PHYSICAL REVIEW B VOLUME 23, NUMBER 10 15 MAY 1981

Electronic structures of β- and α-silicon nitride

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(Received 10 November 1980)

The electronic energy bands of α and β phases of silicon nitride have been calculated using a first-principles orthogonalized linear combination of atomic orbitals method. The potential is constructed from a superposition of atomic charge densities. The basis functions are the atomiclike wave functions contracted from the site-decomposed atomiclike potentials. For β-Si_3N_4, detailed studies of augmenting the basis functions with Si *d* orbitals and additional single Gaussian orbitals for both Si and N atoms, and for the pressurized structure are also performed. The valence bands are composed of mainly N orbitals and the conduction bands are dominated by Si orbitals. It is found that the inclusion of Si *d* orbitals in the basis has little effect on the valence-band structures, but changes conduction bands substantially. The electronic structure of β-Si_3N_4 under pressure up to 29.1 kbars has no appreciable difference from that of ordinary β-Si_3N_4. Furthermore, the density of states of α-Si_3N_4 is very similar to that of β-Si_3N_4. All these indicate that the electronic structure of silicon nitride is completely determined by the local short-range atomic structures.

I. INTRODUCTION

Silicon nitride (Si_3N_4) has been a very useful industrial material with many diversified applications. In the ceramic industry[1] it is used as a material for gas turbines and energy conversion systems because of its unique combination of useful properties such as high strength and compressibility, resistance to corrosion and oxidation, resistance to thermal stress, and flexibility to be molded into desired shapes. In recent years, Si_3N_4 has also found itself to be a very important material in microelectronic industry primarily associated with the metal-nitride-oxide-semiconductor (MNOS) memory devices.[2] There has been almost no communication between scientists interested in these two major applications of Si_3N_4. Since all material properties depend ultimately on the electronic structures, detailed information about its energy-band structure can advance our basic understanding about this important material. Up to this moment, very little theoretical work has been done on the electronic structures of Si_3N_4. This is in sharp contrast to silicon dioxide (SiO_2) where many detailed electronic-structure calculations have been attempted recently.[3] Part of the reason for the long-delayed investigation is due to the rather complicated crystal structure of Si_3N_4, making an accurate calculation a very formidable task. Recently, we reported our preliminary results on the band structures of β-Si_3N_4.[4] Meanwhile some work on the electronic structure of Si_3N_4 began to appear,[5,6] albeit by simple empirical methods.

The linear combination of atomic orbitals method (LCAO), as was reformulated by Lafon and Lin,[7] and with the utilization of Gaussian-type of orbitals (GTO) in basis function,[8] has been very successful in the study of electronic structures of bulk solids[9] and surfaces.[10] In 1975, Ching and Lin[11] extended the LCAO method by orthogonalizing the valence orbitals of each atom to the core orbitals of all the other atoms, thereby eliminating the core basis from the final secular equation, and thus were able to maintain the dimensionality of matrix equations of a complicated system within the manageable level. The method was dubbed the orthogonalized linear combination of atomic orbitals method (OLCAO). It was shown that eigenvalues and eigenvectors of the OLCAO calculation are as accurate as when the core basis is fully included.[11] By computing the matrix elements entirely in the direct space and by choosing a very economic basis set, the OLCAO method became a very powerful tool to study the electronic structures of crystals of high complexity[12] and amorphous materials.[13] This first-principles method is of sufficient efficiency as to to be applicable to large systems yet capable of yielding reasonably accurate results for both the conduction band (CB) and the valence band (VB). It is natural therefore to apply the OLCAO method to the study of energy bands of Si_3N_4. The crystal structures of the α and β phases of Si_3N_4 are fairly complex.[14] The β-Si_3N_4 has a hexagonal structure with two Si_3N_4 molecular units (14 atoms) per unit cell. Each Si atom bonds to four N atoms in an approximate tetrahedral configuration and each N atom links to three Si atoms in an approximate planar position. The Si-N bond distances range from 1.73 to 1.75 Å and the Si-N-Si angles range from 114.5° to 122.5°. The α-Si_3N_4 has a unit cell twice as large and contains twice as many atoms per unit cell. Its local short-range atomic structure is very much like the β phase with only slightly broader bond-length and bond-angle distributions. The β phase is believed to be a more stable phase than the α phase, since the conversion of α phase to β phase has been observed[15] but not vice versa. There has been some speculation[16] about the role the Si d orbitals play in stabilizing the β phase with the potential π bonding of lone-pair Np orbitals with the empty silicon d orbitals. However, this has not been substantiated by the detailed electronic-structure calculations. Recently, it was discovered[17] that in chemical-vapor-deposited (CVD) Si_3N_4, the holes are the dominating charge carriers in contrast to the case of SiO_2 where the electrons are the majority charge carriers.[18] Application of Si_3N_4 to the MNOS memory devices requires detailed knowledge about the electron states of this material, especially near the band gap.

