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Structural Characterization of Amorphous Silicon Nitride by Molecular Dynamics Simulation†

Norimasa UMESAKI*+

Abstract

Computer simulation using the molecular dynamics (MD) technique have been carried out on amorphous silicon nitride ($a-Si_3N_4$) with simple Busing-type potentials. From the MD simulation, the following points have been deduced:

(1) The average Si-N bond length obtained from our MD results is $r_{Si-N}=1.74$ Å, and its coordination number $N_{Si/N}$ is 3.95. The bond angle around a Si and a N atom, ∢ N-Si-N and ∢ Si-N-Si, are found to be 109.8°±12.36° and 127.08°±16.63°, respectively. The obtained ∢ N-Si-N value is in a very good agreement with that of a tetrahedral bond angle (=109.47°). Therefore, the short-range structural arrangement of $a-Si_3N_4$ is composed of the tetrahedral bond angle (=109.47°). Therefore, the short-range structural arrangement of $a-Si_3N_4$ is composed of the tetrahedral SiN_4 units. Our MD results also indicate that there exist only a small number of defects such as dangling bonds.

(2) Our MD results are in good agreement with the reported X-ray and neutron data. The $a-Si_3N_4$ structure can be reproduced by our MD simulation.

KEY WORDS: (Amorphous Silicon Nitride) ($a-Si_3N_4$) (Molecular Dynamics Simulation) (MD Simulation)

1. Introduction

Silicon nitride (Si_3N_4) is known as a potentially useful refractory ceramic. Recently, it has been shown that the amorphous silicon nitride ($a-Si_3N_4$) prepared by chemical vapor deposition (CVD) method[1] can be used as an important dielectric layer in microelectronic technology for its high dielectric constant, high density, high resistance against radiation, high temperature stability and its high barrier against alkali-ion migration or impurity diffusion[2]. For silicon oxide there is a long history of research and development, and a huge amount of data have been accumulated. On the other hand, for silicon nitride much less is known because the urgent necessity for materials with high dielectric constants and resistance against alkali-ion migration have obliged the Si_3N_4 to be used in practical silicon device processes without sufficient research background.

Radial distribution functions (RDF) of $a-Si_3N_4$ were reported from X-ray[3], pulsed neutron[4] and electron[5),6] scattering experiments and EXAFS analyses[7),8]. The X-ray diffraction result[3] has suggested that the short range structure of CVD $a-Si_3N_4$ resembles that of crystalline $\beta-Si_3N_4$ but includes some deficiency of stoichiometric valence numbers in the coordination between nearest neighboring atoms[4]. The neutron result[4] gave information on the short range structure of $a-Si_3N_4$, that is, the Si-N bond length and its coordination numbers $N_{Si/N}$ and $N_{N/Si}$, and indicated the existence of voids. A modeling of atomic arrangement using plastic balls and spokes with a Keating-type potential[9] was examined. Unfortunately, the model structure has been constructed under the unsuitable structural rules. Vibrational excitation of $a-Si_3N_4$ was briefly described by Raman spectroscopy[10].

Molecular dynamics (MD) simulation has been used extensively as an aid to developing an understanding of the local coordination characteristics of amorphous materials and/or glasses. No MD calculation for covalently bonded $a-Si_3N_4$ has been tried to elucidate the local structure and to check the experimental results obtained.

The aim of the present study is to seek the characteristics of the atomic scale structure of $a-Si_3N_4$ by a MD simulation with simple Busing-type potentials.

