

Electronic structure and charge transfer in α - and β - Si_3N_4 and at the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface

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Using a self-consistent linear combination of atomic orbitals method based on density-functional theory in a local-density approximation, the electronic structure in the high-temperature ceramics α - Si_3N_4 and β - Si_3N_4 and at the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface have been calculated. The resulting charge transfer suggests that the ionic formula can be written as $\text{Si}_3^{+1.24}\text{N}_4^{-0.93}$. For the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface, the silicon atoms from the silicon side lose some electrons to the nitrogen atoms of the silicon nitride side forming Si-N bonds at the interface. The calculated electronic density of states spectrum of Si $2p$ core levels for this interface is in good agreement with x-ray photoemission spectroscopy experiments. [S0163-1829(98)06928-8]

I. INTRODUCTION

The knowledge of the electronic structure, charge distribution, and charge transfer in a material is essential for determining the electrostatic energies, for characterizing the chemical reaction, and for predicting the bonding behavior among the atoms.¹⁻⁵ Particularly, for the ceramic material of silicon nitride (Si_3N_4) and its interface structures with silicon, the chemical bonds responsible for microstructures are neither typically ionic nor covalent. A detailed understanding of the electronic structure and the bonding behavior in these materials is indispensable for material studies. In the calculations of mechanical properties or molecular-dynamics simulations, the interatomic potentials involve Coulomb terms for these materials. The effective charges and charge transfers in the materials can be extracted from the analyses of experimental data.¹⁻³ However, in many cases the experimental information is not available, and the empirical or semiempirical methods are not based on fundamental understanding. It has been demonstrated for more than twenty years that the first-principles methods yield quite reliable electronic structure information and other ground-state properties. The purpose of the present study is to obtain information on the electronic structure, the charge distribution, and charge transfer in silicon nitride and for the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface by using the linear combination of atomic orbitals (LCAO) method.

Silicon nitride has a prominent role as ceramics for high temperature, high strength applications owing to its outstanding mechanical properties.⁶⁻⁸ Because of its high strength and hardness, high decomposition temperature, and resistance to corrosion and wear, Si_3N_4 has been used as a high-temperature material for engine components and cutting tools. There is great interest in the Si_3N_4 film on *c*-Si surface among other interface structures (for a review see, e.g., Ref. 9), both in the experimental research and electronics industry.⁹⁻²⁰ It is a material sought for device applications due to its higher density, higher dielectric constant, and promising radiation hardness as compared to SiO_2 . The $\text{Si}(111)/\text{Si}_3\text{N}_4$ interface has been studied experimentally us-

ing different methods.^{16,17,20} One of the most important defects at the interface is the $\text{Si}\equiv\text{N}_3$ defect that is referred to a Si atom backbonded to three N atoms and associated with a dangling bond. This defect was shown to account for the majority of deep traps that have been extensively studied electrically. Due to the complexity of the $\text{Si}(111)/\text{Si}_3\text{N}_4$ interface, especially its structure, the fundamental understanding of the electronic and mechanical properties is far behind the work of experimental studies and engineering.¹⁶⁻²¹

The underlying LCAO method is based on using the atomic orbitals as the basis to expand the electronic eigenfunction of a many-atom system. This method is very attractive in dealing with complex materials with a large number of atoms per unit cell.²²⁻³⁰ In the present study of the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface, a supercell of 52 atoms was used. Because of the broken symmetry at the interface, the computation for such a system is far more complex than a crystal of the same size of unit cell with a perfect lattice.

The calculated effective charges and charge transfer for these materials have been successfully used in related molecular-dynamics simulations by one of the authors and collaborators, which was reported elsewhere³¹ along with a brief announcement of the data from this calculation. In the present paper, we report the detailed calculation procedures and relatively complete information for the calculated electronic structure and charge transfer in silicon nitride, the free $\text{Si}_3\text{N}_4(001)$ surface, and the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface. Especially, we show that the charge transfer in these three cases is closely related to the Si-N bond. In the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface layer, the Si atoms on the silicon side lose some electrons to the N atoms of the silicon nitride side and form Si-N bonds across the interface. The calculated results indicate that one Si-N bond would associate with a charge transfer of about 0.31 electrons/bond. The remainder of this paper is organized as follows. In Sec. II, the method and formulas used in the study will be briefly described. The calculated results will be presented in Sec. III, and a conclusive summary is given in Sec. IV.

II. METHODS

The methods described herein are based on self-consistent calculations using an expanded LCAO package from Ames

Laboratory, Department of Energy (DOE). The exchange-correlation interaction of the many-electron system is described by the density-functional theory in a local-density approximation. Therein, we used the Ceperley-Alder form of the exchange-correlation potential. Test calculations by this and other groups show that the widely used forms of different parametrizations of the exchange-correlation potential give essentially very similar results of electronic structure. Furthermore, the procedure itself has been tested by this and other groups, and is found to give results of comparable accuracy to those obtained using other first-principles methods.²²⁻³⁰ Since the atoms in the Si(111)/Si₃N₄(001) interface do not possess a magnetic moment, a spin-polarized calculation (using the exchange-correlation potential in a spin-density functional) yields practically the same electronic structure as a non-spin-polarized computation.