We have published some preliminary results on the band structures of β-Si_3N_4 using a simple overlap of atomic potential model (OAP).[4] In the present paper, we furnish the results of detailed studies of both α and β phases of Si_3N_4 using a more realistic potential constructed from the overlap of atomic charge densities (OAC). In Sec. II we outline our method of calculation, the results of band-structure calculations on β-Si_3N_4 and α-Si_3N_4 are presented in Sec. III, together with investigation of the effects of Si d orbitals and the extended basis set on the band structures. The electronic structures of β-Si_3N_4 with crystal parameters determined under isotropic pressure of 29.1 kbars are also studied. In Sec. IV we discuss our calculated results in connection with available experimental information and in comparison with SiO_2 whenever appropriate. In the last section, some concluding remarks are made and possible direction for further work is pointed out.

II. METHOD

In the electronic-structure calculation with the direct-space OLCAO method, the only input is the atomic position of each atom in the crystal and the free-atom Hartree-Fock wave functions calculated within the self-consistent-field scheme.[19]

To construct the crystal potential, we first calculate the atomic Coulomb potential:

$$V_{\text{Coul}}(r) = -\frac{Z}{r} + \int \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|}\, d\vec{r}' \tag{1}$$

where $\rho(\vec{r})$ is the free-atom electron charge density obtained from the free-atom wave functions. To obtain the exchange part of the potential within the OAC model, we calculate the bulk-electron charge density $\rho_B(\vec{r})$ at many points around each atom and numerically fit the overall exchange potential V_x (with exchange parameter α equal to $\frac{2}{3}$)

$$V_x = -(\tfrac{3}{2})\,\alpha[3\rho_B(\vec{r})/\pi]^{1/3} \tag{2}$$

with functionals $V_{\text{exch}}(r-\vec{R}_\nu)$ centered at each lattice point $\vec{R}_\nu$. By refitting the sum

$$V(r) = V_{\text{Coul}}(r) + V_{\text{exch}}(r) \tag{3}$$

for each atom nonlinearly to a spherically symmetric Gaussian form of the type

$$V(r) \approx -\frac{Z}{r}\, e^{-\alpha_i r^2} + \sum_j C_j e^{-\beta_j r^2}, \tag{4}$$

we obtain a site-decomposed atomic potential $V(r)$ for each type of atom consistent with the OAC model of the bulk potential. The parameters for the Si and N potentials thus obtained are listed in Table I.

To obtain the atomiclike wave functions for the construction of basis, we select a set of even-tempered Gaussian exponents and use the individual Gaussians as basis functions to solve the associated eigenvalue problem for each single atom with the site-decomposed atomic potential $V(r)$. The resulting eigenvalues can be easily identified as 1s, 2s, 2p, ... etc. The normalized coefficients of the eigenvectors of the corresponding atomic states constitute the contracted atomiclike wave functions $\psi_{i,\alpha}(r)$ for an orbital i of α-type atom. This process of contraction[20] enables us to construct atomiclike wave functions of different types of atoms and different types of orbital angular momenta with the same set of Gaussian exponents, thus severely cutting the number of multicenter integrals needed in a first-principles calculation of electronic structures of complicated structures or systems with heavy atoms. The contracted atomiclike wave functions for Si and N used in the present calculation are listed in Table II.

With the basis functions and site-decomposed atomic potentials determined, we construct the

TABLE I. Gaussian exponents β_j and the associated coefficients C_j for atomiclike potentials of Si and N.

Silicon		Nitrogen	
C_j	β_j	C_j	β_j
1.833 151	1077.792 300	1.097 265	133.692 534
7.624 258	181.721 424	4.685 410	27.444 189
12.990 950	45.996 693	10.318 862	5.725 644
28.114 372	14.506 908	−2.457 151	1.019 076
−9.457 271	2.907 426	−0.409 600	0.991 608
−3.098 209	0.699 137	−0.422 885	0.347 688
−0.733 154	0.163 381	−0.032 554	0.072 328
$\alpha = 9.404349$		$\alpha = 3.412736$	

TABLE II. Contracted atomiclike wave function.