2. 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:

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*Present address: Material Physics Department, Government Industrial Research Institute, Osaka, 1-8-31, Midorigaoka, Ikeda, Osaka 563, Japan

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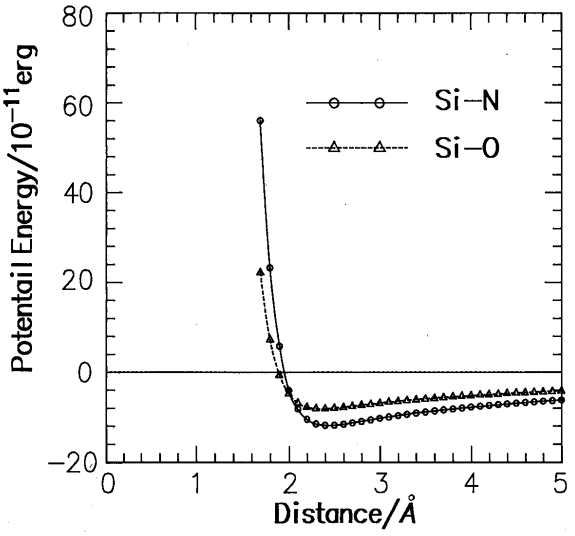

Fig. 1 Potential curves calculated for Si-N and Si-O from the Busing-type potential equation.

Table 1

	Relative atomic mass W	Formal charge Z	Crystal radius a	Compressibility b
Si	28.09	+4	1.012	0.080
N	26.98	-3	1.756	0.085

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

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 ion i and j, f_0 a force constant arbitrarily taken here to be 1kcal·mol^{-1}·$Å^{-1}$, and a_i and b_i are the crystal constant and compressibility of atom i, respectively. As shown in **Figure 1,** we empirically determined the potential parameters given in **Table 1.** Note the long tails of the potentials, which are the result of strong Si-N interaction. This figure also gives Si-O interaction for comparison.

A cube (basic cell) was assumed for all MD calculations. The edge length of the basic cell was calculated from the observed density value of the CVD a-Si_3N_4 ($\rho=2.60$g/cm^3)[3]. The number of particles within a basic cell was 420 (180 for Si^{4+} and 240 for N^{3+}) for a-Si_3N_4. The time increment Δt must be sufficiently short to satisfy the conditions of energy conservation. We choose here $\Delta t=2.5\times10^{-15}$sec which corresponds to a mean fluctuation of internal energy smaller than 0.1 per cent. In evaluating the potential energy and force, the Coulombic term was calculated at each time step by the application of the Ewald method[11]. Our MD calculations were made on personal computer systems - NEC PC-9801RA (CPU80386/16MHz+WTK3167) and PC-RA21 (CPU80386/20MHz+II2C87) by the use of a NDP-FORTRAN386 compiler. For 420 particles, a single time step was about 15 seconds. In most cases, the 3000 time steps after equilibrium were used for calculations of various properties. The average temperature for a-Si_3N_4 was 300K.

3. Results and Discussion

Figure 2 shows the structural view of a typical instantaneous configuration of a-Si_3N_4 at 300K form our MD

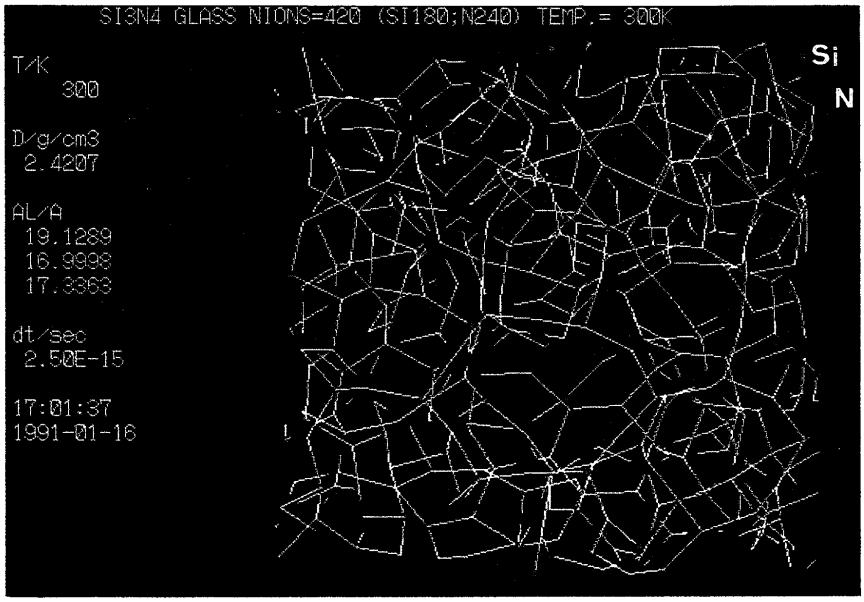

Fig. 2 Structural view of a typical instantaneous configuration of the MD-simulated a-Si_3N_4 at 300K.

