Structural properties of amorphous silicon nitride

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We developed an empirical potential for interactions between Si and N to describe silicon nitride systems using the Tersoff functional form. The fitting parameters were found using a set of *ab initio* and experimental results of the crystalline phase. Using this empirical model, we explored the structural properties of amorphous silicon nitride through Monte Carlo simulations, and compared them to available experimental data. The good description of the a-SiN$_x$ system for a wide range of nitrogen contents ($0 < x < 1.5$) shows the reliability of this model. [S0163-1829(98)00637-7]

I. INTRODUCTION

Silicon nitride[1] is a material of great technological interest due to its mechanical and electronic properties that make it suitable for several applications. Silicon nitride has high density, high melting temperature, low mechanical stress, and strong resistance against thermal shock. Due to its superior mechanical properties at high temperatures, it has been considered as a prototypical material for uses in engine components and cutting tools.[2,3] It has high dielectric constant, large electronic gap, high-energy barrier for impurity diffusion, and high resistance against radiation. These properties led to applications in microelectronic devices as a gate dielectric in thin-film transistors,[4,5] as a charge storage medium in nonvolatile memories,[6,7] and in solar cells. Although considerable effort has been spent in studying silicon nitride, much is still unknown about its macroscopic and microscopic properties.

Silicon nitride is prepared by several processes: sputtering, chemical vapor deposition, and glow-discharge decomposition. Changes in deposition conditions provide considerably different film properties. On the other hand, as electronic devices become smaller, higher quality films are required. Therefore, understanding structural and electronic properties of silicon nitride becomes essential in order to control the film properties under fabrication.

Theoretical investigations have been carried out to unveil the properties of silicon nitride. The electronic structure, lattice parameter, and bulk modulus of crystalline β-Si$_3$N$_4$ were studied through *ab initio* calculations.[3] Semiempirical methods[8–10] explored properties of amorphous SiN$_x$ for $0 < x < 1.6$. Although *ab initio* and semiempirical methods have been successful in describing microscopic properties of materials, computational cost prevents their extensive use to systems larger than a few hundred atoms. However, many problems of interest require thousands to hundreds of thousands of atoms and time scales of nanoseconds for a proper description. Since these problems are computationally too expensive to be explored using methods involving electronic calculations, empirical methods have been developed as al-

ternative models to study structural properties. Although these methods, provide a considerably poorer description of interactions in the material, they are computationally efficient and can handle systems involving thousands to millions of atoms. Specifically in the case of silicon nitride, to our knowledge, there are two empirical models in the literature.[11,12] Those models have been used to identify a number of structural properties of silicon nitride.[11,13,14] However, their transferability to a wide range of SiN compositions was never tested. Those empirical models have not explored the Si-Si interactions so that they lack reliability when dealing with pure or almost pure silicon.

Here we introduce an empirical potential for Si-N interactions using the Tersoff functional form.[15–17] The Tersoff potential, originally developed for pure silicon, has already been successfully used and tested over the last few years.[18] Therefore, this functional form, with the Si-Si interactions described by the original Tersoff potential,[17] appears to be the best candidate to describe Si-N interactions. This paper is organized as follows: In Sec. II we discuss the functional form and the fitting strategy. In Sec. III we test the potential for amorphous SiN$_x$ system in a wide range of nitrogen contents using Monte Carlo simulations, and discuss the structural properties of the amorphous phase. In Sec. IV, we present final remarks.

II. THE INTERATOMIC POTENTIAL

A. The functional form

Empirical potentials have already been developed for SiN. Umesaki *et al.*[11] developed a model based on a two-body interaction consisting of a Coulombic and a repulsive term. They explored the structural properties of stoichiometric amorphous SiN$_{1.33}$ through molecular dynamics (MD) simulations. Vashishta and co-workers[12–14] developed an empirical model that included two- and three-body interactions. The two-body terms consist of steric repulsion between atoms, charge-dipole interaction, and Coulomb interaction due to charge transfer between Si and N. The three-body terms describe the covalent nature of bonding between Si and N.

