Relative stability of $P6_3/m$ and $P6_3$ structures of β-Si_3N_4

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The relative stability between the $P6_3/m$ and $P6_3$ structures of β-silicon nitride (β-Si_3N_4) crystal has been examined using the *ab initio* pseudopotential method. We have performed the relaxation of atomic positions in the unit cell according to the Hellmann-Feynman forces for several sets of lattice constants around the experimental ones. For each set of lattice constants, the $P6_3/m$ structure is naturally recovered through the relaxation from the $P6_3$ initial configurations. There exist no energy minima of the $P6_3$ structure for the examined sets of lattice parameters. Thus it is concluded that the ground-state structure of β-Si_3N_4 has $P6_3/m$ symmetry contrary to a recent orthogonalized-linear combination of atomic orbitals calculation. However, the energy increases by the displacements of the z coordinates of N atoms constituting a coplanar configuration on the (0001) plane are very small. This should be concerned with the conflicting experimental observations.

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Silicon nitride (Si_3N_4) is an important material as a structural ceramic and as a dielectric insulator. The atomic configuration of the Si_3N_4 crystal is very complex with a large number of atoms in the unit cell. The fundamental structural aspect of Si_3N_4 is still critically unresolved and causes uncertainty as mentioned in publications on crystal-structure-related research.[1,2] Under usual pressure and temperature, there are two crystal forms of Si_3N_4, α-Si_3N_4, and β-Si_3N_4. Concerning the space group of β-Si_3N_4, a disagreement among researchers in this field has remained for many years.[3–16] Two atomic structures have been experimentally proposed for β-Si_3N_4, one with the mirror symmetry in the space group of $P6_3/m$ (Refs. 4, 5, and 11–15) and the other without mirror symmetry in the space group of $P6_3$ (Refs. 3, 6, and 16). For the higher-symmetry $P6_3/m$ structure, one-half of the atoms are exactly located on the plane $z=\frac{1}{4}c_0$ and the other half are exactly on $z=\frac{3}{4}c_0$ as shown in Fig. 1. Two nitrogen atoms (N1 group, atoms 1 and 2 in Fig. 1) in the unit cell are at special positions $(2c)$, where these atoms are coplanar with the neighboring Si atoms. The remaining six N atoms belong to the N2 group (atoms 3–8 in Fig. 1). For the noncentrosymmetric $P6_3$ structure, the z coordinates of N atoms deviate from $z=\frac{1}{4}c_0$ or $z=\frac{3}{4}c_0$ as shown in Fig. 1. Thus none of the N atoms are exactly coplanar with the neighboring Si atoms.

The exact stable structure of β-Si_3N_4 at zero temperature is still unresolved. Only recently, the relative stability between the $P6_3/m$ and $P6_3$ structures has been studied by first-principles calculations using the orthogonalized-linear combination of atomic orbital (OLCAO) method[9] based on the density-functional theory (DFT) with the local density approximation (LDA).[17,18] In this study, the relaxation of the internal parameters was achieved using a simple finite-difference method. This study showed that the $P6_3$ structure is more stable than the $P6_3/m$ structure.

The relative stability between the $P6_3/m$ and $P6_3$ structures is concerned with the shape of the potential energy surface in the multidimensional hyperspace of the inner coordinates and lattice parameters. This kind of information is not necessary enough in Ref. 9. We think that the plane-wave pseudopotential method is very suitable to the present problem, because the relaxation of complex configurations can be performed according to the Hellmann-Feynman forces easily and accurately if the plane-wave cutoff energy is enough large. It should be noted that the relative stability and shape of potential energy surface can be examined directly by tracking the relaxation behavior as described in the present paper.