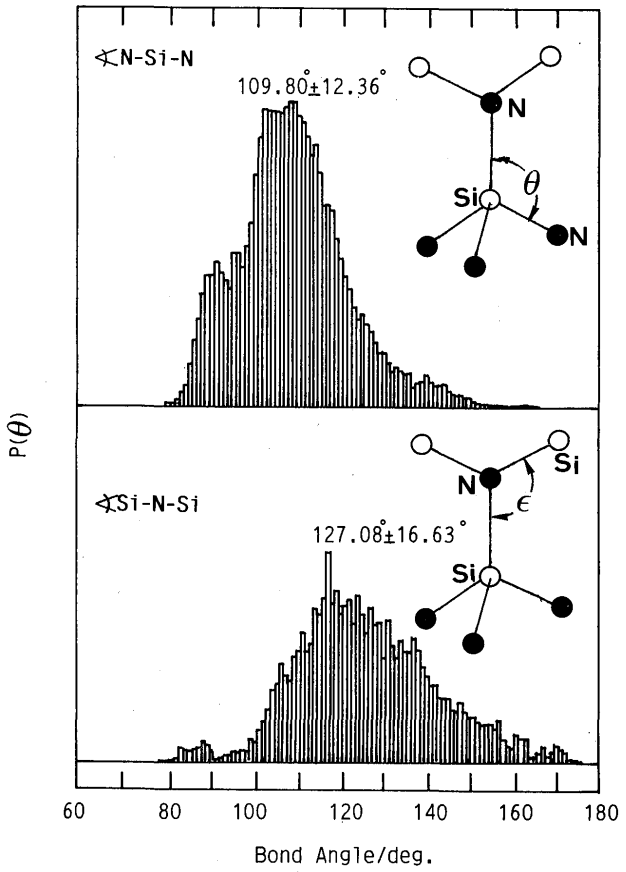

Fig. 3 Plots of distributions of ∢ N-Si-N tetrahedral angle and ∢ Si-N-Si intertetrahedral angle of the MD-simulated a-Si_3N_4 at 300K.

simulation. As shown in this figure, silicon atoms form nearly regular SiN_4 tetrahedra with a peak around 109° in ∢ N-Si-N angel distribution as shown in **Fig. 3,** 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[12] and β[13], with the same SiN_4 tetrahedral units. The ∢ N-Si-N tetrahedral angle (109.8°) obtained from our MD-simulated a-Si_3N_4 is almost equal to the bond angle (109.28°) of an ideal tetrahedron and to the bond angle obtained (109.8°) from the neutron diffraction result listed in **Table 2.** The Sin_4 tetrahedral units reported from the X-ray/neutron scattering analyses[3),4)] are accurately reproduced by our MD simulation with the simply ionic form potentials. However, the ionic approximation result suggests that wide distributions (±12.36°) of the ∢ N-Si-N tetrahedral angle are caused by the lack of directionality in the ionic potentials. The ball-and-stick model[9)] gives a bond-angle distribution (±5.7°) which is too narrow. In addition to showing the wide scatter of the intertetrahedral (∢ Si-N-Si) angle, the angular analysis reveals that the mean bond angle is 127.08°±16.63°. This bond angle is quite close to a plane triangle (120°). Unfortunately, there is no experimental work concerning the ∢ N-Si-N and ∢ Si-N-Si bond angle distributions of short range structure in a-Si_3N_4 until now. Therefore, the ∢ N-Si-N and ∢ Si-N-Si bond angle distributions in a-Si_3N_4 will be a matter of controversy for some time.

