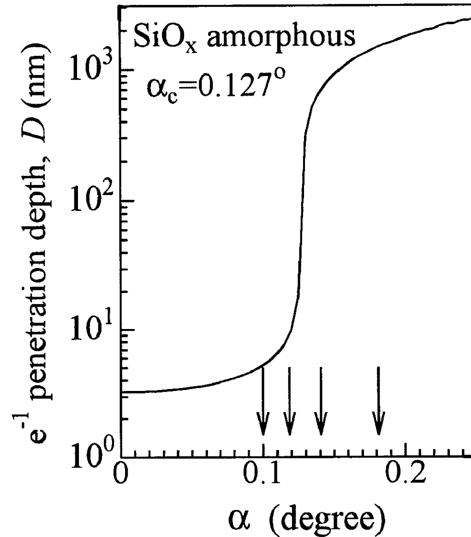



**Figure 4.** Calculated 1/e penetration depth in $SiO_x$ amorphous film grown without $N_2$ gas using the experimental critical angle of 0.127° in Fig.3. The incident angles used for the present measurements in Fig.5 are indicated with arrows.

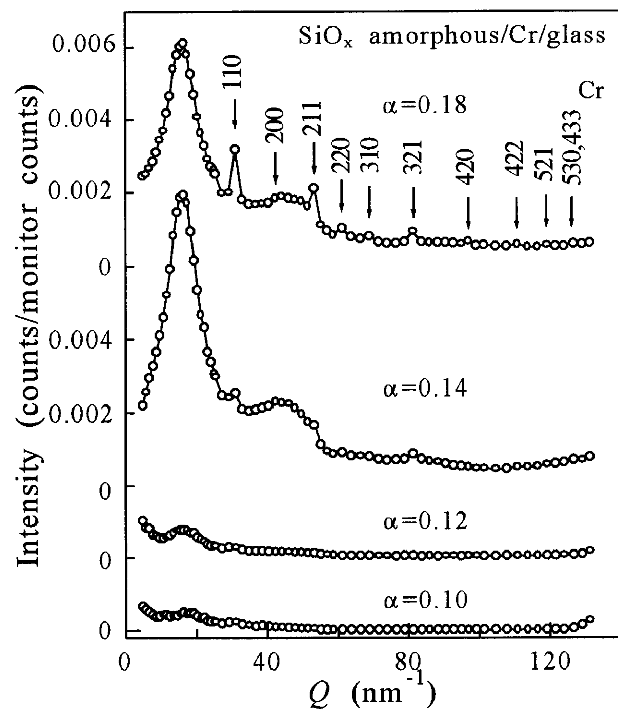



**Figure 5.** Scattering intensity profiles of a $SiO_x$ amorphous film of 200 nm thick grown on Cr polycrystals at various incident angles $\alpha$ in the vicinity of its critical angle.

The penetration depth calculated by eq.(6) for the $SiO_x$ film grown without $N_2$ gas, using the critical angle of 0.127° experimentally determined in Fig.3 is shown in Fig.4. From this figure, it is seen that the penetration depth changes from the order of $10^3$ nm to 1 nm by reducing the angle of incidence across the critical angle. The scattering intensities from the $SiO_x$ amorphous film in Fig.5 were observed at four incident angles in the vicinity of the critical angle as they are indicated with arrows in Fig.4. Quit sharp Bragg peaks of the polycrystalline Cr substrate are observed in the scattering profile at $\alpha$=0.18°. These peaks almost disappear in the measurement at $\alpha$=0.14° just above the critical angle. They completely disappear at $\alpha$=0.12° and 0.10° below the critical angle. Thus, it is clearly seen that the scattering intensity from the amorphous thin film can be obtained with the GIXS method in the vicinity of the critical angle without being prostrated by the scattering intensity from the substrate. It must be also noted in Fig.5 that the scattering intensity rapidly decreases at the measurements below the critical angle. The drastic decrease in the penetration depth of x-rays below the critical angle which is shown in Fig.4 results in the drastic reduction of the sample volume contributing to scattering. Consequently, in the measurement below the critical angle, the only scattering intensity from the thin amorphous film can be obtained without any contribution from the substrate, but on the other hand, the scattering intensity decreases enormously. In the present measurement, referring to the scattering profiles in Fig.5, the incident angle of $\alpha$=0.14° just above the critical angle was selected for the measurement to compare the atomic structures of $SiO_x$ amorphous films due to the difference of the atmosphere including $N_2$ gas or not during production of the films. The small peaks by Cr in the intensity profile at $\alpha$=0.14° were eliminated by removing a few points at the positions of the small peaks of Cr, such as 110, 211, 310 and 321.