We calculate the total energy and Hellmann-Feynman forces using the plane-wave pseudopotential method[19] based on the DFT-LDA. In order to reduce the number of required

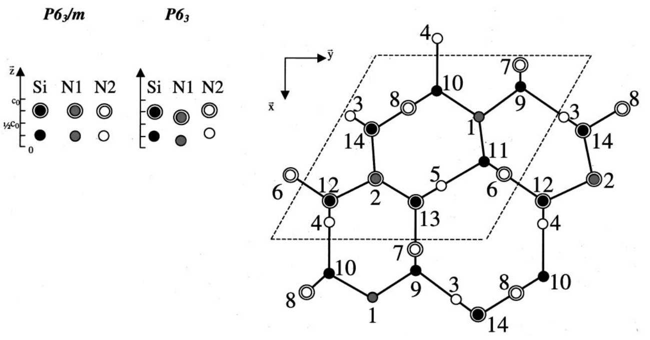

FIG. 1. Atomic arrangement in the unit cell of $P6_3/m$ or $P6_3$ structure including atoms from neighboring cells. Main differences between the $P6_3/m$ and $P6_3$ structures are the z coordinates of N atoms.

plane waves, Troullier-Martins- (TM-) type[20] pseudopotentials in the separable Kleinman-Bylander[21] form were employed. Details of the electronic configurations and cutoff radii for the construction of Si and N pseudopotentials are given in our preceding paper.[22] We use the conjugate gradient technique[23] to efficiently obtain the electronic ground state. We used six special $\vec{k}$ points in the irreducible part of the Brillouin zone (BZ) and a plane-wave cutoff energy of 65 Ry. These conditions were examined in our preceding paper. Both the $P6_3/m$ and $P6_3$ structures have the same irreducible part of the BZ, because the necessary region in the BZ can be reduced to half by time-reversal symmetry even in the case of $P6_3$. Thus we use the same $\vec{k}$ points for both structures with the same lattice parameters.

In our preceding paper[22] we determined the most stable configuration for the $P6_3/m$ symmetry, where we performed relaxation of the lattice constants and atomic positions with the constraint of the $P6_3/m$ symmetry. In the present paper, we examine the stability of the $P6_3$ structure as compared with the $P6_3/m$ structure. For several sets of lattice parameters, we perform a relaxation of atomic positions according to the atomic forces with the constraint of the $P6_3$ symmetry from the initial atomic positions of the experimentally proposed $P6_3$ structure[3] or of the recently optimized $P6_3$ structure.[9] To preserve $P6_3$ symmetry in the relaxation, N1 atoms in Fig. 1 are fixed in the *x-y* plane and their *z* coordinates are relaxed. The N2 atoms in Fig. 1 are allowed to move in all $\vec{x}$, $\vec{y}$, and $\vec{z}$ directions. The Si atoms can be relaxed in the *x-y* plane with their *z* coordinates fixed to the value of $\frac{1}{4}c_0$ or $\frac{3}{4}c_0$. Thus a total of six independent atomic parameters are optimized for each set of lattice constants. Atomic displacements in the relaxation are given by simply multiplying the Hellmann-Feynman forces by some factor. Transformation of atomic displacements into changes in atomic parameters is easy, because the atomic forces also have the same symmetric property. For each relaxation run, we observe a variation of total energy and atomic coordinates. The initial *z* atomic parameters of N1 and N2 atoms are not 0.25 for the $P6_3$ structure. If the *z* atomic parameters of N1 and N2 atoms become 0.25 in the relaxation, it means that the $P6_3/m$ structure is naturally recovered from the $P6_3$ structure, and thus the $P6_3/m$ structure is more stable.