That model has been tested by comparing structural properties from MD simulations with experimental results: bond lengths for both crystalline and amorphous $SiN_{1.33}$ are in agreement with experimental data, the static structure factor is in agreement with neutron-scattering experiments, and elastic properties are within 10% from experimental data.[14] It has been used to study several structural properties such as interfaces[13] and fracture.[14] Although those models have been successful in describing a number of systems, their transferability to structures away from the ones used in the fitting is still controversial. For example, they have never been tested for low nitrogen concentrations, in which the system is essentially amorphous silicon. It looks more natural to develop a model for SiN starting with one that has already been successful in describing pure silicon. The Tersoff potential,[15–17] originally developed for silicon, is the best candidate. That model, fitted to density-functional theory results for several Si polytypes, has been extensively tested over a wide range of properties and systems.[18] It was later extended to multicomponent systems,[17] such as SiC and SiGe.

The Tersoff potential is a bond-order potential composed of a two-body expansion which depends on the local environment. The total energy E is given by the sum over all n atoms of the energy of site i (E_i):

$$E = \sum_{i=1}^{n} E_i = \frac{1}{2} \sum_{i \neq j}^{n} V_{ij}, \tag{1}$$

where V_{ij} is the interaction energy between atoms i and j and is a combination of repulsive and attractive terms.

$$V_{ij} = f_c(r_{ij}) \{ f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \}, \tag{2}$$

where r_{ij} is the distance between atoms i and j.

The functions f_R and f_A represent, respectively, the repulsive and attractive interactions:

$$f_R(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij}),$$

$$f_A(r_{ij}) = -B_{ij} \exp(-\mu_{ij} r_{ij}).$$

Here, f_c is a cutoff function that goes smoothly to zero between two distances (R and S):

$$f_c(r_{ij}) = \begin{cases} 1, & \text{if } r_{ij} < R_{ij} \\ \frac{1}{2} + \frac{1}{2} \cos \frac{\pi(r_{ij} - R_{ij})}{(S_{ij} - R_{ij})}, & \text{if } R_{ij} < r_{ij} < S_{ij} \\ 0, & \text{if } r_{ij} > S_{ij}. \end{cases} \tag{3}$$

The parameter b_{ij} is a bond-order term that determines the strength of the attractive interaction:

$$b_{ij} = \chi_{ij} (1 + \beta_i^{n_i} \zeta_{ij}^{n_i})^{-1/2n_i}, \tag{4}$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}), \tag{5}$$

$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos \theta_{ijk})^2}, \tag{6}$$

where θ_{ijk} is the angle between ij and ik bonds.

The parameters depend on the atom type. For atoms i and j (of different types), these parameters are

$$A_{ij} = (A_i \times A_j)^{\frac{1}{2}}, \tag{7}$$

$$B_{ij} = (B_i \times B_j)^{\frac{1}{2}}, \tag{8}$$

$$\lambda_{ij} = \frac{(\lambda_i + \lambda_j)}{2}, \tag{9}$$

$$\mu_{ij} = \frac{(\mu_i + \mu_j)}{2}, \tag{10}$$

$$R_{ij} = (R_i \times R_j)^{\frac{1}{2}}, \tag{11}$$

$$S_{ij} = (S_i \times S_j)^{\frac{1}{2}}, \tag{12}$$

where the parameters with single index describe the interaction between atoms of the same type. For interactions between atoms of type m, there are eleven parameters to be fitted: A_m, B_m, λ_m, μ_m, R_m, S_m, β_m, n_m, c_m, d_m, and h_m.

The parameter χ takes into account the strengthening or weakening of heteropolar bonds. For the interaction between atoms of the same type, normally this mixing term is taken equal to 1. For an interaction involving atoms of different types, this number weakens the attractive interaction as result of bond polarity. In our model, while this parameter is 1 for Si-Si interactions, it is set to zero for N-N interactions, remaining only the repulsive term. This is motivated by the fact that the N-N interaction to form an N_2 molecule is so strong, with binding energy of 9.8 eV, that when N_2 is formed inside a crystal, it does not interact with other atoms, and diffuses through the crystal to evaporate on the surface. In our model, to keep the nitrogen stable inside the crystalline structure, we prevent the N_2 formation.