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 than the values of 4,9 and 8 which were calculated by the use of the assumption that there were no dangling bonds and no N-N and Si-Si bonds in a-Si_3N_4. We have found the presence of defects such as dangling bonds in the amorphous structure of Fig. 2. From the RDF analysis of the neutron scattering data, Misawa et al.[4)] indicated that the existence of defects such as voids is consistent with the deficient coordination numbers obtained, and they revealed that the proportions of atoms Si and N with dangling bonds sitting on the surface of the void were 0.05 and 0.07, respectively. Our MD simulation also gives similar values, 0.07 and 0.05.

In order to compare the structural information obtained by our MD simulation with that obtained from X-ray[3)]/neutron[4)] diffraction results, we calculated the total struc-

Table 2 Average nearest-neighbor distances r_{ij} and coordination numbers N_{ij} of atoms j around any origin atom i from the MD simulation, X-ray[3)], neutron[4)] and EXAFS[8)] data.

	Si–N				N–N		Si–Si	
	MD cal.	Neutron[4)]	X-ray[3)]	EXAFS[8)]	MD cal.	Neutron[4)]	MD cal.	Neutron[4)]
r_{ij}/Å	1.74	1.729	1.75	1.71	2.65	2.83	3.02	3.01
N_{ij}/atoms	3.95	3.70	—	3.90	8.3	7.7	7.09	6.5
θ/deg					109.8°	109.8°	127.08°	121.0°

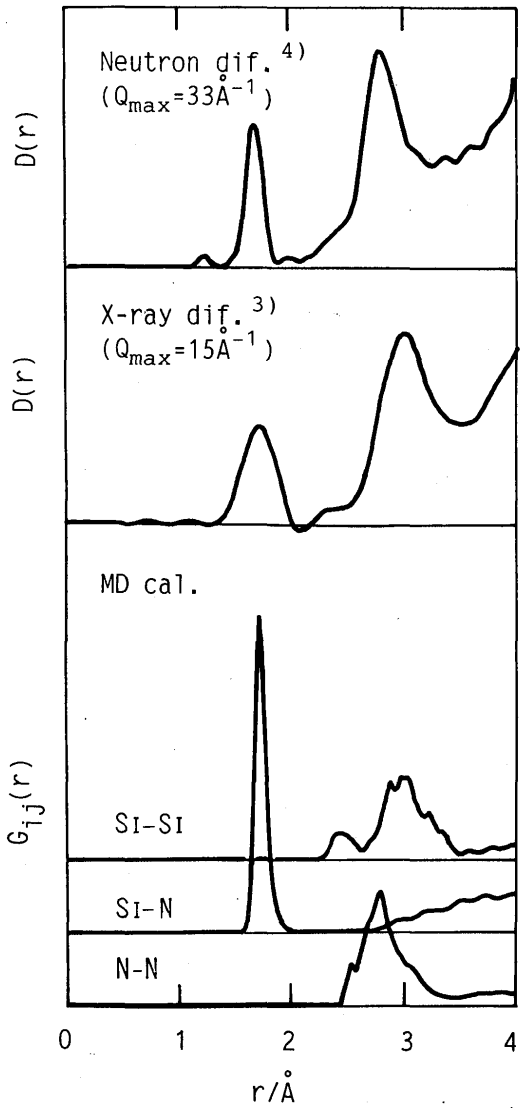

Fig. 4 Comparison of the pair correlation functions $G_{ij}(r)$ of atomic pairs N-N, Si-N and Si-Si in the MD-simulated a-Si_3N_4 at 300K with the experimental RDF curves[3),4)].

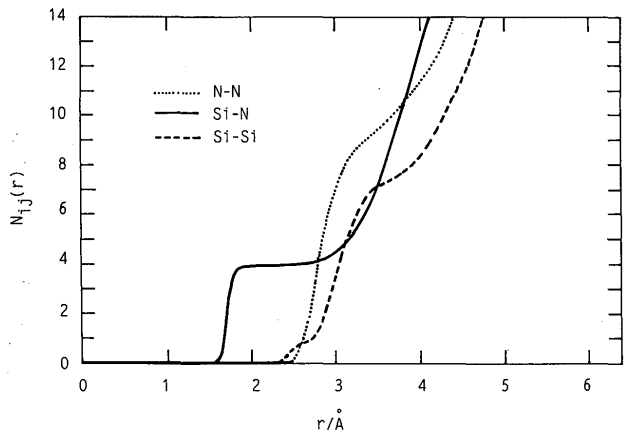

Fig. 5 Distribution of the coordination number $N_{ij}(r)$ of atomic pairs N-N, Si-N and Si-Si in the MD-simulated a-Si_3N_4 at 300K.