In the LCAO method the electronic eigenfunction, $\Psi_{\mathbf{k}n}(\mathbf{r})$, of a many-atom system associated with an energy $\varepsilon_{\mathbf{k}n}$, is expanded by the atomic orbitals

$$\Psi_{\mathbf{k}n}(\mathbf{r}) = \sum_{\alpha m} C_{\alpha m}(\mathbf{k}n) \Phi_{\alpha m}(\mathbf{k}, \mathbf{r}), \quad (1)$$

where $\Phi_{\alpha m}(\mathbf{k}, \mathbf{r})$ is a Bloch wave that is expressed by the atomic orbitals as

$$\Phi_{\alpha m}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i\mathbf{k} \cdot \mathbf{R}_{\mathbf{l}}} u_{\alpha m}(\mathbf{r} - \tau_m - \mathbf{R}_{\mathbf{l}}), \quad (2)$$

where $u_{\alpha m}$ is the shell function of an atomic orbital in the α th state of the m th atom at position τ_m ; $\mathbf{R}_{\mathbf{l}}$ is the translation vector of the lattice; \mathbf{k} is a wave vector in the Brillouin zone; $\varepsilon_{\mathbf{k}n}$ is the energy of the n th electronic state at the k point. The coefficients $C_{\alpha m}$ are calculated from the secular equation

$$HC = \varepsilon_{\mathbf{k}n} SC, \quad (3)$$

where H and S are the matrix of the Hamiltonian and overlap, respectively. The electronic charge density ρ is calculated from the electronic eigenfunctions,

$$\rho(\mathbf{r}) = \sum_{\text{occ}} |\Psi_{\mathbf{k}n}(\mathbf{r})|^2 \quad (4)$$

where the summation extends over all the occupied electronic states.

The integrated total electron charge should be equal to the contribution of the electrons from all the atoms in the material. However, the effective charge associated with the individual atoms in the condensed state of the material could be different from the value of neutral atoms because of chemical reactions. The effective charge and related charge transfer among the atoms of different species in the material is one of the quantities to characterize the nature of the chemical reaction and bonding behavior. A knowledge of this quantity is sought for understanding various physical and chemical properties in molecules and solid-state materials. However, to evaluate reliably the effective charge and charge transfer for a material is still a very difficult task.

One of the practical approaches to evaluating the effective charge of an atom in a quantum calculation using the method

of linear combination of atomic orbitals is to count the contribution of the atom to the coefficients of the electronic eigenfunctions of the system. This is done by substituting Eqs. (1) and (2) into Eq. (4), which yields

$$\rho(\mathbf{r}) = \sum_m \rho_m(\mathbf{r}). \quad (5)$$

In Eq. (5) the effective charge associated with atom m is introduced as

$$\begin{aligned} \rho_m(\mathbf{r}) &= \frac{1}{N} \sum_{\mathbf{l}\alpha} \sum_{\mathbf{l}'m'\alpha'} \sum_{\mathbf{k}n} f_{\mathbf{k}n} C_{\alpha m}^*(\mathbf{k}n) C_{\alpha' m'}(\mathbf{k}n) e^{-i\mathbf{k} \cdot (\mathbf{R}_{\mathbf{l}} - \mathbf{R}_{\mathbf{l}'})} \\ &\quad \times u_{\alpha m}(\mathbf{r} - \tau_m - \mathbf{R}_{\mathbf{l}}) u_{\alpha' m'}(\mathbf{r} - \tau_{m'} - \mathbf{R}_{\mathbf{l}'}), \end{aligned} \quad (6)$$

where $f_{\mathbf{k}n}$ is the Fermi distribution for the electronic state with an energy $\varepsilon_{\mathbf{k}n}$ at the k point in the Brillouin zone. Other notations are the same as defined before. In developing Eqs. (5) and (6), there is no other approximation.

This effective charge in Eq. (6) may be interpreted as a portion of the electronic charge most likely carried by and moved along with the atom. The charge transfer is found from the difference of the effective charge and the neutral charge of the atom. In a bulk material the atoms can be in neutral or ionic states. Based on test calculations on various materials, it was often found that the calculated total charge density $\rho(r)$ is not dependent on the employed basis sets using neutral atomic orbitals or ionic ones. This is largely due to the self-consistent variational principle. However, in a material involving soft valence atomic shells, the difficulties in evaluating the effective charge and charge transfer become more prominent. Our experiences and test calculations indicate that a proper basis set of atomic orbitals in suitable ionic states usually provides more reliable prediction of the effective charge. In this study, the atomic orbitals are computed using an atom calculation program from Ames Laboratory, DOE. The ionic states of atoms in a bulk material are determined from the calculated charge transfer in a self-consistent fashion or from experimental findings.

III. RESULTS

A. Electronic structure and charge transfer in α and β -Si₃N₄

The α -phase silicon nitride has a hexagonal structure.³²⁻³⁴ It is in the space group C_{3v}^4 . The lattice constants used in the calculation are $a = 7.818 \text{ \AA}$ and $c = 5.591 \text{ \AA}$ as reported from the experimental measurement by Kato *et al.*³² There are 28 atoms per unit cell. In the self-consistent calculation, a mesh of 20 k points with the proper weights in the irreducible Brillouin zone was used. A comparison of the calculated total energy with a test calculation using a mesh of five k points only revealed a small difference of about 0.0001 Ry. This is an indication of the satisfactory convergence with respect to the number of k points.