B. Fitting procedure and tests

In this section we describe the fitting procedure used to search for the parameters of Si-N and N-N interactions. The procedure combined two ingredients: the database of relevant silicon nitride properties and the strategy of finding the parameters that best describe those properties in the database. The database consisted of a set of *ab initio* and the experimental data, which included experimental lattice parameter of the crystalline β-Si_3N_4,[19] *ab initio* value for average binding energy of β-Si_3N_4,[3] experimental equilibrium interatomic distance and binding energy of the N_2 molecule,[20] and the *ab initio* result for the structure of the N-Si bonds in the Si_3NH_9 molecule.[21] The best set of parameters is determined using a least-squares approach,[22] with each configuration in the database weighted appropriately. All parameter values are allowed to vary at once through a simulated annealing process. For the Si-Si interactions, we used parameters from the original Tersoff potential.[17]

Table I gives the best set of parameters for all interactions and Fig. 1 shows the term V_{ij} for such interactions. From the figure, the Si-N interaction is considerably stronger and gives a shorter equilibrium distance than the Si-Si interaction. The

TABLE I. Best set of the parameters that define the Si-Si (Ref. 17), and the Si-N interactions obtained from a simulated annealing fit to the database described in the text.

	N	Si
A (eV)	6.36814×10^3	1.8308×10^3
B (eV)	5.11760×10^2	4.7118×10^2
λ (Å^{-1})	5.43673	2.4799
μ (Å^{-1})	2.70000	1.7322
β	5.29380×10^{-3}	1.1000×10^{-6}
n	1.33041	7.8734×10^{-1}
c	2.03120×10^4	1.0039×10^5
d	2.55103×10^1	1.6217×10^1
h	-5.62390×10^{-1}	-5.9825×10^{-1}
R(Å)	1.80	2.70
S(Å)	2.10	3.00
$\chi_{\text{Si-}N}$	0.65	

N-N interaction has only the repulsive term. Figure 2 gives the bond-order term b_{ij} (centered on Si and N) as function of the angle between two bonds for three different coordinations. The angle in which the term b_{ij} is maximum corresponds to the strongest attractive interaction, and therefore the most preferable one. This angle, which is controlled by the parameter h, is around 110° for both Si and N.

The reliability of this model in describing silicon-nitride systems was tested over several properties and structures. To perform the tests we used Monte Carlo simulations[23] at room temperature (300 K) with periodic boundary conditions and 756 atoms. The internal stress was released by allowing volume relaxation (NPT ensemble).[23,24]

There are two stable crystalline structures for Si$_3$N$_4$: α and β.[19,25,26] The local bonding is similar in both cases, differing by the number of atoms in the primitive cell. In the simpler structure (β), believed to be the most stable, the N atoms form bonds with three Si first neighbors in a near planar structure (sp^2 hybridization). The Si atoms form bonds with four N first neighbors in a near tetrahedral struc-
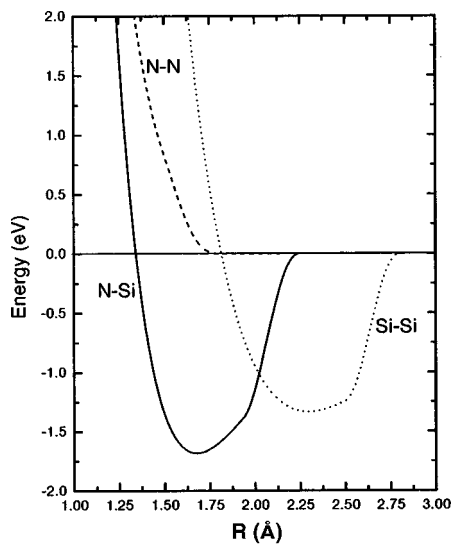

