A density functional study on the electronic structures of TiN solid

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The electronic structures of TiN bulk have been studied by using different theoretical formalisms, and the DFT method, especially the BLYP method can produce reasonable results. The band structure of TiN(001) surface is also investigated and two σ type surface states are presented in our results. The state located at 2.9 eV below E_F in angle resolved photoemission in (ARPES) is well reproduced in this work, which consists essentially of $2p_z$ orbital of surface N atom. Another surface state is associated with the bands originated from 3d orbital of surface Ti atom. Furthermore, the elastic constants of TiN are also calculated by using BLYP method.

Keywords Transition metal mononitrides, density functional theory, band structure, density of state (DOS), surface states, elastic constants

Introduction

Transition-metal monocarbides, mononitrides and monoxides (MX, M = metal, X = C, N, O) have attracted a great deal of attention for a long time because of the very interesting physical properties these materials exhibited, especially for nitrides and carbides. They possess high hardness, high melting point, and metallic conductivity (Table 1).[1-3] These remarkable properties lead them to be used as coatings for cutting tools, wear resistant surfaces, refractory materials, and conducting barriers in the electric industry. Although these compounds mostly crystallize in the rock salt structure, which is typical of materials with ionic crystals, they also show properties of compounds of covalent bonding. According to these properties they exhibit that three kinds of chemical bonding, ionic, covalent and metallic bonding might exist in these compounds, and three degrees of the bonding are varied with the types of X atom, which results in the different properties. For example, the hardness of TiC is greater than TiN and Ti, as well as the melting points (Table 1).

Table 1 Some physical properties of metal Ti, TiC and TiN

Species	Hardness (kg/mm^2)	Melting point (℃)	Electrical resistivity (μΩ·cm)
Ti	200	1600	42
TiC	3000	3140	200
TiN	2000	2930	20

Many investigations for MX compounds have sought to reveal the special relations between such extraordinary properties and the electronic structures. Experimentally, intensive spectroscopic studies have been performed on these compounds to obtain the band structures and the density of states (DOS) of their valence band,[4-10] such as X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS), angle resolved photoemission (ARPES), and electron energy loss spectroscopy (EELS) *etc.*;

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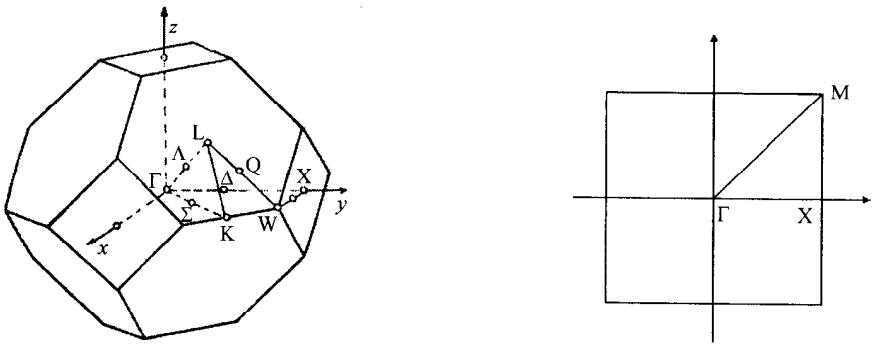
theoretically, numerous band structure calculations have been carried out, most of them have been summarized in review articles by Neckel and Schwarz.[11,12] The general methods used in theoretical investigations include argument plane wave (APW) method,[13] linear muffin-tin orbital (LMTO) method,[14,15] and extended Huckel tight-binding (EHT) method.[16] The APW methods including the linearized APW method were extensively used, especially to study the band structures of these compounds, and the LMTO method is most applicable for studying the physical properties of the compounds. Ahuja *et al.* have recently calculated the elastic properties of TiX by using the LMTO method.[14] Since some physical properties are sensitive to the theoretical method and the parameters used in above calculations, quantitative discrepancies can be found between theoretical results and experiments, although they can get reasonable results in some aspects. In general, the experimentally determined bands are somewhat deeper below the Fermi level (E_F) and smaller in dispersion than the calculated bands.[11,17] Furthermore, in comparison with the bulk studies, there are few theoretical reports on the surface of these compounds, especially using the methods based on the first principle. Therefore, in order to get a better understanding of the bonding characters of these compounds in chemical viewpoint, it is necessary to study the electronic structures of these compounds systematically by using more accurate theoretical method. In this paper, we present a density functional theory (DFT) study on the electronic structures of the bulk and the (001) surface of TiN. Moreover, the elastic property of TiN is calculated by using DFT method, and the comparisons are made between our results and other theoretical calculations as well as spectroscopic studies.