The calculated electronic band structure of α -phase Si₃N₄ (see Fig. 1) agrees well with other well converged calculations.²¹⁻²³ Its analog for β -phase Si₃N₄^{35,36} is very similar to the structure of the α phase as discovered by others and our calculations.^{22,23}

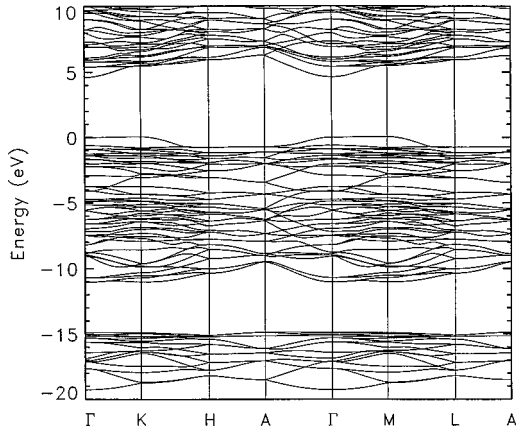


FIG. 1. The electronic band structure of the α -phase Si_3N_4 . The zero of the energy was set at the top of the valence band at the Γ point.

From Fig. 1, the direct band gap at the Γ point can be determined to be about 4.7 eV. It is very close to the smallest indirect band gap of other transitions and lies in the range of experimental values.^{37–40} The large disparity of the experimental data for the band gap from 4.0 to 5.5 eV is mainly attributed to the different experimental methods and sample preparations.

It should be pointed out that some portions of the highest valence band from the Γ point to K and M points in Fig. 1 are quite flat. This will lead to a very large effective mass of holes along these directions.

Using the calculated electronic eigenfunctions, we obtain from Eq. (6) the effective charge of an atom (Q^*) and determine the charge transfer (ΔQ) as the difference of the effective charge and the neutral charge of the atom. The values for α - and β -phase Si_3N_4 are given in Table I.

In one unit cell of Si_3N_4 there are six atoms in the group $6c$; two atoms are in the groups $2a$ and $2b$. From the results of Table I it can be seen that the silicon atoms give away approximately 1.23–1.25 electrons/atom; nitrogen atoms gain approximately 0.91–0.94 electrons/atom. The ionic formula for the silicon nitride may be then written as

TABLE I. (a) Effective charge (Q^*) and charge transfer (ΔQ) in α -phase Si_3N_4 . Space group C_{3v}^4 . (b) Effective charge and charge transfer in β -phase Si_3N_4 . Space group C_6^6 .

		(a)	
Atom	Position	Q^* (electrons)	ΔQ (electrons)
Si(1)	6c	12.761	1.239
Si(2)	6c	12.755	1.245
N(1)	6c	7.928	-0.928
N(2)	6c	7.944	-0.944
N(3)	2b	7.912	-0.912
N(4)	2a	7.908	-0.908
		(b)	
Atom	Position	Q^* (electrons)	ΔQ (electrons)
Si(1)	6c	12.743	1.257
N(1)	6c	7.947	-0.947
N(2)	2b	7.931	-0.931

$\text{Si}_3^{+1.24}\text{N}_4^{-0.93}$. The estimated error in the calculation of the charge transfer is about 10–15%, which is much larger than that in the electronic structure computation. The charge transfer in β -phase Si_3N_4 is very close to the α phase with a difference within the calculation uncertainty. This is due to the fact that the two phases have very similar local atomic configurations. In both of the phases, a Si atom is bonded to four N atoms, and a N atom is bonded to three Si atoms, the bond lengths in the two phases being approximately 1.70–1.78 Å. It should be mentioned again that the calculation error should be considered when a comparison with experimental results is made.

A question may be raised concerning the use of atomic orbitals from the calculation of a neutral atom. Since a Si atom loses about one electron, the ionic atomic orbitals of Si^{+1} was also constructed. The self-consistent calculations were repeated on α -phase Si_3N_4 using these atomic orbitals, and it was found that the calculated effective charge and charge transfer of Si and N atoms using the Si^{+1} orbitals are very close to the data reported in Table I with the differences within the estimated calculation uncertainty.

For one Si-N bond, the silicon atom may transfer about 0.31 electrons to the nitrogen atom. This calculated value of charge transfer for one Si-N bond is very close to the so called “one-third rule” in silicon nitride, which is extracted from experimental data and used in molecular-dynamics simulations.^{1,3} It should be noted that in the evaluation of effective charge and charge transfer the well-constructed atomic orbitals from the atom calculation including core and valence states should be used. In other methods using a procedure of orthogonalization, the overlap matrix elements between the core states of an atom and the valence states of other atoms are orthogonalized to be zero. The orthogonalized basis in a many-atom system is slightly different from the true atomic orbital. The charge-transfer calculation using an orthogonalized basis will bring in an extra calculation uncertainty.

B. Free $\text{Si}_3\text{N}_4(001)$ surface

Before we turn to the complex structure of the interface $\text{Si}(111)/\text{Si}_3\text{N}_4$, let us examine the $\text{Si}_3\text{N}_4(001)$ surface. Both the α - and β -phase Si_3N_4 have a layered structure in the hexagonal lattice.^{32–36} One sheet of Si_3N_4 has three silicon atoms (on one atomic layer) bonded to four nitrogen atoms (three of the N atoms are on an atomic layer and the fourth is on a slightly shifted atomic layer). The interlayer interaction is weaker than the intralayer interaction. It is energetically more favorable to cleave or grow silicon nitride in a layer structure. The surface of Si_3N_4 will be one sheet of the silicon nitride. On the top of the surface, three nitrogen atoms (belonging to $6c$ positions in Si_3N_4) and three silicon atoms (also in $6c$ positions) have dangling bonds. The fourth nitrogen atom (belonging to $2b$ positions in Si_3N_4) is still bonded to three silicon atoms on the layer and has no dangling bond.

