

# All-Electron Mixed-Basis Calculation of Structurally Optimized Titanium Nitride Clusters \*

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*Ab initio* total energy calculations based on the local density approximation (LDA) and the adiabatic approximation has attracted considerable attention as a conceptually new method. It is capable of describing dynamically the stability and reactivity of clusters, surfaces and bulk materials at finite temperatures, in principle, without using any adjustable parameters. Consequently, Ohno *et al.* have developed the all-electron mixed-basis approach which is applicable to the molecular dynamics of objects in any atomic environment. Titanium Nitride has unique features, such as self-lubricity, high wear resistance, high melting point, and high hardness, and the application to artificial bone and cutting tools, among others, is expected. We calculated optimized structures of titanium nitride micro clusters and compared these with silicon nitride which is tetravalent also. Both TiN<sub>2</sub> and SiN<sub>2</sub> clusters form isosceles triangles. The Ti–N bondlengths in TiN and TiN<sub>2</sub> are much shorter than in the bulk.

(Received January 17, 2002; Accepted February 8, 2002)

**Keywords:** *ab initio*, conjugate gradient method, electronic-structure, electronic states, nano cluster

## 1. Introduction

*Ab initio* total energy calculations<sup>1,2)</sup> based on the local density approximation (LDA)<sup>3)</sup> coupled with the adiabatic approximation<sup>4,5)</sup> are an important tool for understanding processes at the atomic level. It is capable to of describing dynamically the stability and reactivity of clusters, surfaces and bulk materials at finite temperatures without using any adjustable parameters. Consequentially, Ohno *et al.* have developed the all-electron mixed-basis approach which is applicable to the molecular dynamics of objects in any atomic environment.<sup>6–9)</sup>

The mixed-basis means that a combination of both plane waves (PWs) and atomic orbitals (AOs) is used as basis functions for expanding the wavefunctions. The introduction of AOs reduces considerably the computational load of the PW-expansion method.<sup>10)</sup> In particular, in the all-electron mixed-basis method, not only valence AOs but also core AOs are incorporated and pseudopotentials are not used. Historically, the all-electron mixed basis method was first formulated by Bendt and Zunger,<sup>11)</sup> who incorporated just core AOs in the PW-expansion method. However, the method<sup>6,12)</sup> used in the present study is independent and different from Bendt and Zunger's because our method incorporates valence AOs in the basis set also.

The present paper deals, for the first time, with the structural optimization of transition metal nitride clusters in the all-electron mixed-basis approach. Here, as an example we consider titanium clusters. Bulk titanium nitrides might someday be used for artificial bone and cutting tools because TiN has properties such as self-lubricity, good wear resistance, high melting point, and high hardness. However, the properties of titanium nitride clusters are not known. Therefore, as a initial investigation, we calculated the geometry and electronic

structure of small TiN clusters.

## 2. All-Electron Mixed-Basis Method

The all-electron mixed-basis method provides an accurate technique for the electronic states calculation. We solve self-consistently the Kohn-Sham equation<sup>3)</sup>

$$H\psi_i = \varepsilon_i\psi_i, \quad (1)$$

where  $H$  is the Hamiltonian,  $\varepsilon_i$  is the Kohn-Sham eigenlevel with wave function  $\psi_i$  of level  $i$  by expanding the wave functions as a linear combination of plane waves (PW)s and atomic orbitals (AO)s as follows:

$$\psi_i(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \chi_i(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} + \sum_n \sum_v \tau_i(n, v) \varphi_v(\mathbf{r} - \mathbf{R}_n), \quad (2)$$

where  $\sqrt{\Omega}$  is the volume of the unit cell,  $\chi$  is the expansion coefficient,  $n$  labels the atom,  $v$  is the index of the AO,  $\varphi$  represents an atomic orbital, and  $\mathbf{R}_n$  is the position of nucleus  $n$ . Here, core AOs are computed using the Herman-Skillman atomic code<sup>13)</sup> with a logarithmic radial mesh. Valence AOs are generated in the same way but their tail is truncated smoothly inside non-overlapping spheres of radius  $r_c$  prescribed at the outset. The same Coulomb and exchange-correlation potentials are evaluated separately for PWs and for AOs, respectively, in reciprocal space and in real space (along the radial direction in the atomic spheres), as accurately as possible. In other words, PW–PW, AO–PW and AO–AO contributions to the charge density and the potential are calculated separately.

To achieve self-consistency of electronic states and to orthogonalize different electronic levels, we adopt a conjugate gradient (CG) method combined with the Gram-Schmidt orthogonalization method.<sup>14)</sup> In the CG method the electronic states are moved along the CG direction on the energy sur-

\*This Paper was Presented at the Autumn Meeting of the Japan Institute of Metals, held in Fukuoka, on September 23, 2001.