Computational details

The crystal structure of TiN is the fcc rocksalt structure, and the lattice parameter used in this paper is 0.4242 nm. In the calculation, a (11s8p3d/4s3p2d) basis set was adopted for the Ti atom.[18] Since the use of sp shells (s and p orbital sharing the same exponent) reduces the time required to compute the integrals considerably, for the N atom, the standard 6-21G basis set augmented with one set of d-like polarization function was employed. Fig. 1 shows the Brillouin zones (BZ) used in the band calculations of the bulk and the (001) surface of TiN, and the energy eigenvalues of fifty K points were resolved. In the study of the elastic property, for the cubic crystal, there are three independent elastic constants, C_{11}, C_{12} and C_{44}. We first calculated the total energy of the unit cell with different deformations for the lattice, then the elastic constants were obtained by performing a polynomial fit of total energy as a function of the deformation of lattice. All the calculations were carried out by using CRYSTAL95 program which deals with periodic systems based on the *ab initio* method.[19]



(a) For the bulk of TiN (b) For the (001) layers of TiN

Fig. 1 Brillouin zones used in the band calculations.

Results and discussion

Comparisons of methods

In order to select a suitable method to describe the electronic structures of TiX compounds, let us first compare the results of the band structure calculations for TiN, achieved by use of the Hartree-Fock (HF) and the DFT formalism, respectively. Several DFT methods, LDA, VBH, BPW and BLYP methods are used, and for each of them, the correlation and exchange functional are Vosko-Wilk-Nusair and Dirac-Salter functional,[20,21] Barth-Hedin correlation and exchange functional,[22] Perdew-Wang and Becke functional,[23,24] Lee-Yang-Parr and Becke functional,[24,25] respectively. Comparing with the LDA and VBH methods, the generalized gradient approximation (GGA) is taken into account for both BLYP and BPW methods. The electronic structure researches of the molecular systems show that, in general, the BLYP method including the hybrid DFT method, B3LYP can provide more reasonable results than other DFT methods, especially for the systems containing transition metal atoms. In the solid field, however, the LDA method is extensively used and has been proven to be a very useful approximation for describing the electronic properties of solid compounds.

In Figs. 2 and 3 the band structures and the total DOSs of TiN calculated by the HF and different DFT methods are listed, respectively. The ARPES experiment was performed by Johansson et al. to determine the energy band dispersion for a $TiN_{0.83}$ crystal along the symmetry direction Γ-Δ-X.[10] Table 2 presents a comparison of the experimental energies for some critical points along Γ-Δ-X direction with calculated energy eigenvalues including the data obtained from the APW band structure calculation. Some conclusions can be summarized as follows:

(1) Although the profile of the band structure resulting from the HF method differs slightly from bands obtained by the DFT methods, some positions of the valence bands below E_F in the HF picture are far deeper than those obtained from other methods and experimental results (Table 2). Hence, the HF formalism only can provide qualitative results, which indicate the exchange corrections should be concerned for this class of compounds.

Table 2 Comparison of experimental with calculated energies for selected states for TiN[a]

Methods	States			
	Γ_{15}	X_3	X_5'	X_4'
Experimental[10]	−3.4±0.1	−2.3±0.3	−4.0±0.2	−6.4±0.2
HF	−9.6	−5.0	−11.9	−15.5
BLYP[b]	−2.6	−2.6	−3.7	−6.2
APW[c]	−2.2	−3.2	−3.3	−5.6

[a] The energies in eV relative to the Fermi level. [b] The results of BPW, LDA and VBH methods are very close to BLYP's. [c] See the reference 11.