tural factros S(Q) in reciprocal space and the pair correlation functions $G_{ij}(r)$ in real space from the MD results. In ordinary X-ray/neutron diffraction measurements, the scattering intensity of X-ray/neutron beams is the primary structural information in reciprocal space. On the other hand, in MD simulation, positions of atoms as a function of time are the primary information. Therefore, the instantaneous structure is the most straight forward way of presenting the result of MD-derived simulation. The pair correlation function for the atomic species i and j, $G_{ij}(r)$, is obtained from the positional data accumulated during the final equilibrium (in the actural computation, the distance interval, Δr, is taken to be 0.1 Å.).

$$G_{ij}(r)=\left(\frac{V}{N_iN_j}\right)\left(\frac{n_{ij}(r)}{4\pi r^2}\right), \tag{2}$$

where $n_{ij}(r)$ is the time-averaged number of atomic pairs between i and j within a distance range from $r-\Delta r/2$ to $r+\Delta r/2$, N_i and N_j are the numbers of atomic species i and j in the basic cell, and V is the volume of the basic cell. The running coordination number, $N_{ij}(r)$, which is important in characterizing the coordination state of atoms, is given by

$$N_{ij}(r)=\sum_{r=0}^{r}\frac{n_{ij}(r)}{N_i}. \tag{3}$$

The pair correlation functions $G_{ij}(r)$ and the distribution of the coordination number $n_{ij}(r)$ of the atomic pairs N-N, Si-N and Si-Si in a-Si_3N_4 at 300K are illustrated in **Figs. 4** and **5.** Experimental RDF curves obtained from X-ray[3)] and neutron[4)] diffraction measurements are also shown in Fig. 4 for comparison. The MD-simulated $G_{ij}(r)$ curves indicate good agreement with the experimental RDF curves in their shapes and peak positions, as shown in this figure. The first peaks at 1.73~1.75 Å of the experimental RDF curves[3),4)] correspond to the Si-N nearest-neighbor pair. The second peaks of the RDFs at 3.0 Å in X-ray[3)] and at 2.8 Å in neutron[4)] results are composed of the nearestneighbor pairs N-N and Si-Si. Because of a difference of atomic scattering factors between X-ray and neutron diffractions, the N-N correlation is dominant in the X-ray RDF whereas the Si-Si correlation is dominant in the neutron RDF. Therefore, the second peak around 2.8 Å in the neutron RDF mainly corresponds to the N-N correlation, and that around 3.0 Å in the X-ray RDF corresponds to the Si-Si correlation.

As noted above, we discussed the structure of a-Si_3N_4 in terms of the calculated and the experimental correlation functions, which are widely used to investigate the structure of amorphous materials for their clear-cut meaning. In the experimental RDF, however, detailed information on