	Gaussian exponents	Coefficient					
		1*s*	2*s*	3*s*	2*p*	3*p*	3*d*
	0.150 000	0.000 314 8	0.004 914 6	1.111 022 7	0.018 536 0	−1.104 317 4	1.410 770 6
	0.257 644	−0.000 862 4	−0.007 304 3	−0.233 880 6	−0.046 152 9	0.372 931 1	−0.709 275 1
	0.503 922	0.001 075 3	−0.051 684 3	0.321 739 6	0.095 692 5	−0.383 069 5	0.362 437 5
	1.452 210	−0.001 657 4	−0.564 714 0	−0.410 086 6	0.290 106 2	0.089 295 9	0.004 042 9
	3.927 140	0.007 537 5	−0.522 396 1	−0.194 540 0	0.516 740 6	0.131 292 9	0.020 013 2
Si	12.815 600	0.170 841 0	0.066 704 5	0.017 820 3	0.265 928 4	0.069 308 4	0.001 281 8
	30.639 500	0.402 651 0	0.197 925 9	0.061 649 1	0.057 559 9	0.013 292 3	0.0
	77.606 400	0.344 502 4	0.113 815 5	0.032 978 7	0.027 380 5	0.006 934 4	
	214.004 000	0.160 204 8	0.047 114 2	0.013 845 0	0.003 442 6	0.000 763 9	
	657.466 000	0.052 616 2	0.014 227 5	0.014 088 3	0.001 058 0	0.000 269 5	
	2 330.010 000	0.012 544 5	0.003 374 5	0.000 980 7	0.000 054 7	0.000 010 7	
	10 380.200 000	0.002 860 6	0.000 756 1	0.000 217 7	0.000 014 7	0.000 003 8	
		1*s*	2*s*	2*p*			
	0.150 000	0.020 294 1	0.446 642 8	−0.742 463 6			
	0.257 644	−0.052 557 9	−0.002 397 6	0.310 371 5			
	0.503 922	0.058 204 1	0.558 476 4	−0.482 134 6			
	1.452 210	−0.034 994 3	0.183 836 0	−0.227 692 4			
N	3.927 140	0.390 121 5	−0.191 784 8	−0.114 260 4			
	12.815 600	0.442 148 2	−0.138 517 1	−0.026 972 6			
	30.639 500	0.186 662 7	−0.045 628 4	−0.003 684 6			
	77.606 400	0.104 731 3	−0.025 161 5	−0.001 774 0			
	214.004 000	0.030 976 6	−0.006 846 3	−0.000 152 3			
	657.466 000	0.010 086 7	−0.002 287 5	−0.000 063 1			
	2 330.010 000	0.002 108 2	−0.000 461 8	−0.000 001 4			
	10 380.200 000	0.000 506 2	−0.000 113 1	−0.000 000 9			

Hamiltonian of the crystal as

$$H = -\frac{\nabla^2}{2} + \sum_{\nu,\alpha} V(\vec{r} - \vec{R}_\nu - \vec{\rho}_\alpha) \tag{5}$$

and the Bloch function:

$$b_{j,\alpha} = \sum_{\nu} e^{i\vec{k}\cdot\vec{R}_\nu} \psi_j(\vec{r} - \vec{R}_\nu - \vec{\rho}_\alpha), \tag{6}$$

where j denotes the atomic orbitals and $\vec{\rho}_\alpha$ is the position of α^{th} atom in the ν^{th} cell. Since the wave functions and potentials are both linear combinations of GTO, the overlap and Hamiltonian matrix elements can be evaluated exactly using techniques of Gaussian transformation.[8] Using the orthogonalization to the core technique[11] the dimension of the matrix equation can be greatly reduced. The final secular equation is

$$|H'_{i\alpha,j\beta}(\vec{k}) - E(\vec{k}) S'_{i\alpha,j\beta}(\vec{k})| = 0 \tag{7}$$

where ′ indicates the matrix elements are evaluated in the orthogonalized space and does not cover the core orbitals. Solution of (7) gives us energy bands and wave functions of the valence and unoccupied states. The density of states (DOS) are calculated based on the eigenvalues and eigenfunctions of properly weighted eighteen $\vec{k}$ points in the irreducible part of the Brillouin zone (BZ). When a minimal basis is used in the calculation, it is convenient to resolve the DOS into its atomic and orbital components using Mulliken's population analysis.[21] When the basis function contains extended orbitals or unoccupied orbitals such as Si d orbitals, the wave functions have greater uneven mixing and resolution into orbital DOS using Mulliken's prescription may not be fruitful.

III. RESULTS

A. Band structures

The calculated energy bands of β-Si_3N_4 along the symmetry lines with a minimal basis set of $1s, 2s, 2p_x, 2p_y, 2p_z$ for N and $1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z$ for Si are shown in Fig. 1. The top of VB is at a point about 0.3 of ΓA and the bottom of the CB is at Γ giving an indirect band gap of 6.77 eV. These band structures are very similar to the earlier result[4] calculated using the OAP model where an indirect band gap of 5.54 eV was obtained. In Fig. 2, the similar result for α-Si_3N_4 is presented. The doubling of the number of atoms in the unit cell results in the doubling of the number of bands and a very flat VB top.