(2) As other theoretical methods, the bands derived by the DFT method below E_F are still somewhat higher than the experimentally determined bands. However, the bands obtained by using the DFT scheme yield better agreement with experiment than those obtained by using the APW and LMTO methods. A significant improvement made by the DFT method is that it can produce reasonable energy gap between the X_3 and X_5' points. The X_3 and X_5' point is separated in the APW calculation by only an energy gap of about 0.1 eV,[11] and no significant separations between them can be seen in the LMTO study.[14] An energy gap obtained by the DFT method is about 1.1 eV which agrees with the experimental value 1.2—2.2 eV.

(3) In the spectroscopic studies of TiN, two dominat peaks located at −5.3 eV and −16.4 eV are observed[8] (The values of energy in this paper are relative to E_F). For the peak at −5.3 eV, the structures in the DOS calculated by the DFT, APW and LMTO methods are well reproduced in the experimental spectrum (Fig. 3). However, the peak at −16.4 eV in the experimental spectrum is further below E_F than the calculated DOS maximum. The corresponding peakin the DOS derived by the LDA, VBH, APW and LMTO methods is found to lie about 0.5 to 1.0 eV near the E_F,[11,14] whereas the results of the BLYP and BPW methods (about −16.2

eV) agree much better with the experimental spectrum. It can be deduced that the GGA correction must be considered to describe those bands far below E_F.

According to the results above mentioned, we choose the BLYP method to perform further investigations of the electronic structures of TiN.

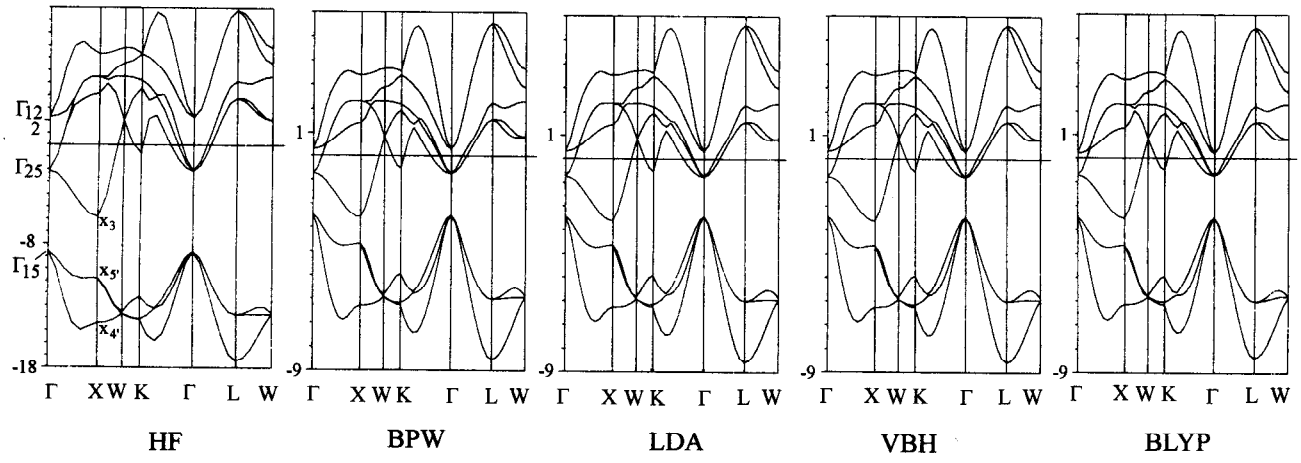


Fig. 2 Band structures for TiN bulk by using different methods (the Fermi level is set at zero energy).