FIG. 1. The $V_{ij}(r)$ term for Si-Si (dotted line), Si-N (full line), and N-N (dashed line) interactions. Energies are in eV.
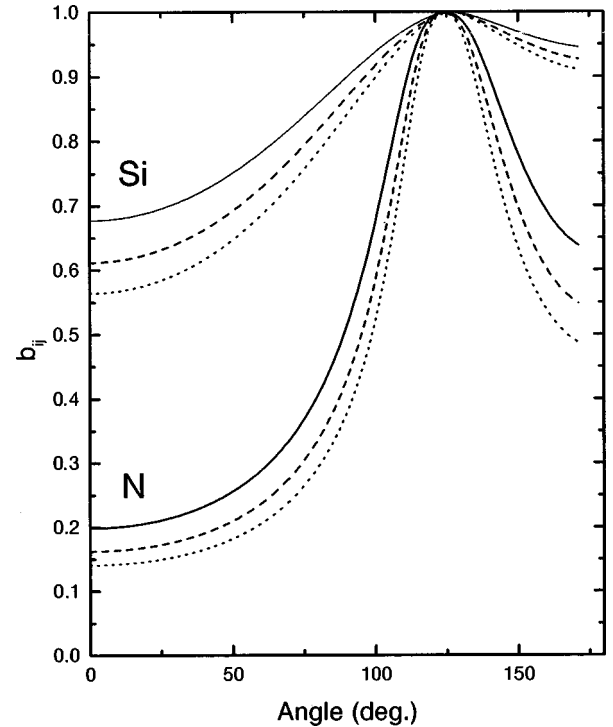

FIG. 2. The term b_{ij} which controls the attractive interaction as function of the angle between bonds. It is presented for the interactive term centered at both N and Si atoms for various coordinations: $Z=4$ (dotted line), $Z=3$ (dashed line), and $Z=2$ (full line).

ture (sp^3 hybridization). Table II shows the results of binding energy and lattice parameter for the β phase. The results are in good agreement with *ab initio*[3,27] and experimental data.[19,28] Since β and α crystalline phases have similar bonding, their binding energies (per atom) are very close, with the binding energy for the α phase being slightly smaller (0.01 eV higher) than the one for the β phase. Due to the strong bond between Si and N atoms, silicon nitride has a large bulk modulus. Using our model, the bulk modulus for the β phase is 2.40 Mbar, in good agreement with *ab initio*[3] and experimental results.[29]

TABLE II. Properties of β crystalline phase computed using this model as compared with *ab initio* and experimental data. Binding energies (E_B) are given in eV/atom, lattice parameter (a) in Å, and bulk modulus (B) in Mbar.

	Exp.	*ab initio*	This work
a (Å)	7.606 [a]	7.61 [b]	7.513
	7.595 [c]	7.586 [d]	
E_B (eV)	–	-5.307 [b]	-5.305
		-5.342 [d]	
ρ (g/cm^3)	3.19 [c]	3.17 [b]	3.32
B (Mbar)	2.56 [e]	2.65 [b]	2.40
		2.82 [d]	

[a]Reference 28.
[b]Reference 3.
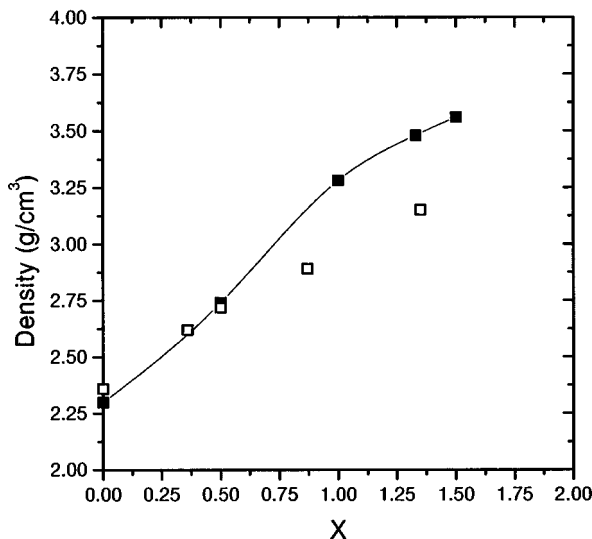[c]Reference 19.
[d]Reference 27.
[e]Reference 29.

FIG. 3. The density (in g/cm^3) of amorphous silicon nitride (SiN$_x$) computed by Monte Carlo simulations compared to experimental results ($\square$) (Ref. 30).