The electronic structure of the unrelaxed $\text{Si}_3\text{N}_4(001)$ surface was calculated using the self-consistent LCAO method. 28 atoms in one unit cell of the two-dimensional $\text{Si}_3\text{N}_4(001)$ slate were used to simulate the free surface structure. The

layer structure was based on the atomic arrangements of the β -phase Si_3N_4 .^{33,34} Four Si_3N_4 sheets containing 12 atomic layers were used in the calculation.

The self-consistent calculation revealed that the charge transfer from the surface silicon atoms (having one dangling bond) is about 1.10 electrons/Si atom, which is smaller than the silicon charge transfer (1.24) in the bulk Si_3N_4 . Correspondingly, the surface nitrogen atoms with one dangling bond gains about 0.79 electrons/N atom, which is also smaller than the charge transfer of the N atom (0.93) in the bulk. It is very interesting to see that the fourth surface nitrogen atom without a dangling bond gains about 0.94 electrons/N atom, which is very close to the charge gain of nitrogen atom in the bulk Si_3N_4 given in Table I. The reduced charge transfer for the surface silicon and nitrogen atoms is attributed to the dangling bonds.

C. Si(111)/ Si_3N_4 (001) interface

Six layers of Si 2×2 (111) containing 24 atoms were matched to the Si_3N_4 (001) surface. The mismatch of the lattice constants of the two slates of materials is only about 1%, which is relatively small compared to other geometries of the interface. Since the silicon nitride is mechanically much harder than the silicon crystal, the Si(111) layers were expanded along x and y directions to match the Si_3N_4 lattice parallel to the interface. In this study using the LCAO method, a supercell of 52 atoms for the interface structure was used; see Table II for the coordinates. In the x - y plane parallel to the interface, periodic boundary conditions were applied. The two translation vectors (\mathbf{a}_1 and \mathbf{a}_2) on the x - y plane were chosen from the β -phase Si_3N_4 lattice. The Si_3N_4 (001) slate includes twelve atomic layers (four Si_3N_4 sheets with three layers each). The interface structure in perspective view is shown in Fig. 2. Outside of the Si(111) and Si_3N_4 (001) layers there is an empty space in the supercell.

Since the Si-N bond is much stronger than Si-Si and N-N bonds in Si_3N_4 , the interface of Si(111)/ Si_3N_4 (001) tends to have a maximum number of Si-N bonds. A numerical computation was performed to search the geometry of the interface by maximizing the total number of Si-N bonds at the interface. Further relaxation of the interface was not included in the construction of the interface structure. A Si 2×2 (111) layer has four Si atoms/cell. Three of the four Si atoms (small dark shaded spheres) of the first Si(111) layer near the interface directly bond to the three N atoms (large spheres) of Si_3N_4 (001) layer as shown in Fig. 2. Each of these nitrogen atoms has one dangling bond before matching the Si(111) layer onto the Si_3N_4 (001) surface. The fourth Si atom of the first Si(111) layer is on the top of another N atom, which is bonded to three Si atoms of the first Si_3N_4 sheet. The three Si atoms (the small lightly shaded spheres) of the first Si_3N_4 sheet at the interface still have one dangling bond that generates the defects of $\text{Si} \equiv \text{N}_3$.

Within the self-consistent LCAO method for the Si(111)/ Si_3N_4 (001) interface three k points with proper weights in the two-dimensional Brillouin zone were used. A comparison with results of the one k point (Γ point) calculation showed only a small difference of the charge distribution. This is an indication that three k points with proper

TABLE II. Atomic positions for the Si(111)/ Si_3N_4 (001) interface structure used in our calculation. The two translation vectors on the x - y plane parallel to the interface are $\mathbf{a}_1 = (0.0, 7.5950, 0.0)$ Å, $\mathbf{a}_2 = (6.5775, -3.7975, 0.0)$ Å. (a) The Si atomic positions of the Si(111) film used in the interface structure. The atom type 1 refers to Si atoms. (b) Positions of the Si and N atoms of Si_3N_4 (001) layers. Here atom type 1 is referred to Si atoms; atom type 2 is referred to N atoms.

Position No.	Atom-Type	x (Å)	y (Å)	z (Å)
1	1	1.2570	2.0282	3.6956
2	1	1.2586	5.8257	3.6956
3	1	4.5465	3.9255	3.6956
4	1	4.5448	0.1280	3.8543
5	1	0.1599	0.1299	4.4793
6	1	3.4478	-1.7703	4.4793
7	1	0.1616	3.9274	4.4793
8	1	3.4494	2.0272	4.4793
9	1	0.1599	0.1299	6.8306
10	1	3.4478	-1.7703	6.8306
11	1	0.1616	3.9274	6.8306
12	1	3.4494	2.0272	6.8306
13	1	2.3524	0.1289	7.6143
14	1	5.6402	-1.7713	7.6143
15	1	2.3540	3.9264	7.6143
16	1	5.6419	2.0262	7.6143
17	1	2.3524	0.1289	9.9656
18	1	5.6402	-1.7713	9.9656
19	1	2.3540	3.9264	9.9656
20	1	5.6419	2.0262	9.9656
21	1	1.2570	2.0282	10.7493
22	1	4.5448	0.1280	10.7493
23	1	1.2586	5.8257	10.7493
24	1	4.5465	3.9255	10.7493

weights will be sufficient for this self-consistent calculation. The $1s$, $2s$, and $2p$ states of Si and the $1s$ state of N were treated as core states, being fully occupied. The core charge density was considered to be the same as the neutral atoms. However, the core energy levels of the atomic states may still shift along with the Hamiltonian of the system in the self-consistent calculation. Our test calculations show that the calculations using the spin-density functional find practically the same electronic structure since the atoms in the Si(111)/ Si_3N_4 interface do not have a net magnetic moment.