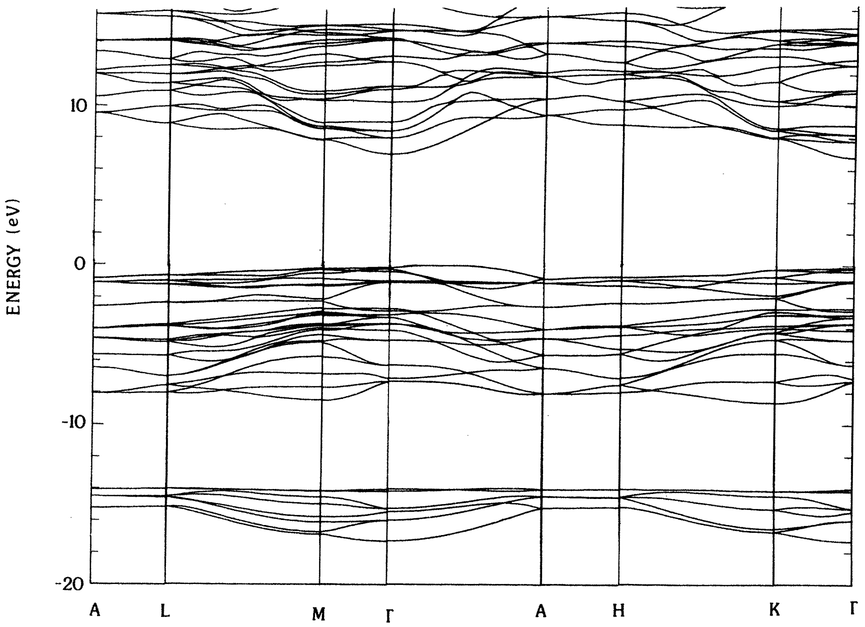

FIG. 1. Band structure of β-Si_3N_4 using minimal basis set.

The minimum of CB is still at Γ and a band gap of 6.90 eV is obtained. The α-Si_3N_4 has a structure approaching that of amorphous Si_3N_4 (a-Si_3N_4), thus the band structure itself is less meaningful. What is important is the DOS which will be discussed later on.

In Fig. 3 we show the band structure of β-Si_3N_4 with the basis function including the Si d orbitals. In comparison with the minimal basis result of Fig. 1, we note that the VB remains practically the same, but the CB is substantially changed. The indirect band gap is now 6.49 eV. When the

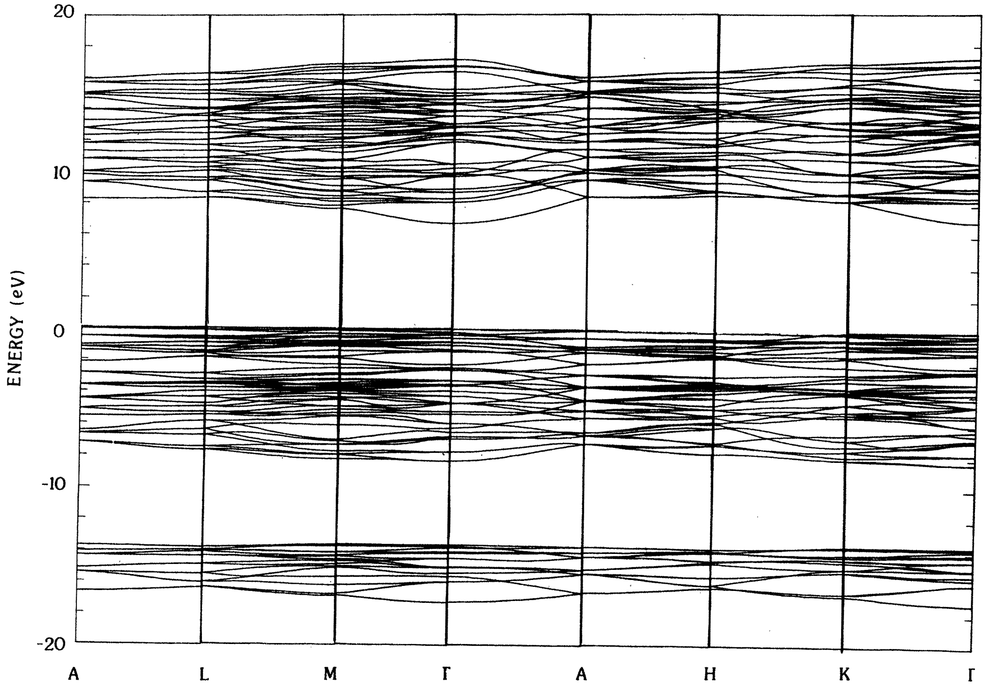

FIG. 2. Band structure of α-Si_3N_4 using minimal basis set.