The good description of local bonding and mechanical strength shows the reliability of this model for silicon-nitride systems. In the next section we study the amorphous silicon nitride in a wide range of nitrogen contents and compare the structural properties of a-SiN to recent experimental data.[30]

III. STRUCTURAL PROPERTIES OF AMORPHOUS SiN$_X$

Most of the silicon nitride produced by different processes has reasonably high hydrogen concentrations.[1] However, here we discuss theoretical calculations of systems having only Si and N species. This certainly provides a partial picture of a realistic system. In a forthcoming publication, we present a theoretical study of the hydrogen role in silicon-nitride systems.

In this section we discuss the structure of amorphous SiN$_x$ ($x = 0, 0.5, 1.0, 1.33,$ and 1.5) and compare the results with recent experimental data.[30–32] The amorphous SiN$_x$ for each x was created by a simulated annealing process. The simulations were performed using 756 atoms and periodic boundary conditions. The relaxation of both the atoms and the cell volume were allowed during the simulation. For each x, the simulation started at a very high temperature ($T > 6000$ K), when the material was essentially liquid. The temperature was slowly reduced in a simulated annealing scheme until it reached room temperature (300 K). Then the statistical properties were computed over several configurations.

Figure 3 shows the density of the material as a function of nitrogen content. The density increases with x, consistent with experimental data.[30] For $x=0$, we find a density of 2.31 g/cm^3 as compared to experimental value[30] of 2.35 g/cm^3. For all nitrogen contents, we find the density in reasonably good agreement with experimental data.

Figure 4 shows the total radial distribution function $g(r)$. As x increases, the behavior of $g(r)$ changes considerably. At $x=0$, the system is amorphous silicon and the radial dis-
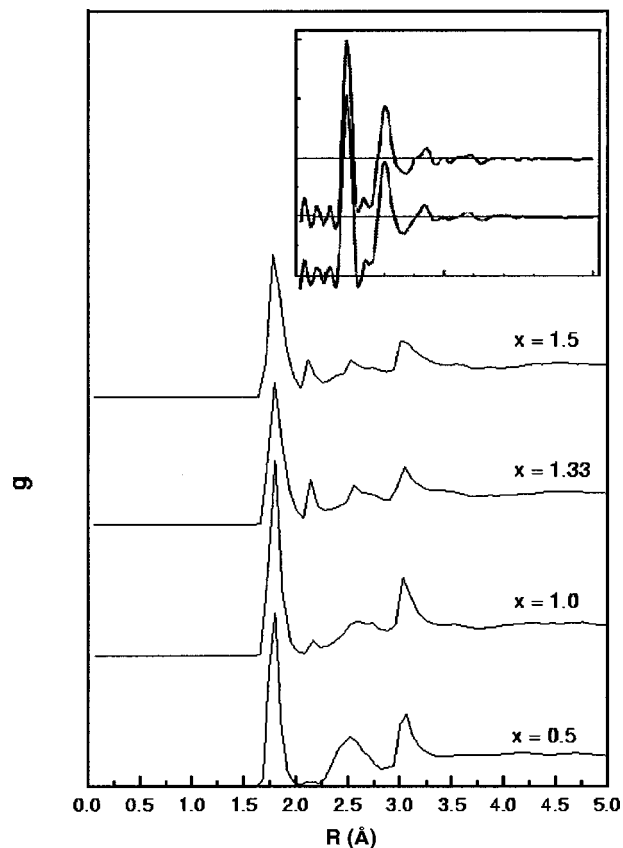

FIG. 4. The total correlation function $g(r)$ for $x=$ 0.5, 1.0, 1.33, and 1.5. The experimental result (Ref. 31) for $x=1.33$ is presented in the insert.