The penetration depth of x-rays at 0.14° evaluated by eq.(4) is larger than the total thickness of the $SiO_x$ films. This is consistent with the fact that the small Bragg peaks of Cr were observed in the scattering profile of Fig.5. Because the total thickness of the present $SiO_x$ film is 200 nm, it is expected that the structural information from all through the film is obtained in the present GIXS measurement. Thus, the data was analyzed with the method for intensity data by the ordinary diffraction geometry. The interference functions of the two $SiO_x$ amorphous films are compared in Fig.6. For a reference, the interference function obtained in the $SiO_2$ glass with the ordinary x-ray diffraction is also shown in the figure. The essential features of the functions for these amorphous thin films resembles that for the $SiO_2$ glass. This indicates that the basic net work structures formed by $SiO_4$ tetrahedra observed in $SiO_2$ glass would be also found in the present $SiO_x$ amorphous films.

The radial distribution functions (RDFs) estimated by the Fourier transformation of the interference functions in Fig.6 are shown in Fig.7. As it has been expected in the interference functions in Fig.6, the essential RDF profiles resemble each other. The coordination numbers and atomic distances has been determined by fitting the experimental interference functions to the ones calculated by the following equation with the non-linear least-squares method[8].

$$Qi(Q) = \sum_{j=1}^{n}\sum_{k=1}^{m_{jk}} c_j N_{jk} e^{-b_{jk}Q^2} \frac{f_j f_k}{\langle f \rangle^2} \frac{\sin(Qr_{jk})}{r_{jk}} + 4\pi\rho_o \sum_{j=1}^{n}\sum_{k=1}^{n} \frac{c_j c_k f_j f_k}{\langle f \rangle^2} e^{-B_{jk}Q^2} \frac{QR_{jk}\cos(QR_{jk}) - \sin(QR_{jk})}{Q^2} \tag{7}$$

In Figs.6 and 7, the dotted curves correspond to these calculated ones. The coordination numbers and atomic distances determined in the present samples by this least-squares method, are summarized in **Table 1**.

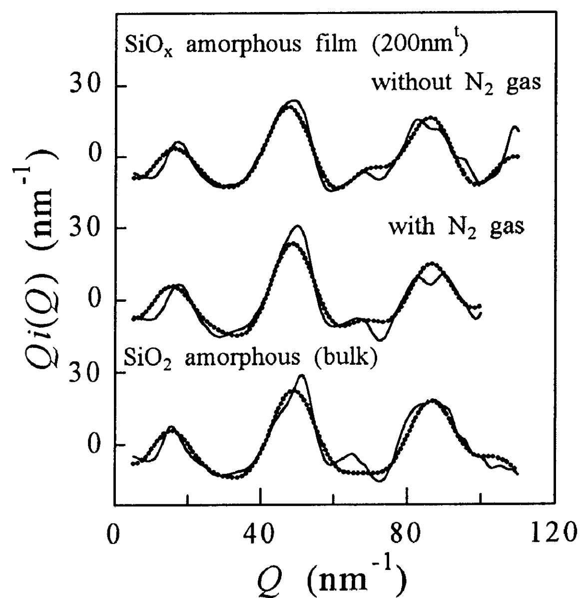



**Figure 6.** Interference functions of $SiO_x$ amorphous films grown in the atmosphere without and with $N_2$ gas are compared. As a reference, the interference function of $SiO_2$ glass is also shown.

**Table 1** Coordination numbers and atomic distances of $SiO_x$ amorphous films grown in the atmosphere without and with $N_2$ gas, and the bulk $SiO_2$ glass. The errors of the atomic distances and coordination numbers are ±0.001nm and ±0.2, respectively. The densities of the $SiO_x$ amorphous films with and without $N_2$ gas evaluated from the reflection profiles are 2.27 and 2.24 g/cm$^3$, respectively. Incidentally, the density of $SiO_2$ glass is 2.204g/cm$^3$.

| Sample | Si-O | | O-O | | Si-Si | |
|---|---|---|---|---|---|---|
| | $r$/nm | $N$ | $r$/nm | $N$ | $r$/nm | $N$ |
| $SiO_x$ amorphous thin films | | | | | | |
| without $N_2$ gas | 0.168 | 3.8 | 0.268 | 5.5 | 0.308 | 4.6 |
| with $N_2$ gas | 0.161 | 4.2 | 0.268 | 6.2 | 0.310 | 4.8 |
| $SiO_2$ glass | 0.161 | 3.9 | 0.266 | 6.3 | 0.310 | 4.6 |

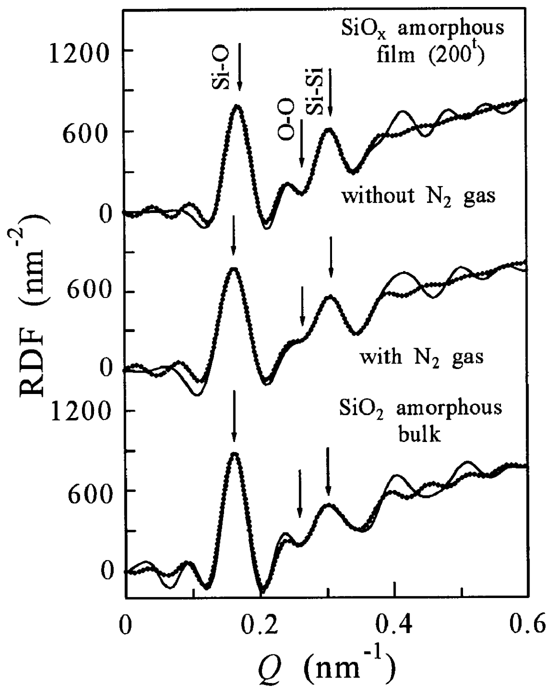



**Figure 7.** Radial distribution functions (RDFs) of $SiO_x$ amorphous films grown in the atmosphere without and with $N_2$ gas are compared. The RDF of $SiO_2$ glass is also shown.