The calculated Si $2p$ density of states (DOS) for the Si(111)/ Si_3N_4 (001) interface structure is shown in Fig. 3. The heights of the peaks of the density of state depend on the number of the atomic layers of Si(111) and Si_3N_4 (001) used in the calculation. In the experimental measurements, it depends on the probing depth into the interface. The distribution of the energy level of the Si $2p$ states was attributed to the broken symmetry at the interface. Near the interface, the Si atoms in different atomic layers experience different environments of atomic configurations. This broken symmetry due to the interface leads to the energy shift of the atomic core levels as shown in Fig. 3 for the Si $2p$ states, featuring two major peaks. One of the peaks is around -98 to -99 eV, which is the contribution of the Si(111) film near

TABLE II. *Continued.*

Position	Atom type	x (Å)	y (Å)	z (Å)
25	1	5.4304	-1.3777	2.1767
26	1	2.6691	-0.2165	2.1767
27	1	5.0554	1.5942	2.1767
28	1	1.1471	5.1752	-2.1767
29	1	3.9083	4.0140	-2.1767
30	1	1.5220	2.2033	-2.1767
31	1	1.1471	5.1752	0.7256
32	1	3.9083	4.0140	0.7256
33	1	1.5220	2.2033	0.7256
34	1	5.4304	-1.3777	-0.7256
35	1	2.6691	-0.2165	-0.7256
36	1	5.0554	1.5942	-0.7256
37	2	2.1666	-1.0246	0.7627
38	2	4.6069	2.4334	0.7627
39	2	6.3815	-1.4089	0.7627
40	2	4.4108	4.8221	-0.6884
41	2	1.9706	1.3641	-0.6884
42	2	0.1960	5.2064	-0.6884
43	2	4.4108	4.8221	2.2139
44	2	1.9706	1.3641	2.2139
45	2	0.1960	5.2064	2.2139
46	2	2.1666	-1.0246	-2.1396
47	2	4.6069	2.4334	-2.1396
48	2	6.3815	-1.4089	-2.1396
49	2	2.1925	3.7975	-2.2081
50	2	4.3850	0.0000	2.1454
51	2	4.3850	0.0000	-0.7569
52	2	2.1925	3.7975	0.6942

the interface. Another major peak around -100.5 to -102 eV is the Si $2p$ states from the Si_3N_4 side near the interface. Both peak positions agree well with x-ray photoemission spectroscopy (XPS) experimental data of -99.7 and -102.8 eV.¹⁶ The shift of the two major peaks is approximately 3.1–3.5 eV, which is in agreement with the experimental result of 3.15 eV.¹⁶ The calculated Si $2p$ core energies also agree with the experimentally measured binding energies within 1%. The substructure around -100.5 eV is the contribution of Si atoms at the interface from the first Si_3N_4 sheet near the interface. The relaxation of the atoms near the interface may lead to disorder effects, which can smooth the substructure of the DOS spectrum in some degree as demonstrated in the studies for amorphous materials.^{26,27} The good agreement of the calculated DOS spectrum with the experimental results indicates that the major structures of the calculated results using the self-consistent LCAO method are reasonably reliable.

Some contour diagrams of the valence charge-density map for the Si(111)/ Si_3N_4 (001) interface structure are shown in Figs. 4 and 5. A two-dimensional contour diagram of the valence charge density on a plane perpendicular to the interface is given in Fig. 4. This plane cuts through the N(2*b*) and N(6*c*) atoms of the first Si_3N_4 sheet near the interface as marked in Fig. 4. Here the labels N(2*b*) and N(6*c*) refer to the N atoms of Si_3N_4 at 2*b* and 6*c* positions. The silicon atoms on the first Si(111) layer near the interface can also be

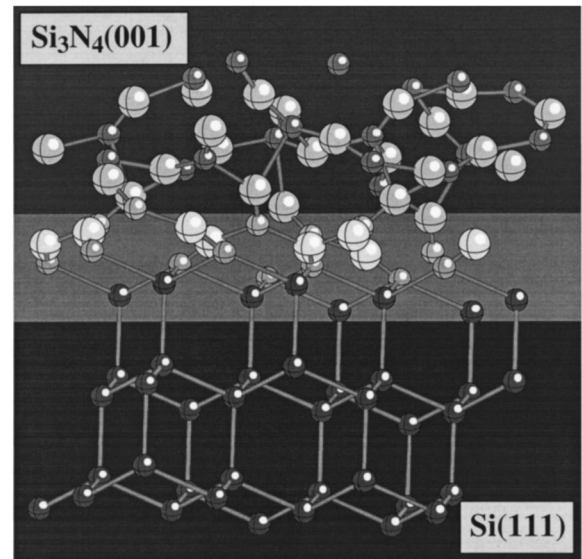


FIG. 2. The atomic structure of the Si(111)/ Si_3N_4 (001) interface used in the study. The small dark shaded spheres are the Si(111) atoms; the small lightly shaded spheres are the Si atoms of the Si_3N_4 side; and the large spheres are the N atoms of the Si_3N_4 side. The interface region is indicated by a bright strip.