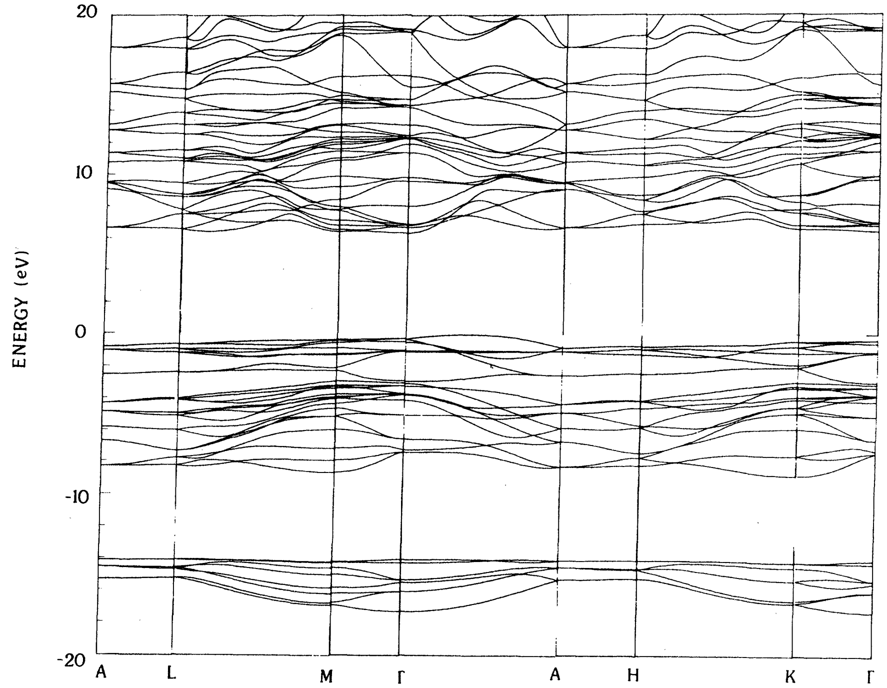

FIG. 3. Band structure of β-Si_3N_4 with Si*d* orbitals included in the basis set.

basis function is further augmented by two *s* type (exponent = 0.15, 0.257 644) and one *p* type (exponent = 0.15) of GTO for both Si and N atoms in addition to Si 3*d* orbitals, the basis function achieves a much greater variational freedom and the CB changes drastically. The VB is again relatively unchanged and the band gap is further reduced. We have also calculated the band structures of β-Si_3N_4 under pressure using the crystal parameters determined by Herndon and Jorgensen[22] using the time-of-flight neutron-diffraction techniques. The results are very similar to the ones without pressure. The above results are succinctly summarized in Table III.

B. Density of states

The total DOS and partial DOS for Si and N for α- and β-Si_3N_4 calculated with a minimal basis set are shown in Figs. 4(a), 4(b), and 4(c), respectively. Although the band structure of α-Si_3N_4 differs from that of β-Si_3N_4 in appearance, their DOS are remarkably similar with only slight variations in very subtle structures in the CB. This proximity of electronic DOS between the two phases is the direct consequence of the similar local atomic arrangements in these two crystals. For example, in β-Si_3N_4, the average Si–N bond length is 1.736 Å, the average N-Si-N angle is 108°50′, and the N atom is on average only 0.07 Å out of the Si_3 plane. The corresponding figures for α-Si_3N_4 are 1.738 Å, 109°11′, and 0.14 Å. Since the α phase, with a larger distribution of Si–N bond lengths and Si-N-Si angles, and with twenty-eight atoms per unit cell, can mimic *a*-Si_3N_4 which has essentially the same local bonding configurations, we thus expect the DOS of *a*-Si_3N_4 to be virtually the same as those presented in Fig. 4.

In Fig. 5, we display the same DOS of β-Si_3N_4 and with the one calculated by including Si *d* orbitals in the basis function. Clearly, the VB DOS is practically the same as that from a minimal-basis calculation. Of particular interest is that the leading peak near the top of VB which originates from the N lone-pair orbitals, is hardly changed at all. Inspection of eigenvectors of the states at the top of VB show negligible mixing of Si 3*d* orbitals, thus the speculation[16] that the empty Si *d* orbitals should interact with N lone-pair orbitals seems to be not validated and the invocation[16] of $(p-d)\pi$ bonding in stabilizing the Si_3N_4 structure needs to be reexamined. We will return to this point in the next section. The CB DOS in this case is, of course, considerably changed; this is mainly attributed to the increased variational freedom attained by the Bloch function due to the enlarged basis set. The CB edge is thus lowered and results in a decrease of the band gap; however, the characteristic of CB-edge wave function is not changed and still consists mainly of Si 3*s* orbitals. When the basis functions are further supplemented by single GTO, the Bloch function

TABLE III. Summary of band structure of β-Si_3N_4 for different potential models and size of basis functions. A=β-Si_3N_4 using OAP model and minimal basis set. B=β-Si_3N_4 using OAC model and minimal basis set. C=β-Si_3N_4 using OAC model with Si d-orbitals. D=β-Si_3N_4 using OAC model with extended basis.

	Energy (eV) and symmetry point			
	A	*B*	*C*	*D*
Lowest CB	5.54 (Γ)	6.77 (Γ)	6.49 (Γ)	4.72 (0.95 *AP*)
Top VB	0.0 (0.3 ΓA)	0.0 (0.4ΓA)	0.0 (0.4 ΓA)	0.0 (0.4 ΓA)
Bottom 1st VB	−10.64 (*K*)	−8.65 (*K*)	−8.75 (*K*)	−9.00 (*K*)
Top 2nd VB	−14.89 (Γ)	−14.08 (Γ)	−14.03 (Γ)	−14.24 (*L*)
Bottom 2nd VB	−19.07 (Γ)	−17.32 (Γ)	−17.24 (Γ)	−17.60 (Γ)
Indirect band gap	5.54	6.77	6.49	4.72
1st VB width	10.64	8.65	8.75	9.00
2nd VB width	4.18	3.24	3.21	3.36
Separation 1st and 2nd *VB*	4.25	5.43	5.28	3.36
m_e^*/m_e	0.63	0.47	0.27	0.19
m_h^*/m_e	3.7	2.9	2.5	3.0

attains even more variational freedom. The DOS for this calculation is shown in Fig. 6. Again, as expected, the VB DOS remains essentially the same with further changes in the CB.

