



The structural correlation and mechanical properties in amorphous silicon nitride under densification

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ABSTRACT

Molecular dynamics simulations of amorphous silicon nitride ($a\text{-Si}_3\text{N}_4$) with various densities ranging from 2.43 to 3.40 g cm^{-3} were carried out to investigate their structural correlation and mechanical properties. The local structure was analyzed through the pair radial distribution functions, bond angle distributions and simplex statistics. The simulation reveals that although the fractions of structural units SiN_x and NSi_y strongly change with the density, the partial bond angle distributions of these structural units are identical for all constructed models. This result has enabled us to establish a relationship between the bond angle distributions and the fractions of structural units. Based on the analysis of simplex statistics, we found that all samples contain both the perfect and distorted tetrahedrons (SiN_4). These perfect tetrahedrons (PTEs) may connect to each other via common nitrogen to create a large cluster- or poly-PTEs. The largest poly-PTE consists of 45.6% Si in the sample with a density of 3.02 g cm^{-3} and 1.3% Si with the lowest density. We also found that even though at the high density the sample contains a remarkable number of voids in which the radius is larger than 1.1 Å. From uniaxial deformation of samples, the Young's modulus, yield and flow stress were determined. The strain hardening and softening become more pronounced as density increases.

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1. Introduction

Covalent amorphous materials, such as silicon nitride ($a\text{-Si}_3\text{N}_4$), alumina ($a\text{-Al}_2\text{O}_3$), or silica ($a\text{-SiO}_2$), should be investigated separately from metallic glasses [1] and glassy polymers [2] due to fundamental differences in the type of atomic bonding environments. Bonding between all atoms in covalent amorphous materials is of a strong and directional nature. The structure of $a\text{-Si}_3\text{N}_4$ is created by networks of high-valence silicon cations with strongly bonded nitrogen anions in their first coordination shells. This structure is determinant of its properties and strongly dependent on its thermo-mechanical history [3]. Due to high mechanical strength and high resistance to wear, corrosion and thermal shock, $a\text{-Si}_3\text{N}_4$ is widely used in automotive, chemical, and cutting-tool industries. Thin films of $a\text{-Si}_3\text{N}_4$ deposited by chemical vapor deposition (CVD) [4] and physical vapor deposition (PVD) [5] techniques have been widely applied throughout the decades. The radial distribution functions (RDF) and local structures of $a\text{-Si}_3\text{N}_4$ films were determined from X-ray [6], neutron [7] and electron [8] scattering experiments. According to their measurements, the Si–N bond length is 1.729 Å [7] and 1.75 Å [6,8], whereas the Si coordination number is 3.63, 3.87 [6] and 3.70 [7]. The N–Si–N and Si–N–Si bond angles are determined as 109.8° and 121°, respectively [7]. Different models for

$a\text{-Si}_3\text{N}_4$ have been constructed by classical molecular dynamics (MD) [9–14], density functional schemes [15–19] and the continuous random network model [20]. These models with various densities from 2.0 to 3.2 g cm^{-3} showed that the atomic structures are in agreement with the experiments in terms such as the bond lengths, coordination numbers and bond angles. Although $a\text{-Si}_3\text{N}_4$ systems with various densities have intensively studied both experiments and simulations, many of its aspects are still not specified; for instance, the variation of bond angle distributions (BAD) and coordination numbers upon compression is not fully understood. The parameters of BAD are often used to interpret various properties in silica such as photoemission binding energies and vibrational properties [21]. Theoretically and experimentally, the charge transfer from Si to O in silica depends sensitively on the Si–O–Si bridging bond angle, and therefore a similar result might be anticipated for the Si–N–Si bond angle even though no pertinent calculations are available as yet [22]. Regarding the point defects in Si_3N_4 and the analogous defects in SiO_2 , Pacchioni and Erbetta [23] found that there is a close resemblance of the nature of the transitions of a K center in Si_3N_4 and an E' center at the surface of SiO_2 . The experiments have only shown the deficient coordination numbers which are caused by the defects such as voids [7], vacancies in its matrix itself [6] and dangling bonds [24]. Meanwhile, the over-coordinated Si and N atoms have been shown by ab initio simulations [15,19]. In fact, the cubic spinel $\gamma\text{-Si}_3\text{N}_4$, in which Si atoms occupy both tetrahedral and octahedral sites and all the N atoms are tetrahedrally bonded, can be obtained from both hexagonal α - and $\beta\text{-Si}_3\text{N}_4$ upon compression [25].

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The mechanical properties of a-Si₃N₄ systems have been studied by both experiments [26–28] and simulations [10,29,30]. The results show that the Young's modulus in the range from 70 to 320 GPa depends on the change of the structures corresponding to the variation of the density. Omeltchenko et al. [10] reported that a significant growth of pores has been observed at the densities below 2.6 g cm⁻³, and these micro-pores have a significant effect on the mechanical properties. However, the deformation on the local structures of a-Si₃N₄ systems at a large strain has not been observed yet.

Therefore, the purpose of this work is to study the structural correlation based on a relation between the BAD and the fractions of structural units, and the deformation at a large strain under a-Si₃N₄ densification. The analysis of simplex statistics has also been used to study the local structures of a-Si₃N₄ systems. In addition, the radial distributions of voids in all a-Si₃N₄ samples are also calculated and presented here.