seen in Fig. 4. Each line of the contour diagram has a constant charge-density value; the difference of the charge density of any two consecutive lines was kept constant. There is a dense distribution of the contour lines around the atomic sites. This clearly indicates that the charge density near the nuclei changes rapidly. It is evident from Figs. 4 and 5, that the size of the nitrogen atom is much larger than that of silicon atom. The sizes of the silicon and nitrogen atoms may be estimated as $R_{\text{N}}=1.15$ Å and $R_{\text{Si}}=0.61$ Å, respectively. The bonding behavior of the Si and N atoms near the interface can be seen from the relatively denser distribution and a more complex structure of the contour lines than that of the interstitial region. The electron charge in the bonding area cannot be clearly identified as to associate with a specific atom.

Figure 5 shows the valence charge-density maps on the Si_3N_4 side near the interface. Figure 5(a) is the first Si_3N_4

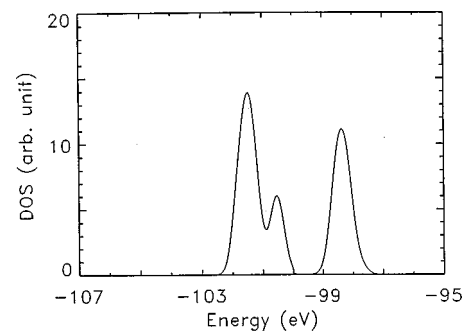


FIG. 3. The calculated Si $2p$ core spectrum of the density of states for the interface structure of Si(111)/ Si_3N_4 (001). An arbitrary unit was used for the density of states. The peak of DOS around the energy at about -98.5 eV is the contribution of Si(111) atoms; the peak structure from the energy of -100 to -102.4 eV is attributed to the Si $2p$ core levels of the Si_3N_4 (001) side.

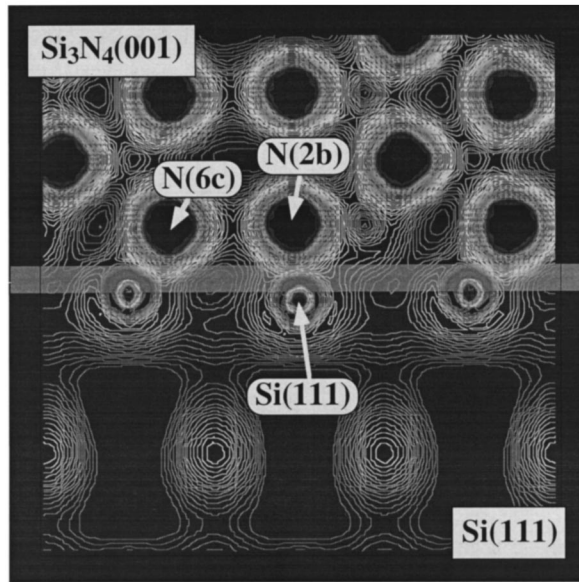
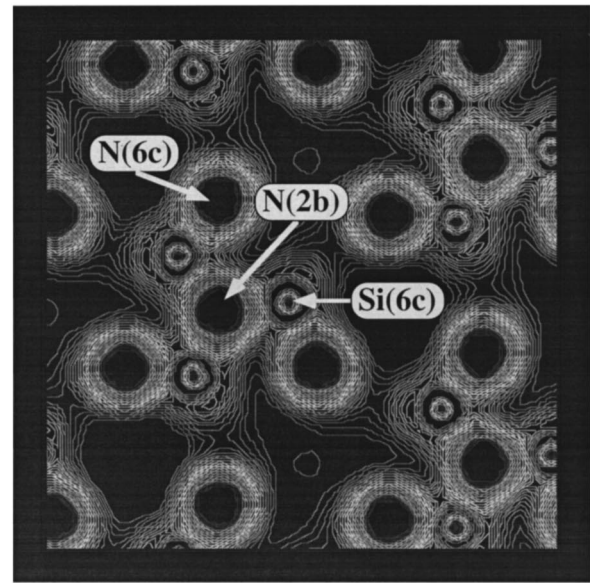


FIG. 4. The valence charge-density map on a two-dimensional plane perpendicular to the Si(111)/Si₃N₄(001) interface. The labels N(2*b*) and N(6*c*) refer to the N atoms of Si₃N₄ at 2*b* and 6*c* positions.