In Fig. 7, we compare the DOS of β-Si_3N_4 with and without pressure. The calculation includes Si d obitals in the basis set. As is evident, the difference is negligible. According to Herndon and Jorgenson,[22] up to a pressure of 29.1 kbars the volume of β-Si_3N_4 only diminishes by 1.3%. With a much smaller change in Si–N bond lengths (average 1.73 Å) and N-Si-N angles (average 109°25′), it appears the pressure only tends to adjust the tetrahedron units with little distortion in the intraunit bond lengths and bond angles. Thus the present result on DOS demonstrates again the fact that the local geometry totally controls the electronic properties in Si_3N_4, since even up to a pressure of 29 kbars, distortions in bond lengths and bond angles are minimal, reflecting the unique mechanical properties of Si_3N_4 mentioned in Sec. I. In Fig. 6, we also include the experimental results[23] of x-ray photoelectron spectroscopy for comparison to the VB DOS.

The average calculated charge transfer from Si to N is 0.73 electron per Si–N bond for minimal-basis calculation. This is to be compared with 0.57 electron in the OAP calculation and 0.70 electron in the OAC calculation with Si d orbitals included in the basis function. Since the charge-transfer calculation is based on Mulliken's prescription,[21] they can only be trusted as estimates because in Mulliken's scheme it is assumed that the degree of overlap between two atoms is regarded to be equally shared among them. This approximation is obviously less valid when the basis function includes empty orbitals or extended orbitals because of the far greater range of each atomiclike wave function. Thus the partial DOS presented in Fig. 6(b) which shows much greater Si components in the VB region than other cases, is actually fallacious. With a minimal-basis-set calculation, the approximation is a reasonably good one and the calculated charge transfer and partial DOS should be quite reliable.

IV. DISCUSSION

Based on the results presented in the last section, a fair amount of information about the electronic structures of Si_3N_4 has been obtained. The top of the VB consists of N lone-pair orbitals

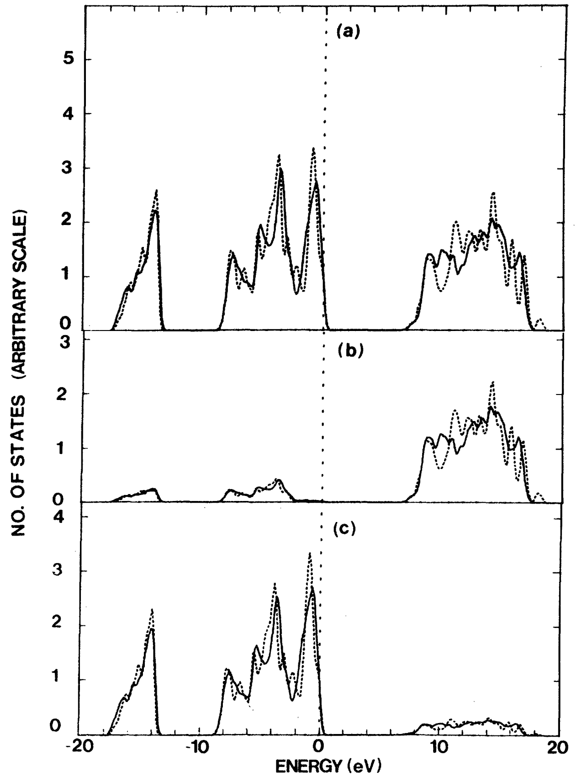

FIG. 4. DOS of β-Si_3N_4 (solid line) and α-Si_3N_4 (dashed line) using minimal basis set. (a) Total DOS, (b) partial DOS of Si, and (c) partial DOS of N.

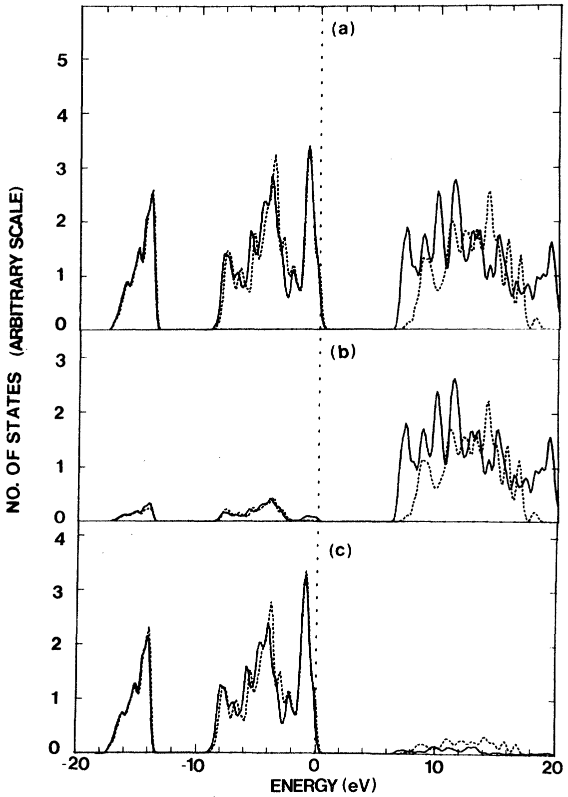

FIG. 5. DOS of β-Si_3N_4: solid line, Si*d* orbitals included in the basis set; dashed line, minimal basis.