We have performed the relaxation for several sets of lattice parameters around the experimental values as shown in Fig. 2. For the initial inner parameters of the atomic positions in the unit cell, we used the experimental ones of the $P6_3$ structure,[3] where the *z* atomic parameters of N1 and N2 atoms are 0.2392 and 0.2628, respectively. Only for set *G* did we used the atomic parameters by the OLCAO calculation,[9] where the *z* parameters of N1 and N2 atoms are 0.2353 and 0.2726, respectively. In Fig. 3, the three-dimensional representations in energy-position space show the relaxation tracks for all sets of lattice constants. For all sets, the total energy is really decreased by the relaxation, and the *z* atomic parameters of N atoms naturally reach nearly 0.25. This means that the $P6_3/m$ symmetry is naturally recovered in the relaxation. The converged structure is not exactly $P6_3/m$, but nearly $P6_3/m$ because the relaxation is stopped by the condition of the atomic force values. For each converged configuration of nearly $P6_3/m$, we forced the *z* atomic parameters of N atoms to be exactly 0.25, and then we performed relaxation of the remaining atomic parameters. The red square in Fig. 3 shows the energy of this exact $P6_3/m$ structure at the end of the track. We have observed that the obtained exact $P6_3/m$ structure is really a little more stable than the nearly $P6_3/m$ structure. And there exist no local energy minima except for the exact $P6_3/m$ structure in each track. Thus it is concluded that the $P6_3/m$ structure is more stable than the $P6_3$ structure for all sets of lattice parameters. It should be noted that both $P6_3/m$ and $P6_3$ structures are dealt with under exactly the same conditions for each set of lattice parameters. Therefore, the uncertainty caused by the DFT-LDA is unsupported with regard to this point.

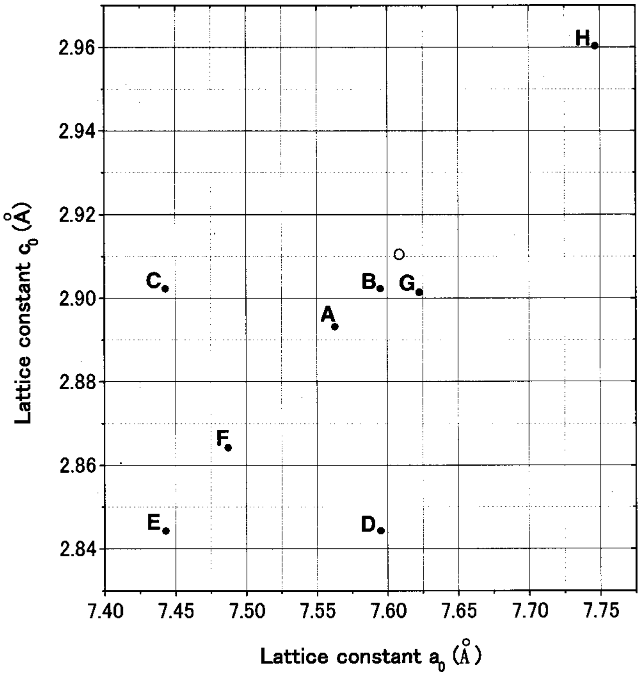

FIG. 2. Map of the lattice constant sets examined in this paper. Set *A* is the lattice parameters of the most stable $P6_3/m$ structure obtained in Ref. 22. Set *B* is the experimental ones proposed as the $P6_3$ structure (Ref. 3). Set *G* is the lattice constants of the $P6_3$ structure obtained by the OLCAO method (Ref. 9). Set *F* is the 1% compression of set *A*. Sets *C*, *D*, and *E* are the 2% compression of the parameters of *B*. Set *H* is the 2% expansion of set *B*. The experimental lattice constants of the $P6_3/m$ structure (Ref. 15) are indicated by ○.

In Fig. 3, the parameter of N2 reaches 0.25 rapidly, whereas the parameter of N1 reaches 0.25 very slowly in each case. It is clear that the total energy increase by the displacement of the *z* coordinate of N1 is very small. In other words, the curvature of the potential energy surface against the *z* atomic parameter of N1 is very small. Thus the atomic force on N atoms of the N1 group is very small when the configuration nearly reaches the $P6_3/m$ structure. However, the atomic force on N atoms of the N1 group has the direction so as to recover the $P6_3/m$ symmetry in the relaxation and is zero in the $P6_3/m$ structure. The present feature of the

