Structure of Amorphous Silicon Nitride (α - Si_3N_4)

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Computer simulation, using the molecular dynamics (MD) technique, has been carried out on an silicon nitride (α - Si_3N_4) with simple Busing-type potentials. Furthermore, the local structure of chemical vapor-deposited (CVD) α - Si_3N_4 has been studied at the Si K-edge by the use of a laboratory XAFS system. From the MD simulation and XAFS results, the short-range structural arrangement of α - Si_3N_4 comprises tetrahedral SiN_4 units. The MD and XAFS results presented in this study also indicate that there exist only a small number defects such as dangling bonds.

1. Introduction

Silicon nitride (Si_3N_4) is well known as a potentially useful refractory ceramics. Recently, it has been shown that the amorphous silicon nitride (α - Si_3N_4) prepared by chemical vapor deposition (CVD)¹⁾ can be used as a dielectric layer in microelectronics technology because of its high dielectric constant, high density, high resistance against radiation, high temperature stability and its high barrier against alkali-ion migration or impurity diffusion²⁾. For silicon oxide, there is a long history of research and development, and a huge amount of data has been accumulated. On the other hand, for silicon

nitride much less is known. The urgent necessity for materials with high dielectric constants and resistance against alkali-ion migration has meant that Si_3N_4 has been used in practical silicon device applications without basic background research on the atomic and electric structures.

Radial distribution functions (r.d.f.) for α - Si_3N_4 were reported from X-ray³⁾, pulsed neutron⁴⁾ and electron^{5,6)} scattering experiments and EXAFS analyses⁷⁻⁹⁾. The X-ray diffraction result³⁾ has suggested that the short-range structure of CVD α - Si_3N_4 resembles that of crystalline α - Si_3N_4 but includes some deficiency in the stoichiometric valence numbers for the

coordination between nearest-neighbor atoms⁴⁾. The neutron scattering data⁴⁾ gave information on the short-range structure of α - Si_3N_4 , i.e., the Si-N bond length and the coordination numbers $N_{\text{Si/N}}$ and $N_{\text{N/Si}}$, and indicates the existence of voids. A modeling study of the atomic arrangement using plastic balls and spokes with Keating-type potential¹⁰⁾ was performed, but, unfortunately, the model structure was constructed according to unsuitable structural rules. Raman spectroscopic measurement on α - Si_3N_4 has also been briefly reported¹¹⁾.

Molecular dynamics (MD) simulation has been used extensively as an aid of developing an understanding of the local coordination characteristics of amorphous materials. No MD calculation has, however, been tried for covalently bonded α - Si_3N_4 , to determine the local structure and to help interpret the experimental results obtained. XAFS spectroscopy has also been used for investigating the structure of disordered materials. However, XAFS experiments in the soft X-ray domain 700 to 3000 eV appear less developed than those in the hard X-ray or VUV regions; the reason may lie in some intrinsic experimental difficulties in terms of monochromators, sample preparation and even theoretical background, etc.¹²⁾. EXAFS investigations

of amorphous silicon alloys were reported, but, unfortunately, the local structure in the silicon nitride compounds reported in these papers⁷⁻⁹⁾ was not fully discussed.

The aim of the present study is to investigate the characteristics of the atomic scale structure of α - Si_3N_4 by an MD simulation with simple Busing-type potential. Furthermore, we examined the local structure of CVD α - Si_3N_4 from the experiments on Si *K*-edge by the use of a laboratory XAFS facility.