similar to SiO_2. The most important finding is that there is no evidence whatsoever that the empty Si *d* orbitals play a crucial role in the chemical bonding of Si_3N_4. By including Si *d* functions in our calculation, we find that the VB is virtually unaffected. The CB do change appreciably when Si *d* orbitals are included or an extended basis set is used, largely because of the increased variational freedom of the Bloch function. This is contrary to previous speculation[16] which is based mainly on the information derived from measurements on molecules containing Si–N bonds such as trisylamine $(SiH_3)_3N$. Our viewpoint is that in a partially ionic and partially covalent solid such as silicon nitride, the wave functions of electrons on each atom can overlap substantially, and the effect of p–d bonding which may be present in molecular cases is totally unimportant in the crystalline cases. The assertion that p–d bonding plays a role in stabilizing the β phase with respect to the α phase can be discounted. Instead, we have to look more carefully into the relation between the oxygen content in α-Si_3N_4 and its metastability.

In comparing the calculated results with experimental data, we found that most experiments were done on CVD Si_3N_4 (Refs. 22–26) rather than single

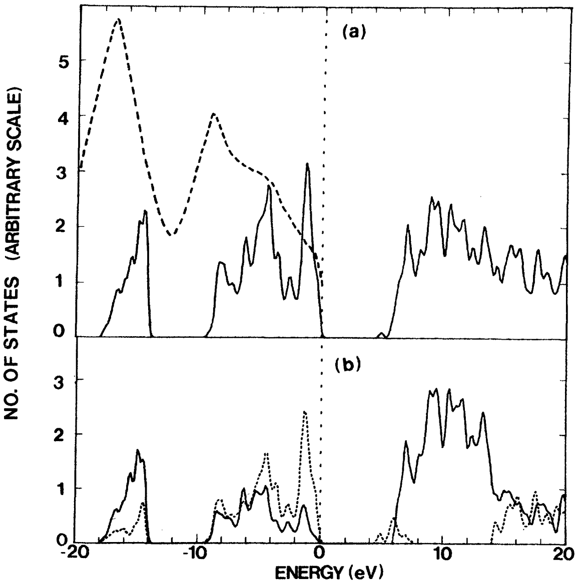

FIG. 6. (a) DOS of β-Si_3N_4 with extended basis set. Dashed line experimental result of Ref. 23. (b) Partial DOS of Si (solid line) and N (dashed line). See text for comment and explanation.

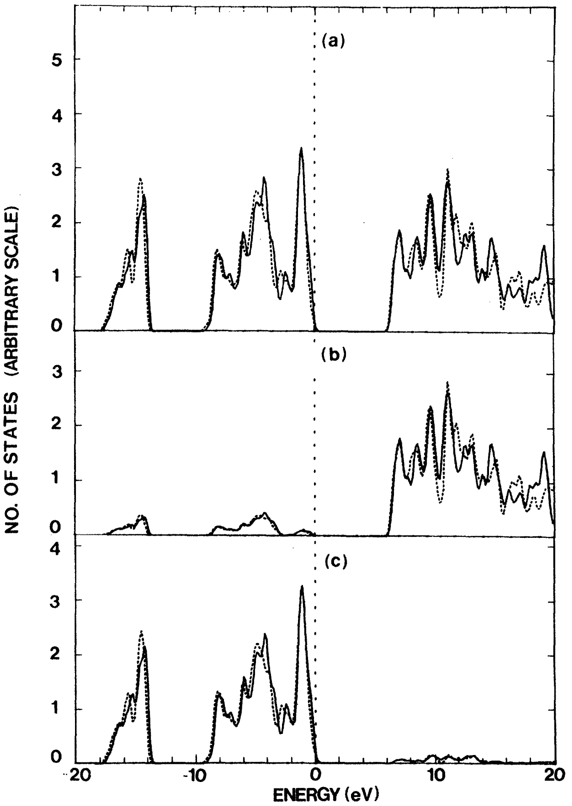

FIG. 7. DOS of β-Si_3N_4 with (dashed line) and without (solid line) pressure, calculated with Si*d* orbitals in the basis set. (a) Total DOS, (b) partial DOS of Si, and (c) partial DOS of N.