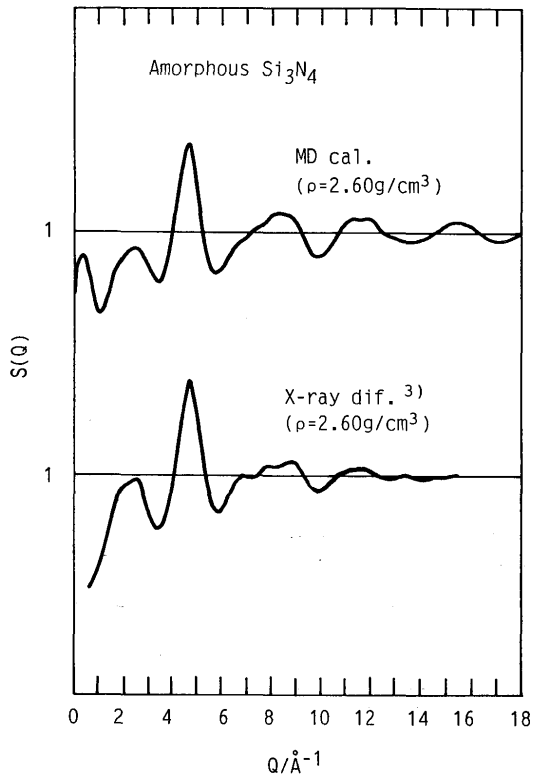

Fig. 6 Comparison of the X-ray structure factor S(Q) of the MD-simulated a-Si_3N_4 with the experimental structure factor[3].

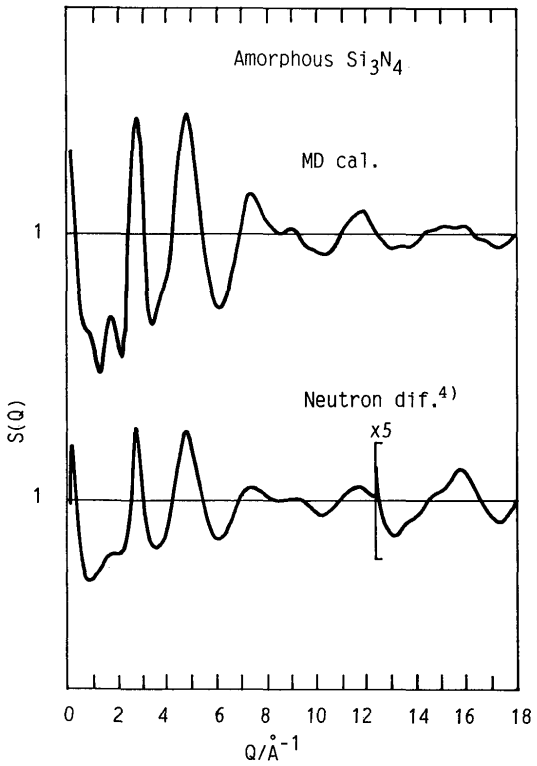

Fig. 7 Comparison of the neutron structure factor S(Q) of the MD-simulated a-Si_3N_4 with the experimental structure factor[4].

structures is averages by peak broadening due to thermal vibration of atoms and by the termination effect of Fourier transformation. For a detailed discussion on the structure of a-Si_3N_4, it is necessary to compare the experimental scattering intensities with the MD-simulated scattering data. We, therefore, calculated the interference function Q·i(Q) and the structure factor S(Q) in reciprocal space from the $G_{ij}(r)$ functions by Fourier transformation. Q is the scattering Vector given by

$$Q=\frac{(4\pi\sin\theta)}{\lambda}, \tag{4}$$

where λ is the incident X-ray or neutron wavelength. The functions Q·i(Q) and S(Q) can be obtained from the following equations:

$$Q\cdot i(Q)=\left(\frac{4\pi N}{V}\right)\left\{\frac{[\sum_i\sum_j N_iN_jf_i(Q)f_j(Q)]}{[\sum_{\text{all}} N_kf_k(Q)^2]}\right\}\cdot \sum_{r=0}^{r}\sum_{r=0}[r(G_{ij}(r)-1)sin(Qr)], \tag{5}$$

where fi(Q) is the atomic scattering factor of atomic species i, and

$$S(Q)=i(Q)+1. \tag{6}$$

Figures 6 and **7** show the total structure factors S(Q) calculated from our MD results. The observed S(Q) curves[3),4)] are also shown in these figures for comparison. It is generally considered that an observed S(Q) may contain some experimental errors, so that no quantitative discussion is possible. However, it can be concluded that the S(Q) curves calculated from our MD results by the use of equations (5) and (6) are in good agreement with those obtained from the X-ray[3)] and the neutron[4)]diffraction measurements. Therefore, our MD simulation is capable of giving a reasonable description of the structure of a-Si_3N_4 by using simple pair potentials.

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