2. Computational procedure

We performed MD simulation for a-Si₃N₄ system containing 3380 atoms in simulation box with periodic boundary conditions (PBC). The Morse type pair potential used for the Si–N interaction was of the form

$$\phi_{ij}(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + D_e \left(e^{-2\beta(r_{ij}-\rho)} - 2e^{-\beta(r_{ij}-\rho)} \right). \quad (1)$$

The Si–Si and N–N interactions were applied by the form of Born–Mayer type pair potential

$$\phi_{ij}(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} e^{-r_{ij}/R_{ij}} \quad (2)$$

where r_{ij} is the distance between an ion of type i and an ion of type j ($i, j = \text{Si, N}$), e is the elementary charge, and $q_{\text{Si}} = 1.05$ and $q_{\text{N}} = -0.7875$ are the effective partial charges. The values $D_e = 3.88516$ eV, $\beta = 2.3266 \text{ \AA}^{-1}$, $\rho = 1.62136 \text{ \AA}$, $A_{\text{Si-Si}} = 105.19$ eV, $A_{\text{N-N}} = 146.6559$ eV, $R_{\text{Si-Si}} = 0.59121 \text{ \AA}$ and $R_{\text{N-N}} = 0.66787 \text{ \AA}$ were adopted to receive a good agreement with the experiment for the partial RDF of models. These parameters are close to the ones used in Ref. [14]. The long-range Coulomb interactions were calculated with the Ewald summation technique.

The Verlet algorithm with a time step of 0.5 fs was adopted and the simulation was executed at a constant volume corresponding to the density of 2.43 g cm⁻³. An initial configuration of model was constructed by the static relaxation (SR) method. The SR calculates the trajectory of atoms under the action of the forces from neighboring atoms in the model at zero temperature. The equilibrium amorphous model was reached after 8000 SR steps from the random initial configuration of atoms in simulation box. The final SR step was taken about 0.001 Å. This configuration had been equilibrated by MD method at temperature of 5000 K for over 50,000 time steps. Then, the sample was cooled down to 3000 K within 60,000 time steps and reached the equilibrium for over 10⁵ time steps. The obtained sample was denoted by M1. Sample M1 was chosen as an input configuration to five higher-density models. These models (M2, M3, ..., M6) were constructed by compression of the model M1 to correspond to the density and relaxed the system to reach the equilibrium at constant volume and temperature (the ensemble NVT). Finally, the samples reduced the temperature to 300 K during the next 675,000 time steps and ran the systems for over 40,000 time steps without any disturbance. In order to improve statistics, all quantities of interest were calculated by averaging over 1000 last configurations during the simulation. To determine the coordination number and BAD, we used the $R_{\text{Si-N}} = 2.25 \text{ \AA}$ which was a cutoff

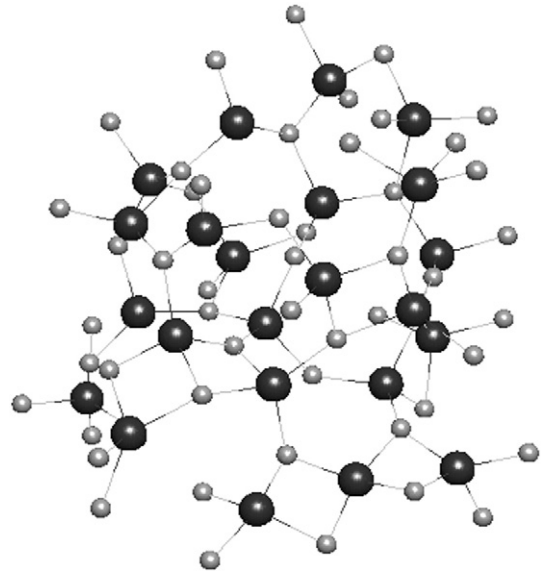


Fig. 1. The structure of the central region in the sample M3: large and small spheres represent Si and N, respectively.

radius as the first minimum after the peak of PRDF for a-Si₃N₄ at the density of 2.43 g cm⁻³. The radial distributions of voids were calculated following the procedure which was described elsewhere [31]. If every atom is considered as a sphere, then there is a part of the system in which no atomic sphere exists. The radius of Si and N atoms is 1.1 and 0.70 Å, respectively. The void is defined as a sphere that can be inserted in contact with four atoms and did not intersect with any atom.

Strain–stress simulations were performed using the computational procedure which can be found elsewhere [32]. Following this procedure, the model was deformed by applying a negative external pressure $P_{\text{ext}} = -n\Delta P$ at each time interval, here n is the number of time steps and ΔP is a small pressure increment chosen to be $\Delta P = 1.0$ GPa. The system was relaxed during each time interval. At each time interval, the model is deformed by a tiny scaling of the coordinates under external pressure, z coordinates are multiplied by $1 + \gamma$, the x and y coordinates by $1 - \nu\gamma$, where γ is a very small number and ν is an approximate of the Poisson's ratio as described in Ref. [33]. The simulations were carried

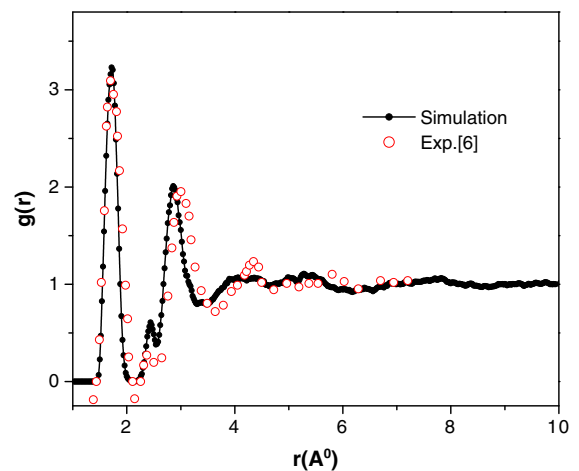


Fig. 2. The total PRDFs of a-Si₃N₄ at the density of 2.62 g cm⁻³ and experimental data [6].

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