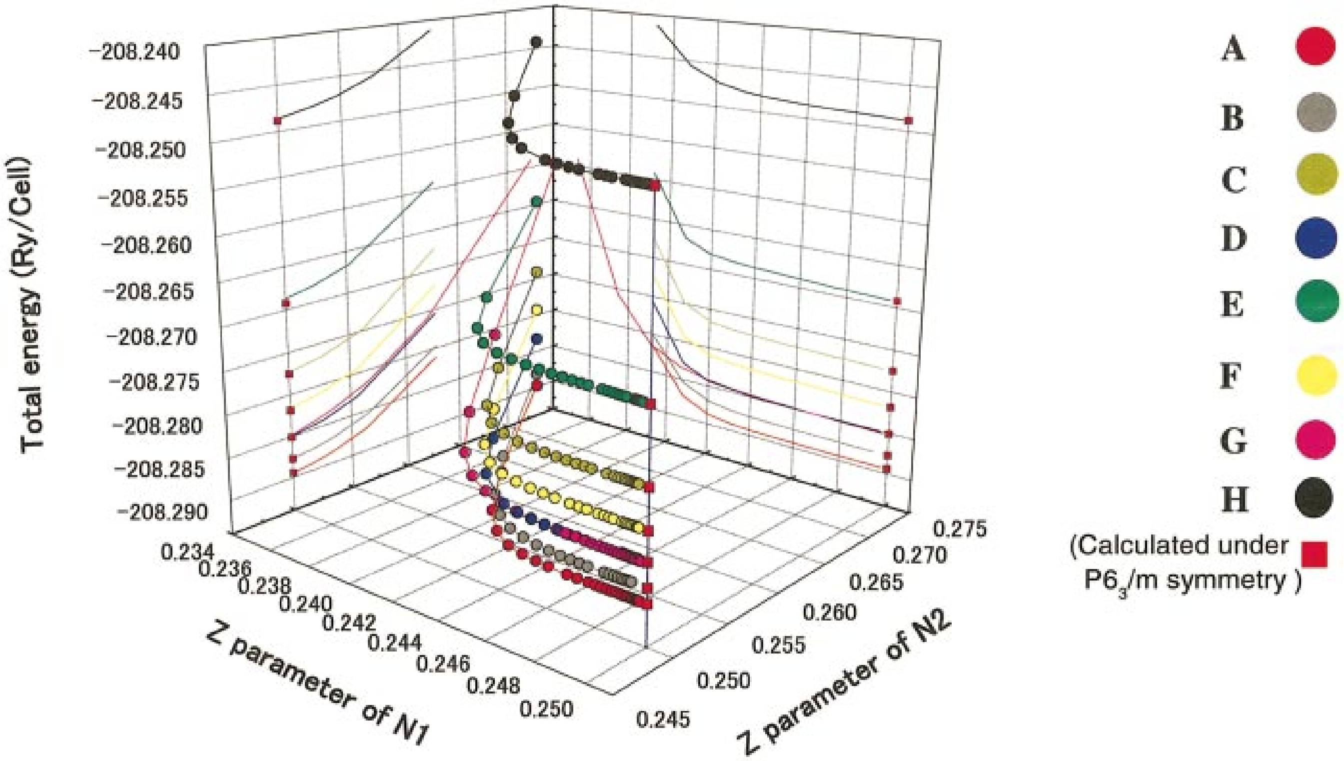

FIG. 3. (Color) The relaxation track from initial $P6_3$ structure for various sets of lattice parameters from *A* to *H*. The tracks are shown three-dimensionally for the total energy and the *z* atomic parameters of N1 and N2.

potential energy surface indicates that the displacement of N atoms of the N1 group along the $\vec{z}$ direction is rather easy. This should cause very slow lattice vibration modes. There should exist a substantial probability of such displacements of N atoms associated with such lattice vibrations or the presence of lattice defects or impurities. This point should be concerned with conflicting experimental observations. It should be noted that the detailed features of the potential energy surface with rather small curvatures can be effectively examined by the present scheme utilizing the Hellmann-Feynman forces, because the forces contain rich information on the potential surface.