It is found in the structural parameters for $SiO_2$ glass in Table 1 that Si atoms are surrounded by 4 oxygen atoms. This indicates that its local unit structure is the $SiO_4$ tetrahedra. The coordination numbers of O-O pairs is about 6 and that of Si-Si pairs is about 4. This implies that the $SiO_4$ tetrahedra are connected by sharing oxygen atoms at the vertices of the $SiO_4$ tetrahedra. That is, the atomic structure of the $SiO_2$ glass is the network structure consisting of the $SiO_4$ tetrahedra. This result is consistent with the results by the previous workers).

By comparing the structural parameters of the $SiO_x$ amorphous thin films and the $SiO_2$ glass in Table 1, the coordination numbers and atomic distances of the $SiO_x$ amorphous film grown in the atmosphere including $N_2$ gas resemble those of the $SiO_2$ glass. On the other hand, a couple of distinct differences are observed in the $SiO_x$ amorphous film grown in the atmosphere without $N_2$ gas. First, the coordination number of O-O pairs is about 10% less than that of another $SiO_x$ film or $SiO_2$ glass. Secondly, the atomic distance of Si-O pairs is about 4% longer than the others. From these observation, it has been deduced that the $SiO_x$ amorphous film grown with $N_2$ gas forms the network structure consisting of $SiO_4$ tetrahdera sharing oxygen at the vertices. This network structure is, however, slightly modified in the $SiO_x$ amorphous film grown without $N_2$ gas. Although the coordination number of Si-O pairs in this modified network structure is almost equal to 4, its atomic distance is larger. Furthermore, in this modified network structure, the number of O-O pairs is much less than 6. This suggests that in the modified network structure the local unit structure would be $SiO_4$ tetrahedra and some of the tetrahedra may not be connected by sharing oxygen atoms located at the vertices of the tetrahedra. The appearance of these network structures in both $SiO_x$ amorphous films are schematically shown in Fig.8. In the network structure observed in the ordinary $SiO_2$ glass or the $SiO_x$ amorphous film grown with $N_2$ gas, all oxygen atoms have 6 nearest neighboring oxygen atoms. When the network is disconnected as it is shown in Fig.8(b), oxygen atoms which have no neighboring tetrahedra have only 3 nearest neighboring oxygen. Thus, the average coordination numbers of O-O pairs decrease in the modified network structure of Fig.8 (b). It is easily imagined that the atomic distance of Si-O pairs might be longer in the modified network structure as it is shown in Fig.8 (b) than that in the complete network structures in Fig.8 (a). The $SiO_x$ amorphous film grown without $N_2$ gas gives a striking contrast to that of the amorphous $SiO_x$ film grown with $N_2$ gas. It is expected that this difference in the network structure is closely related with the fact that the $SiO_x$ amorphous films grown with $N_2$ gas is a better insulator than the one grown without $N_2$ gas. In the above discussion, however, the role of $N_2$ gas has not been clearly understood yet. According to the observation by the infrared spectroscopy[10], it has been reported that nitrogen atoms is taken in the Si-O network structure. Therefore, it is plausible that by adopting nitrogen atoms in the network structure, the imcoplete network structure in Fig.8(b) may be fixed to form the complete network structure in Fig.8(a).

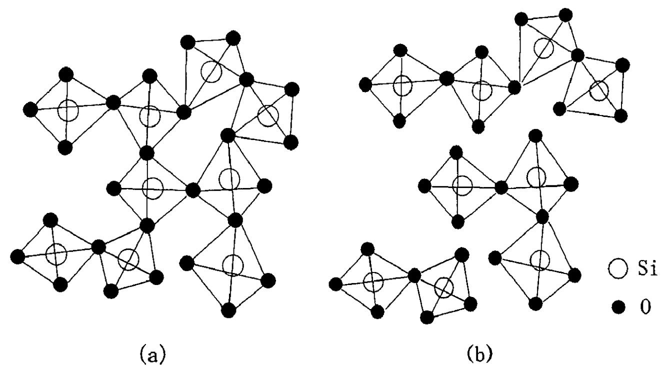



Figure 8. The schematic diagram of the two different network structures measured in the two $SiO_x$ amorphous films grown (a) with and (b) without $N_2$ gas.

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