2. Experimental

2.1 MD simulation

The most important factor in MD models is the accuracy of the potential equation which is chosen to simulate the forces between atoms. In this study, the pair potential functions are assumed to consist of simplified Coulombic and repulsive terms:

$$u_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp \left[\frac{(a_i + a_j - r_{ij})}{b_i + b_j} \right] \quad (1)$$

where z_i is the formal charge number of atom i (e.g., +4 for Si^{4+}), e the unit charge, r_{ij} the distance between ions i and j , f_0 a force constant, arbitrarily taken here to be 1 kcal·mol⁻¹·Å⁻¹, and a_i and b_i are the crystal radii and compressibility of atom i , respectively. We empirically determined

the potential parameters given in Table 1. In order to check the validity of the set of potential parameters used, an MD simulation of α - and β -Si₃N₄ crystals^{13,14}) has been performed, and these crystal structures have been stably reproduced at 300K.

Table 1 Potential Parameters for Eq. (1).

	Relative atomic mass, W_i	Formal charge, Z_i	Crystal radius, a_i	Compres- sibility, b_i
Si	28.09	+4	1.012	0.080
N	26.09	-3	1.756	0.085

A cubic basic cell was assumed for all the MD simulations. The edge length of the basic cell was calculated from the observed density of CVD a-Si₃N₄ ($\rho=2.60\text{g/cm}^3$)³). The number of particles within a basic cell was 420 (Si:180; N:240) or 1260 (Si:540; N:720) for a-Si₃N₄. The time increment, Δt , must be sufficiently short to satisfy the conditions of energy conservation. We choose here $\Delta t=2.5 \times 10^{-15}\text{s}$ which corresponds to a mean fluctuation in the internal energy of <0.1%. In evaluating the potential energy and force, the Coulombic term was calculated at each time step by the application of the Ewald method¹⁵). In most case, the 3000 time steps after equilibrium were used for calculations of the various properties. The average temperature was 300K.

2.2 XAFS measurements

The sample of a-Si₃N₄ was prepared from a gaseous mixture of NH₃ and H₂-carried SiCl₄ by the chemical vapor-deposition technique at a deposition temperature 1300°C and under a total gas pressure of 20torr. Details of the sample preparation have been reported in a previous paper¹). The average density of the sample was 2.6g/cm^3 .

We have performed the transmission experiments at the Si K-edge of the sample films by the use of the laboratory XAFS facility which consists of rotating anode X-ray generator, vacuum X-ray path, bent PET(002) ($2d=8.742\text{\AA}$) crystal monochromator and solid state detector (SSD). We used the conventional vacuum system maintained inside the X-ray path by means of a thin beryllium window at the front of the rotating anode X-ray generator. Details of the X-ray spectrometer used here have already been described in the previous paper¹⁶).

The Si K-edge absorption spectra of the CVD a-Si₃N₄ have been collected up to about 400eV above the absorption edge for EXAFS studies and up to about 60eV for XANES studies. The additional measurements were also made on the silicon-based crystalline materials such as

α/β - Si_3N_4 , c-Si, β -sialon ($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$; $z=2$) and quartz SiO_2 .

The obtained data were analyzed according to a standard procedure¹⁷⁾. After the subtraction of the Victoreen-type baseline of pre-edge region, EXAFS spectrum $k^3\chi(k)$ vs. k (in $\text{\AA}^{-1}$) was extracted from the background determined by moving average method or automatic background removal¹⁸⁾. In order to obtain the local structure around silicon atoms, Fourier transformation of $k^3\chi(k)$ and least-square fitting in the filtered k -space were carried out utilizing the theoretical phase and amplitude functions of Mckale and Knapp¹⁹⁾.

3. Results and Discussion

3.1 MD simulation

Fig. 1 Structural view of a typical instantaneous configuration for MD-simulated α - Si_3N_4 at 300K.