Finally, we have examined the dependence of the present essential results on the calculation conditions such as the plane-wave cutoff energy and the number of special $\vec{k}$ points. Only the total energy is calculated using a cutoff energy of 75 Ry and 6 or 12 special $\vec{k}$ points for the initial and final atomic parameters in the relaxation shown in Fig. 3. It can be said that the energy differences between the initial and final configurations do not seriously depend on the number of $\vec{k}$ points and the plane-wave cutoff energy, although the absolute total energy values depend on the calculation conditions. For the lattice parameters of set *A*, the energy difference between the initial and final configurations is 0.008 224 29 Ry/cell for 6 $\vec{k}$ points and 65 Ry. The difference is 0.008 227 73 Ry/cell and 0.008 223 26 Ry/cell for 6 $\vec{k}$ points and 75 Ry and for 12 $\vec{k}$ points and 75 Ry, respectively. For the lattice parameters of set *B*, the difference is 0.007 990 22 Ry/cell for 6 $\vec{k}$ points and 65 Ry. The difference is 0.007 999 35 Ry/cell and 0.007 995 45 Ry/cell for 6 $\vec{k}$ points and 75 Ry and for 12 $\vec{k}$ points and 75 Ry, respectively. For the lattice parameters of set *G*, the difference is 0.026 202 68 Ry/cell for 6 $\vec{k}$ points and 65 Ry. The difference is 0.026 220 58 Ry/cell and 0.026 373 47 Ry/cell for 6 $\vec{k}$ points and 75 Ry/cell and for 12 $\vec{k}$ points and 75 Ry, respectively. Note that the initial atomic parameters for set *G* are those from Ref. 9. It is very important that both the experimental and the calculated $P6_3$ structures[3,9] have higher energy than the $P6_3/m$ structure regardless of the calculation conditions. Of course, the energy difference values for the initial and final configurations are rather small, which are in the same order of numerical errors thought to be associated with $\vec{k}$ points sampling and plane-wave cutoff energy. However, such numerical errors mainly affect absolute total energy values, and the present kind of energy differences for fixed cells are essentially little affected.

We have examined only several sets of lattice parameters in the region of ±2% of the experimental lattice parameters as shown in Fig. 2. However, it does not seem that the potential energy surface is so complicated at least against the lattice parameters. As seen in the converged total energy values of the $P6_3/m$ structures in Fig. 3, it is clear that the energy minimum of the $P6_3/m$ structure exists at the point *A* in the region of ±2%. On the other hand, the shape of each relaxation track itself in Fig. 3 does not reveal significant dependence on the lattice parameters, where only energy values are shifted according to the lattice parameters, except for the track of the point *G* with different initial inner coordinates. These points indicate that the $P6_3/m$ structure is always more stable than the $P6_3$ structure and that there exist no local energy minima for the $P6_3$ structure in this region of lattice parameters. Of course, we do not deny the possibility that the $P6_3$ structure could be more stable than the $P6_3/m$ structure for some other region of the space of lattice parameters. However, it does not seem that such a region should exist at least near the experimental lattice parameters.

We think that the physical origin of the relative stability of the $P6_3/m$ structure may be concerned with some kind of local tensile atmosphere around the N1 atom on the basal plane, where tensile forces of the Si-N bonds should stabilize the planar configuration. If the compressive stress occurs around the N1 atom along the basal plane for some smaller lattice constant of a_0, the N1 atom may stick out of the plane by the compressive forces of the Si-N bonds, which induces the $P6_3$ structure. However, such a phenomenon was not observed for the examined lattice parameters.

From the present examination, it is concluded that the most stable configuration of β-Si_3N_4 in the usual atmosphere has $P6_3/m$ symmetry. In other words, the $P6_3/m$ structure obtained in our preceding study[22] is the most stable phase of β-Si_3N_4. By the way, there exists a dynamical scheme to examine the present problem, which is the first-principles molecular-dynamics method combined with a variable unit-cell shape algorithm. Such a scheme can perform simultaneous relaxation of both lattice parameters and atomic parameters, and has recently revealed the relative stability of the $P6_3/m$ structure for β-C_3N_4.[24] However, if we repeat the relaxation of inner coordinates for each set of lattice parameters, the results should coincide with those of such a simultaneous full relaxation.

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