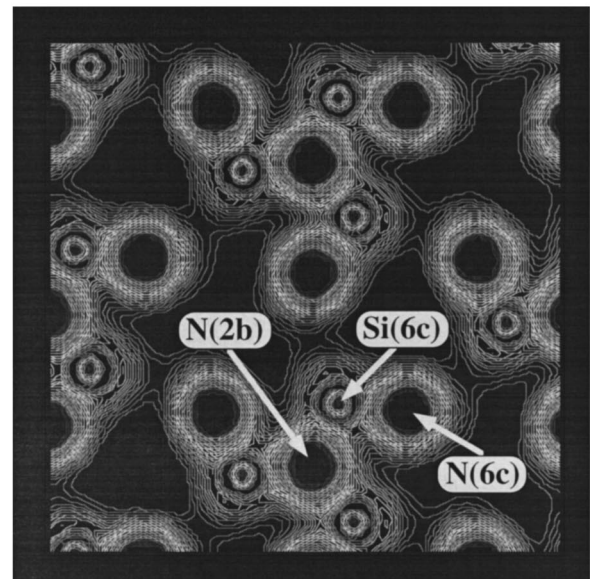
sheet near the interface; Fig. 5(b) is the second Si₃N₄ sheet away from the interface. These two-dimensional maps are on a plane parallel to the interface. The labels Si(6*c*), N(2*b*), and N(6*c*) refer to the Si atom at 6*c*, N atoms at 2*b* and 6*c* positions in the bulk silicon nitride, respectively. There are one N(2*b*), three N(6*c*), and three Si(6*c*) atoms on one Si₃N₄ sheet in a unit cell. The formation of the Si-N bond can be seen from the distribution of the contour lines. The N(2*b*) atom is fully bonded to three Si(6*c*) atoms on one Si₃N₄ sheet. The N(6*c*) atom on the first Si₃N₄ sheet [Fig. 5(a)] has one bond to a Si atom on the same sheet, and one bond to the Si atom of the Si₃N₄ sheet above. It also has one bond to the Si atom of the Si(111) layer that is below the first Si₃N₄ sheet. For the second sheet [see Fig. 5(b)] these N(6*c*) atoms have bonds to the Si₃N₄ sheets lying above and below.

The valence charge density on the silicon side near the interface is shown in Fig. 6. Figure 6(a) shows the charge density on the first Si(111) layer; Fig. 6(b) is for the third Si(111) layer away from the interface. The hexagonal structure of the Si(111) layer is clearly seen from Fig. 6. The Si atoms do not bond each other on this plane as seen from the distribution of the charge density. All the bonds are pointing out of the plane. Whereas the first layer indicates the influence of the interface on the charge density [see Fig. 6(a)], the third layer clearly represents the electronic structure of a bulklike behavior, namely, high charge density around the atom positions and low one in the interstitial regions.

The effective charge and the charge transfer at the interface were carefully examined using the obtained electronic eigenfunction. In the calculation of the effective charge, eight *k* points with proper weights in the irreducible Brillouin zone were used. It should be mentioned again that the full atomic orbitals of core and valence states were included in the calculation of the effective charge. The disorder effect in the interface layer is not included in this electronic structure calculation. Our calculated electronic charge densities



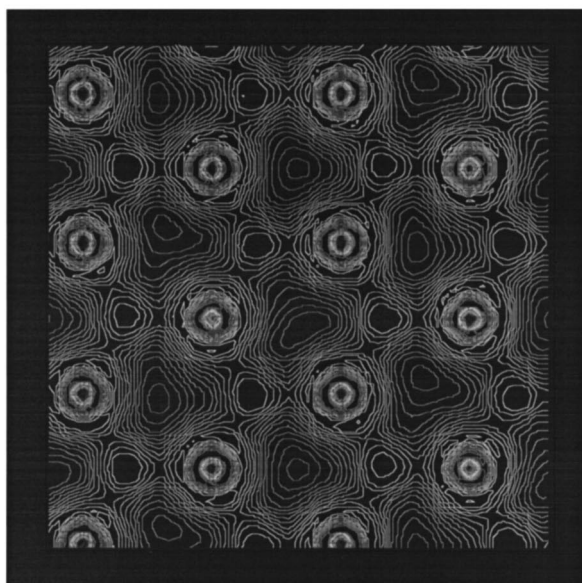
(a)



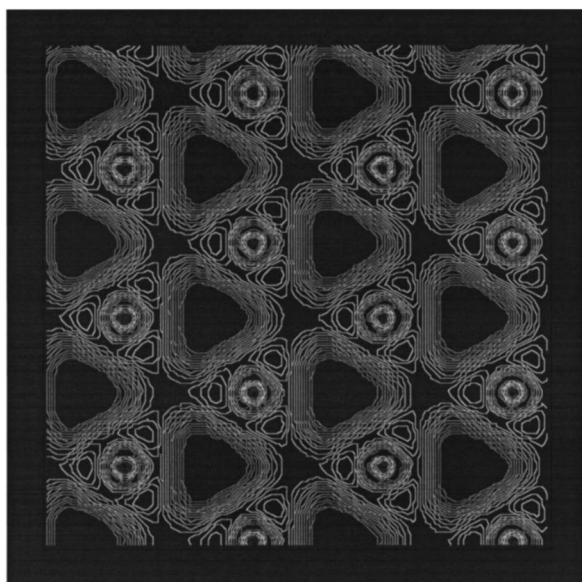
(b)

FIG. 5. The valence charge-density maps on the Si₃N₄ side near the interface. These planes are parallel to the Si(111)/Si₃N₄(001) interface. (a) The first Si₃N₄ sheet; (b) the second Si₃N₄ sheet away from the interface. The label Si(6*c*) refers to the Si atom at 6*c* position in Si₃N₄; and N(2*b*) and N(6*c*) refer to the N atoms at 2*b* and 6*c* positions.

and previous experiences indicate that a charge transfer happens predominantly along the chemical bond of the first-nearest neighbors and depends mainly on the local structure. A long-range disorder may not substantially change the nature of the effective charge and charge transfer in the material. The calculated effective charge Q^* and the charge transfer ΔQ for the selected atomic layers near the interface structure are listed in Table III. Therein, the labels Si1 to Si4, and N1 to N4 refer to the atoms in an order on the plane used in the calculation. Since the symmetry is broken in the region of the interface, the symbols 6*c* and 2*b* do not have an exact meaning in group theory. They only refer to the positions