Fig. 1 shows a structural view of a typical instantaneous configuration of α - Si_3N_4 at 300K from our MD simulation. The silicon atoms form nearly regular SiN_4 tetrahedra with a peak around 109° in $\angle\text{N-Si-N}$ angle distribution. Each silicon atom is coordinated by four nitrogen atoms, and each nitrogen is approximately shared by three tetrahedra in such a way that the SiN_4 tetrahedra are joined only at the corners. It is well known that silicon nitride has two crystalline forms, designated as α -¹³⁾ and β - Si_3N_4 ¹⁴⁾, with the same SiN_4 tetrahedral units. The $\angle\text{N-Si-N}$ tetrahedral angle (109.8°) obtained from our MD-simulated α - Si_3N_4 is almost equal to the bond angle (109.28°) for an ideal tetrahedron and to the bond angle (109.8°) obtained from the neutron diffraction result⁴⁾ listed in **Table 2**. The SiN_4 tetrahedral units reported from X-ray/Neutron scattering analyses^{3,4)} are accurately reproduced by our MD simulation with simple ionic potentials. However, the ionic approximation result suggests that the wide distribution ($\pm 12.36^\circ$) of the $\angle\text{N-Si-N}$ tetrahedral angle is caused by the lack of the directionality in the ionic potentials. The ball-and stick model¹⁰⁾ gives ($\pm 5.7^\circ$) which is too narrow. In addition to showing the wide scatter of the inter tetrahedral ($\angle\text{N-Si-N}$) angle, the angular analysis reveals that the mean bond

angle is quite close to $127.08^\circ \pm 16.63^\circ$. This bond angle is quite close to a plane triangle (120°). The MD results also indicated that most of the SiN₄ tetrahedra were present as the polymerized units such as 6, 7, 8 and 9 membered rings in medium-range order.

Table 2 Average nearest-neighbor distances, r_{i-j} and coordination number, $N_{i/j}$, for atoms j around any origin atom i obtained from our EXAFS result. Included in this table for comparison are data from the MD simulation⁸⁾, X-ray³⁾, neutron⁴⁾ and electron⁵⁾ diffraction.

a-Si ₃ N ₄				
i-j pair	r_{i-j} (Å)	$N_{i/j}$ (atoms)	σ^2_{ij} (Å ²)	θ (deg)
Si-N				
MD cal.	1.74	3.95		
EXAFS	1.77	4.1	0.0057 ^a	
X-ray ³⁾		1.75		
Neutron ⁴⁾	1.729	3.7	0.0050 ^b	
Electron ⁵⁾	1.75			
N-N				
MD cal.	2.65			109.8 ^c
Neutron ⁴⁾	2.83	7.7	0.026 ^b	109.8 ^c
Si-Si				
MD cal.	3.02	7.09		127.1 ^d
EXAFS	2.98	7.5	0.014 ^a	114.7 ^c
Neutron ⁴⁾	3.01	6.5	0.026 ^b	121.0 ^c

a EXAFS Debye-Waller factor

b Root-mean-square displacement of the $i-j$ bond length obtained by Gaussian fitting of the peaks in the rdf curve.

c $\pm 12.36^\circ$

d $\pm 16.63^\circ$

As listed in Table 2, the MD-simulated coordination numbers of $N_{Si/N}=3.95$,

$N_{N/N}=8.30$ and $N_{Si/Si}=7.09$ were smaller the values of 4, 9 and 8 which were calculated assuming that there were no dangling bonds and no N-N and Si-Si bond in a-Si₃N₄. We have found the presence of defects such as dangling bonds in the amorphous structure of Fig.1. Form the rdf analysis of the neutron scattering data, Misawa et al.⁴⁾ indicated that the existence of defects such as voids was consistent with deficient with deficiency coordination numbers obtained, and they estimated that the proportions of Si and N atoms with dangling bonds sitting on the surfaces of voids were 0.05 and 0.07, respectively. Our MD simulation also gives similar values: 0.07 and 0.05.

3.2 XAFS measurements

Fig. 2 shows the X-ray absorption silicon near edge structures for a- and α/β -Si₃N₄, β -sialon, c-Si and quartz SiO₂. These XANES are normalized of the the maximum of absorption for qualitative analysis. In these samples each silicon is four-fold coordination, and hence their spectra are very similar to each other. It can therefore be concluded from these spectra that conventionally-termed 'short range order' of a-Si₃N₄, i.e., the basic structural unit and the relative configuration of adjacent structural units, is similar to that of α/β -Si₃N₄.