tribution function shows a first peak around 2.4 Å, which is the average distance between atoms in the amorphous silicon. As x increases, the peak corresponding to Si-Si bonds decreases. Simultaneously, a peak appears at a shorter distance (around 1.75 Å) corresponding to the Si-N bonds. In the case of $x=1.33$, where there is available experimental data, $g(r)$ is in good agreement with experimental result reached by x-ray scattering[31] shown in the inset of the figure. For $x=1.33$, the first peak in $g(r)$, which corresponds to the Si-N bonds, is found at 1.73 Å in excellent agreement with experimental data of 1.729 Å reached by neutron scattering.[32]

Figure 5 shows the angular distribution function for different nitrogen contents. Here the angular distribution is defined for those angles formed between two bonds, for N-Si-N and Si-N-Si. For the Si-N-Si (centered on the N atoms), the distribution is reasonably narrow and has a peak around 120 ° showing that N bounded to Si displays a sp^2-like hybridization, and therefore a planar structure. This result is in excellent agreement with experimental data[32] that find a preferred angle of 121 °. As the nitrogen content increases, the distribution becomes wider, but still determining a sharp peak around 120 °. The distribution widens as x increases mostly due to the competition between N atoms to form bonds with Si. When there is a saturation of available Si atoms to form bonds with N (for $x>1.33$), this widening becomes more evident. Figure 6 shows the angular distribution for the N-Si-N (centered at the Si atoms). The distribution is considerably wider than in the previous case, even for
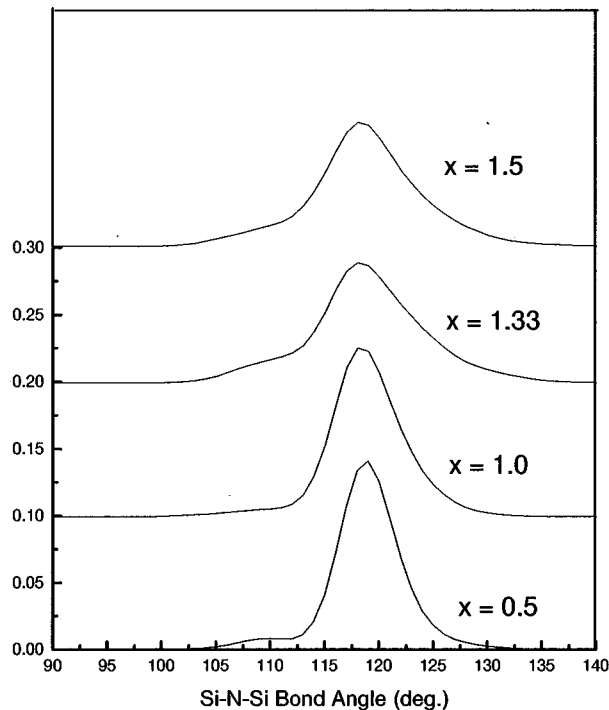
FIG. 5. The angular distribution function between two bonds N-Si centered at an N atom.

FIG. 7. The average coordination number at Si and N sites as function of x. The simulation results (full symbols) are compared to experimental data (open symbols) (Ref. 30). The figure shows $\langle n_{Si}(Si)\rangle(\square)$, $\langle n_N(Si)\rangle(\triangle)$, and $\langle n_{Si}(N)\rangle(\bigcirc)$.

low x, with most of the bonds in the region between 90 ° and 130 °. As x increases, the distribution becomes even wider and a peak moves to lower angles (around 75 °). This small angle peak is characteristic of angular distributions in amorphous structures and comes from atoms with high coordination.

Figure 7 shows the average coordination numbers at Si and N centers for different nitrogen contents as compared to
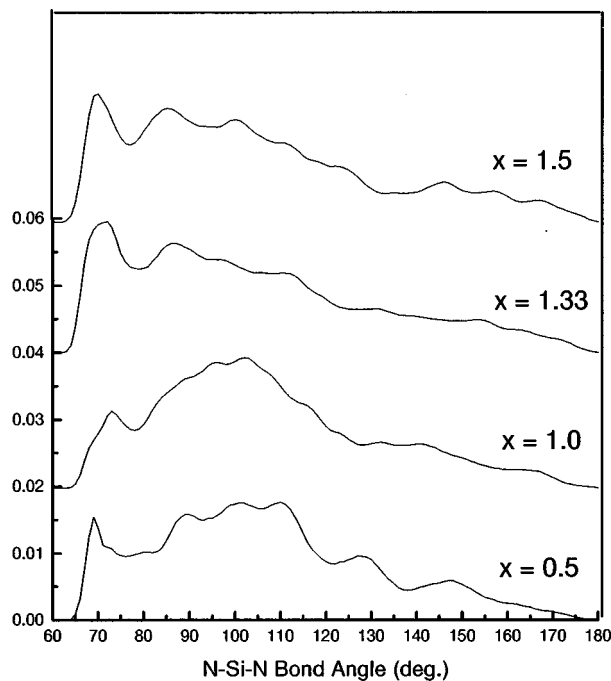