(a)



(b)

FIG. 6. The valence charge density on the Si(111) side. All the planes are parallel to the interface. (a) The first Si(111) layer near the interface; (b) the third Si(111) layer away from the interface structure.

from the bulk Si_3N_4 . The effective charge and charge transfer of Si atoms from the first Si(111) layers near the interface are listed in Table III(a), from which it can be seen that the Si1 to Si3 atoms lose about 0.41 to 0.44 electrons. These three Si atoms are bonded to three N($6c$) atoms of the first Si_3N_4 sheet near the interface by giving away some electrons. Otherwise these three N($6c$) atoms would have a dangling bond at the Si_3N_4 surface. The Si4 atom of Table III(a) has only a charge transfer of about 0.26 electrons that is much smaller than other three Si atoms. The Si4 atom is on the top of the N($2b$) atom which is fully bonded to three Si atoms of Si_3N_4 side and has no dangling bond before the matching of Si(111) layer to the Si_3N_4 surface. Careful data

TABLE III. Effective charge and charge transfer at the interface of Si(111)/ Si_3N_4 (001). (a) First layer of Si at the Si(111) side from the interface. (b) Second layer of Si at the Si(111) side from the interface. (c) Effective charge and charge transfer of N and Si atoms at the first Si_3N_4 (001) sheet from the interface.

(a)			
Atom		Q^* (electrons)	ΔQ (electrons)
Si1		13.56	0.44
Si2		13.59	0.41
Si3		13.59	0.41
Si4		13.74	0.26
(b)			
Atom		Q^* (electrons)	ΔQ (electrons)
Si1		13.75	0.25
Si2		13.86	0.14
Si3		13.66	0.34
Si4		13.77	0.23
(c)			
Atom	Position	Q^* (electrons)	ΔQ (electrons)
N1	$6c$	7.96	-0.96
N2	$6c$	7.92	-0.92
N3	$6c$	7.84	-0.84
N4	$2b$	7.94	-0.94
Si1	$6c$	13.27	0.73
Si2	$6c$	13.11	0.89
Si3	$6c$	13.24	0.76

analysis showed that the Si4-N($2b$) interaction is weaker than other Si-N bonds at the interface.

Table III(b) lists the charge transfer for the four Si atoms on the second Si(111) layer away from the interface. The Si atoms at the third and fourth Si(111) layers away from the interface have no noticeable charge transfer within the calculation uncertainty. This is an indication that the Si atoms in these two layers at the middle of Si(111) film are very close to the bulk properties.

Table III(c) lists the calculated effective charge and charge transfer for the four N atoms and three Si atoms at the first Si_3N_4 sheet near the interface. It is interesting to find that the N atoms at the interface have a charge transfer very close to the value of the N atom charge gain in the bulk silicon nitride. Three of these N atoms gain about 0.93 electrons/atom, the N3 atom has a smaller charge transfer of 0.84 electrons/atom; this inhomogeneity is largely due to the mismatch of the interface. It was found that one Si-N bond would associate with a charge transfer of about 0.31 electrons, which is that of bulk Si_3N_4 . From Table III(c) it can be also seen that the three Si atoms at the first Si_3N_4 sheet near the interface have a charge transfer of about from 0.73 to 0.89 electrons, which is much smaller than the Si charge transfer in the bulk Si_3N_4 . Even the charge transfer of these Si atoms of silicon nitride at the interface is smaller than in the case of the Si atoms at the free Si_3N_4 surface. Further analysis of the data showed that these three Si atoms of the silicon nitride side gained some electrons from the Si(111) atoms. The effective charge of the Si and N atoms at the

second and third Si_3N_4 sheets away from the interface is very close to the case of bulk Si_3N_4 .

IV. CONCLUSION

The electronic structure, the charge distribution, and the charge transfer in α - and β -phase Si_3N_4 , and for the interface structure of $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ have been studied using the self-consistent LCAO method. It is found that the silicon atoms in Si_3N_4 lose about 1.24 electrons/Si atom to the nitrogen atoms which gain about 0.93 electrons/N atom. The ionic formula for the silicon nitride may be written as $\text{Si}_3^{+1.24}\text{N}_4^{-0.93}$. Based on tests using two different sets of atomic orbitals of Si^0 and Si^{+1} , it was found that the effective charge and charge transfer from the two calculations are very close to each other. The quite stable results of the calculated charge transfer are attributed to the stability of the atomic shell orbitals of Si and N. At the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface, the Si atoms on the silicon side lose some electrons to the N atoms of the silicon nitride side and form Si-N bonds across the interface. The calculated results show that one Si-N bond would associate with a charge transfer of about 0.31 electrons/bond from the Si atom to the N atom, which is the same as the bulk Si_3N_4 value. The calculated DOS spectrum of Si $2p$ core levels for the $\text{Si}(111)/\text{Si}_3\text{N}_4(001)$ interface is in good agreement with XPS

experiments. The Si $2p$ levels in the Si_3N_4 side shift down by approximately 3.1–3.5 eV relative to the Si $2p$ states of $\text{Si}(111)$ side.

The study of the relaxation of a complex interface structure like this one is still a challenge for experimental measurements and theoretical calculations, and we expect to see that further relaxation of the interface structure will modify the charge-transfer results.

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