Fig. 2 XANES spectra of CVD a-Si₃N₄ and the reference silicon compounds.

Fig. 3 Fourier transform of CVD a-Si₃N₄ and α/β-Si₃N₄.

Fourier transforms for α/β- and a-Si₃N₄ obtained from the Si EXAFSs are shown in Fig. 3. As shown in this figure, the profile of the a-Si₃N₄ is almost the

same as the profiles of the α/β-Si₃N₄. The first peaks in the obtained Fourier transforms correspond to the Si-N bond in the a-Si₃N₄, and the second peaks are due to the Si-Si bond. The result of the curve fitting to the $k^3\chi(k)$ spectrum of the a-Si₃N₄ is given in Table 2. Included in this table for comparison are our MD simulation and the reported X-ray³⁾, neutron⁴⁾ and electron⁵⁾ diffraction results. The average Si-N bond length obtained from our EXAFS result was $r_{\text{Si-N}}=1.77\text{\AA}$, and its coordination number $N_{\text{Si/N}}$ was 4.1. Hence, the silicon atoms form nearly regular SiN₄ tetrahedra as the basic structural unit in the a-Si₃N₄. It is well known that silicon nitride has two crystalline forms, designated as α- and β-Si₃N₄, with the same SiN₄ tetrahedral units (α-Si₃N₄: $r_{\text{Si-N}}=1.759\text{\AA}$; β-Si₃N₄: $r_{\text{Si-N}}=1.776\text{\AA}$). The average Si-Si bond distance and coordination number were $r_{\text{Si-Si}}=2.98\text{\AA}$ and $N_{\text{Si/N}}=7.5$, respectively. Each silicon atom is also coordinated by four atoms, and each nitrogen is approximately shared by three tetrahedra in such a way that the SiN₄ tetrahedra are joined only at the corners. As listed in Table 2, the EXAFS-derived coordination number of $N_{\text{Si/Si}}=7.5$ was smaller than the value of 8 which was calculated assuming that there were no dangling bonds and no N-N and Si-Si

bonds in a-Si₃N₄. We can estimate from the obtained deficient coordination number of the Si-Si bond that there exist only a small number of defects such as dangling bonds in the a-Si₃N₄. Misawa et al.⁴⁾ indicated the existence of the defects in the a-Si₃N₄. The obtained value for the mean bond angle around a N atom, $\angle \text{N-Si-N} = 114.7^\circ$, is slightly lower than an ideal plane triangle (120°). This result indicates that there are many distorted inter-tetrahedral bonds in the CVD a-Si₃N₄.

4. Conclusion

Computer simulation, using the molecular dynamics (MD) technique, has been carried out on an amorphous silicon nitride (a-Si₃N₄) with simple Busing-type potentials. From the MD simulation, the following points have been deduced: The short-range structural arrangement of a-Si₃N₄ composes tetrahedral SiN₄ units, and medium-range structure consists of a mixture of 6, 7, 8 and 9 membered rings. Our MD results also indicate that there exist only a small number of defects such as dangling bonds. The a-Si₃N₄ structure can be reported by our MD simulation.

X-ray absorption measurement near Si *K*-edge for the CVD a-Si₃N₄ has been performed by the use of a laboratory XAFS system. From the obtained XAFS data, the

following points have been deduced: The XANES spectrum of the a-Si₃N₄ is similar to the XANES spectra of crystalline silicon compounds with Si four-fold coordination. The average Si-N bond length obtained from the EXAFS result is $r_{\text{Si-N}} = 1.77 \text{ \AA}$, and its coordination number $N_{\text{Si/N}}$ is 4.1. Hence, the short-range structural arrangement of the a-Si₃N₄ comprises tetrahedral SiN₄ units.

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