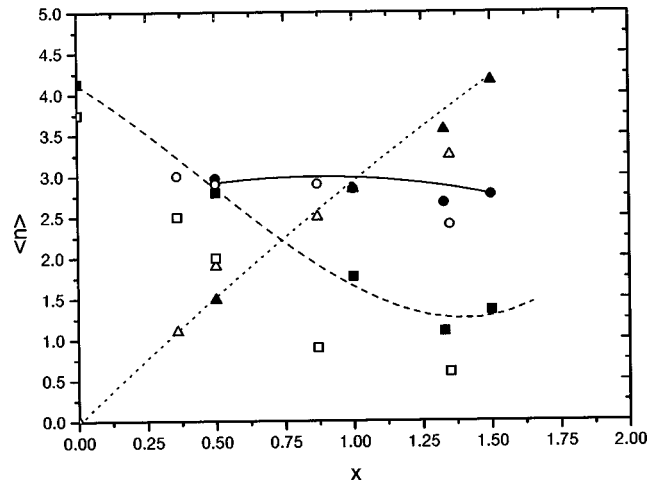FIG. 6. The angular distribution function between two bonds N-Si centered at a Si atom.

experimental results.[30] The figure shows the coordination $n_A(B)$, the average number of neighbors A for atom type B. This coordination is defined as the average number of neighbors inside the radial distribution function up to covalent radius. For $x = 0$ (a-Si), each Si atom has an average coordination of 4.13. As x increases, the N atoms start to compete with Si atoms to form bonds, so that the coordination $n_{Si}(Si)$ falls from 4.13 to about 0.9 at $x = 1.5$. On the other hand, the coordination $n_{Si}(N)$ grows linearly for $x < 1$ from zero to four. The coordination $n_{Si}(N)$ is about 3 for all the range of x. This behavior is consistent with the fact that the N atom has a chemical preference to be bounded to three Si atoms.[33,34] All these results agree very well with experimental results.[30] However, this comparison should be taken with caution. The samples, in which the experiments were performed, had considerably high hydrogen concentrations. Since hydrogen competes with the other atoms to form bonds, the competition between Si-N and Si-Si bonds in the sample is considerably more complex than what is described here.

IV. DISCUSSION AND CONCLUSION

In summary, we presented an empirical potential for silicon nitride using the Tersoff functional form. The model provides a reliable description of systems over a wide range of configurations and nitrogen contents. The structural properties of β phase are in good agreement with *ab initio* and experimental results. The structural properties of amorphous silicon nitride over a wide range of nitrogen concentrations are also in good agreement with available experimental data.

Since this model is an extension of the original Tersoff model for silicon, its reliability for pure silicon systems has already been extensively verified. Therefore, studies involving both pure Si and SiN are within the validity of this model. An interesting system to study is the (100) Si/SiN$_x$ interface. This interface is of considerable interest for microelectronic devices since silicon nitride is generally grown over a silicon matrix.

The good transferability of the model would allow the

study of a number of systems. Recently, several calculations have been performed to study mechanical properties of the silicon nitride.[13,14] This model will allow the extension of such studies to a wide range of nitrogen contents and therefore a careful analysis of mechanical properties as a function of nitrogen contents. Our model does not include long-range interactions, such as Coulomb terms. Although these interactions are not taken into account explicitly, our model is still valid to a large number of configurations and systems. The long range terms are mainly responsible for the chemical preference of Si to bind to N that is implicitly included in our model.

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