crystals. The CVD samples have a structure closest to the amorphous phase of Si_3N_4. Analysis of radial-distribution functions of CVD Si_3N_4 determined by x-ray[27] and neutron scattering experiments[28] indicates very little difference in the local bonding structure of β-Si_3N_4 and a-Si_3N_4. Our calculated DOS of α- and β-Si_3N_4 as well as that of pressurized β-Si_3N_4 show that they are all very similar because of the resemblance in the local short-range bonding character. We expect that the DOS of a-Si_3N_4 will be similar to the crystalline cases, and the comparison between theoretical calculation based on crystalline structure and the experimental measurement on samples which are essentially amorphous is meaningful. The x-ray photoemission data of Weinberg and Pollak[23] are shown in Fig. 6 along with calculated VB DOS; all the main structures are reproduced with relative peak positions in the right order. The lowest peak corresponding to N2*s* bands seems to be 2 eV too high, however there appears to be some uncertainties in determining the VB edge in the experimental data. Furthermore, the effects of trace impurities such as O may also need to be considered. The optical gap measured by the various experiments[26] on various samples of Si_3N_4 ranges from 4.5 to 6.5 eV. Our calculated values of the indirect gap using different potential models and different sizes of basis functions fall within this range. A more definitive value of band gap can only be obtained when a full self-consistent calculation with an enlarged basis function is done. Such an attempt is not warranted at the present time due to the insufficient experimental information on well characterized single-crystal samples. Any discussion on the conduction properties of silicon nitride must take into account the presence of native impurities and defects that are present in the CVD samples. A full treatment on these topics is beyond the scope of the present paper and we refer to Robertson[6] for further details. Nevertheless, it is possible to gain some insight into the conduction properties of Si_3N_4 based on the results of the crystalline electronic structures. The estimated (with extended basis set) hole effective mass is about $3.0m_e$ which is much larger than the electron effective mass of $0.19m_e$. The heavy-hole effective mass is the consequence of the rather flat top of the VB, as would be the case for the bands of lone-pair orbitals. Recent experiments on electric-conductivity measurement[17] indicate that holes are the dominate charge carriers in contrast to the a-SiO_2 where the electrons are much more mobile.[18] In silicon nitride, the conduction is carried by holes which have much greater effective mass. This seems to imply that the hole traps should be much shallower than the electron traps in Si_3N_4. Such an interpretation is consistent with transport measurements on the CVD films of Si_3N_4.[17] More work needs to be done in this area in order to have a much deeper understanding.

V. CONCLUSION

We had calculated the electronic structures of Si_3N_4 using both OAP-model[4] and OAC-model potentials with various sizes of a basis set. The three main conclusions are (1) the empty Si*d* orbitals play a very small role in the VB structure of Si_3N_4, (2) the electronic structure of Si_3N_4 is totally controlled by the local short-range order, thus the α, β, and the amorphous phase of Si_3N_4 will have almost identical DOS, and (3) very satisfactory band structures including CB can be obtained by using a minimal basis set alone. For most purposes, an orthogonalized minimal basis set of four orbitals per atom for nonmetallic materials and nine orbitals per atom for metals should be sufficient to study the electronic structures of most materials. Thus a non-self-consistent, minimal-basis calculation in conjunction with a simple OAP model using the real-space OLCAO method represents the simplest form of first-principles electronic-structure calculation which is parameter independent and has a well defined unique prescription of procedures capable of yielding results of sufficient accuracy, yet is economically feasible to be applied to a variety of complicated systems. Unlike the parametrized tight-binding method,[5,6] the OLCAO method gives reasonable wave functions which can be used to study other microscopic and macroscopic properties or to calculate other physical observables. The method could be applied to a vast class of important materials with highly complicated crystal structures. A logical extension of the present work is to study Si_2N_2O or Si-Al-N-O solid solutions (Sialon), although more crystal-structure information is needed for Sialon. A deep understanding of electronic structures of these materials will be very valuable since these are materials of potential technological importance. Preliminary investigation[29] on Si_2N_2O and Ge_2N_2O indicates that the DOS of these materials can be roughly represented as a superposition of that of Si_3N_4 and SiO_2. Another interesting problem is to study the electronic states of α-Si_3N_4. As pointed out earlier, we do not expect the DOS of α-Si_3N_4 to be significantly different from that of β-Si_3N_4, yet the disordered nature of the amorphous phase could give rise to interesting localization properties of electron states near the band edge. We found that the twofold-coordinated α-SiO_2 (Ref. 30) has localization properties very much different from fourfold-coordinated α-Si.[31] A threefold-coordinated network of α-Si_3N_4 should provide an important intermediate link between the two cases. Furthermore, the charge transfer of about 0.70 electron per Si–N bond in Si_3N_4 is only slightly less than that of 0.77 electron per Si–O bond in SiO_2.[30] The difficulty lies, however, in the construction of sufficiently large periodic structural models of α-Si_3N_4 suitable for such studies.[30] With the radial-distribution function of CVD Si_3N_4 well determined by both x-ray[29] and neutron-scattering experiments,[28] it is only a matter of time before realistic structure models for α-Si_3N_4 will be constructed and more detailed study on the noncrystalline phase of Si_3N_4 which relate more closely to experiment can be performed.

ACKNOWLEDGMENTS

One of us (W. Y. Ching) wishes to thank Dr. J. D. Jorgensen for beneficial discussion on several occasions and for providing us with unpublished data of crystal structures of pressurized β-Si_3N_4. We also thank Dr. J. Robertson for sending us the results of his calculation prior to publication. This work was supported by Department of Energy Contract No. DE AC0279ER10462.

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