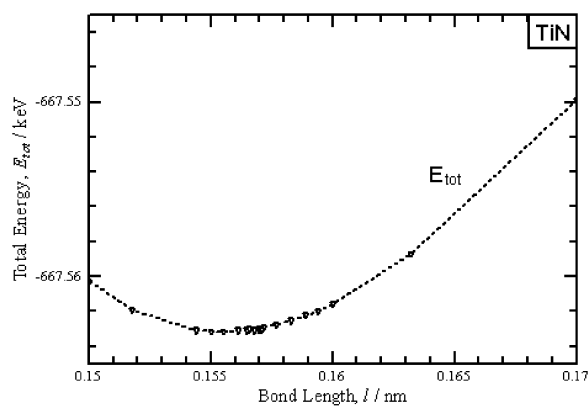


Fig. 1 Total energy vs bond length of TiN.

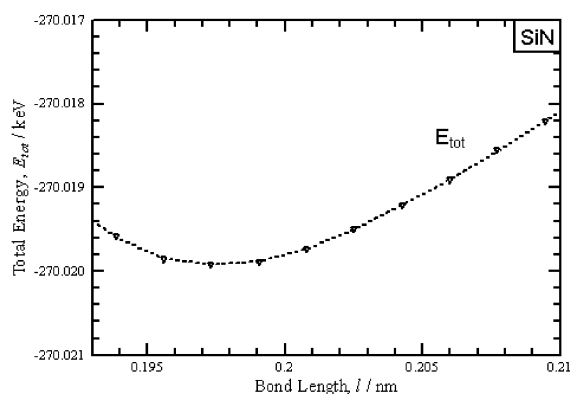


Fig. 2 Total energy vs bond length of SiN.

face. The convergence by CG method is faster than that of the steepest descent (SD) method.<sup>8)</sup>

### 3. Results

We used the all-electron mixed-basis method to calculate the structure of TiN, TiN<sub>2</sub>, SiN, and SiN<sub>2</sub> clusters. The Hamiltonian was diagonalized using matrix diagonalization, SD, and CG methods. Charge self-consistency and the minimization of the atomic forces was achieved using Broyden mixing. For TiN<sub>2</sub> and SiN<sub>2</sub> the local density approximation (LDA) was used, but for clusters with odd numbers of electrons, TiN and SiN, the local spin density approximation (LSDA) was employed.<sup>15)</sup>

The TiN and SiN cluster was calculated in a cubic unit cell with an edge of 0.9 nm. A cutoff energy for PWs of 118.8 eV was chosen, corresponding to 2109 plane waves. In this calculation, the interatomic distance was varied to determine the equilibrium bondlength, see Figs. 1 and 2. In these figures, the minimum of total energy coincides with the zero of the force at about 0.157 (0.197) nm bond length for TiN (SiN). The curvature of the total energy is very different between both sides of the minimum of total energy.

The LDA calculation of TiN<sub>2</sub> (SiN<sub>2</sub>) was performed in a cubic unit cell with an edge of 0.8 (0.9) nm. The cutoff energy for PWs is chosen as 397.2 (313.8) eV corresponding to 9171 plane waves. The structure was relaxed using Broyden's method.

Optimized structures of TiN and TiN<sub>2</sub> are shown in Fig. 3

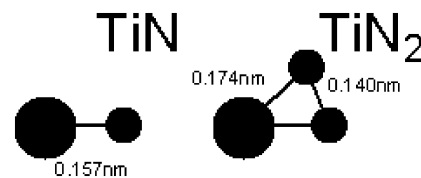
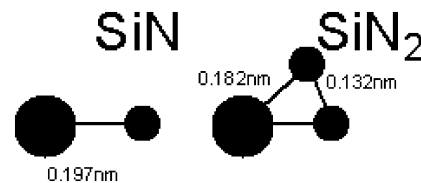
Fig. 3 Optimized structures of TiN and TiN<sub>2</sub>.Fig. 4 Optimized structures of SiN and SiN<sub>2</sub>.

Table 1 Bondlengths in microclusters as computed with the all-electron mixed basis method and as found in bulk TiN with the NaCl type structure.

	Reference	Ti/Si-N (nm)	N-N (nm)
TiN	this work	0.157	—
TiN <sub>2</sub>	this work	0.174	0.140
SiN	this work	0.197	—
SiN <sub>2</sub>	this work	0.182	0.132
TiN (bulk)	exp. <sup>16)</sup>	0.212	—
TiN (bulk)	LDA <sup>17)</sup>	0.209	—

and those of SiN and SiN<sub>2</sub> are shown in Fig. 4. The bond length in TiN is about 0.157 nm while the bond length between Ti–N in TiN<sub>2</sub> is 0.174 nm, and between N–N is 0.140 nm. The optimized structures of TiN<sub>2</sub> and SiN<sub>2</sub> are isosceles triangles. The Ti–N bondlength in micro clusters is much shorter than that in the bulk, see Table 1.

### 4. Summary

We have applied the all-electron mixed basis approach to the titanium nitride micro clusters. Both TiN<sub>2</sub> and SiN<sub>2</sub> clusters form isosceles triangles. The Ti–N bondlengths in TiN and TiN<sub>2</sub> are much shorter than in the bulk. We are now planning to calculate optimized structures of larger clusters.

### Acknowledgements

The authors would like to thank the technical staff of the supercomputing center at IMR for their continuous support of the supercomputing facility.

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