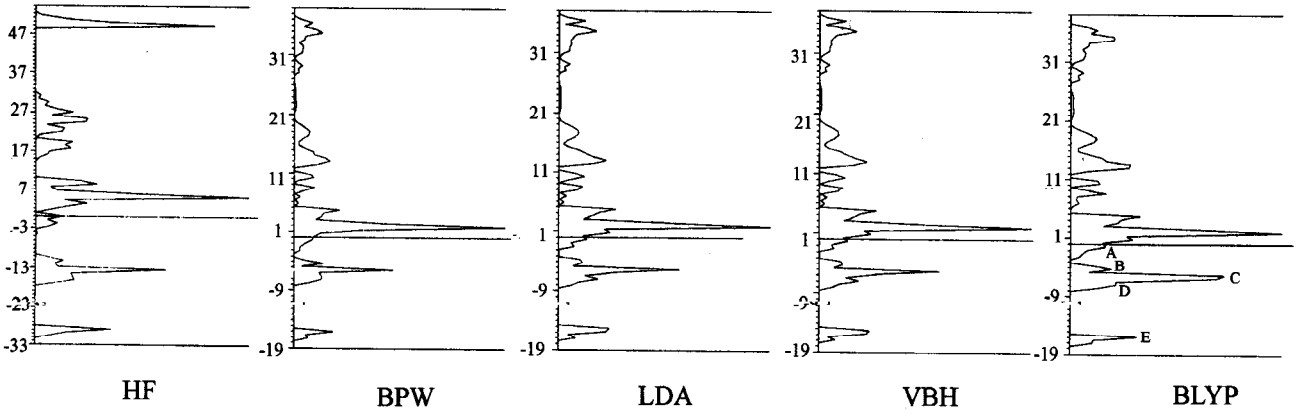


Fig. 3 Calculated total density of states (DOS) for TiN bulk by using different methods.

Electronic structures of TiN *bulk*

To obtain deeper insight into the band structure of TiN, we analyze the constituents of the bands near E_F, which have great influences on the properties of compounds. According to the knowledge of the group theory, the classification of energy states for each K point can be obtained by the irreducible represent (IR) of the point group each K point belongs to.[26] For the origin of BZ, the Γ point, the point group of this K point is T_d, so the energy states of the Γ point are classified into five states according to the IR of T_d group: two nondegeneracy states (Γ_1 and Γ_2), one two-fold degeneracy state (Γ_{12}) and two three-fold degeneracy states (Γ_{15} and Γ_{25}). The energy bands from the Γ_{25} and Γ_{12} states are near E_F and the bands derived from Γ_{15} state are somewhat below E_F (Fig. 2). On the other hand, five 3d orbitals of Ti atom are divided into two groups in the crystal field: one three-fold degeneracy orbital (t_{2g}) and one two-fold degeneracy orbital (e_g). It can be seen that the t_{2g} and e_g orbitals correspond to the Γ_{25} and Γ_{12} states, respectively. The calculated results also show that the bands derived from the Γ_{25} state, which are half occupied, have the components of the 3 d_{xy}, 3 d_{xz} and

$3d_{yz}$ orbitals of Ti atom, and the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals can be found in the unoccupied bands from the Γ_{12} state. For the energetically low-lying bands, which are derived from the three-fold degeneracy state Γ_{15}, they contain the prominent contributions of three 2p orbitals of N atom.

Examining the total DOS calculated by the BLYP method (Fig. 3), we can find that below E_F there are five peaks, A—E located at −0.5, −4.2, −5.3, −7.1 and −16.2 eV, respectively. Except for the peak B, all peaks are observed in the photoelectron spectroscopy, and the prediction peak positions are found to be in satisfactory agreement with the experimental findings.[4] Furthermore, in order to determine the components of the peaks in total DOS, the partial DOSs of Ti 3d orbitals and N 2p orbitals are calculated (Fig. 4). It can be seen that the small shoulder peak A, which very closes to E_F, originates mainly from the Ti 3d orbitals. The shoulder peaks B, D and the dominate feature C are derived from the N 2p orbitals and exhibit also some 3d and 4p contributions of Ti atom, which is expected the mixing covalent bond between Ti 3d and N 2p orbitals. For the energetically low-lying peak E, the dominat contribution is the N 2s orbital.

In order to determine the strength of the covalent bonding, the overlap population (OP) between Ti and N atoms has been calculated by using more diffusion basis set for the Ti atom. The result (0.128) also indicates the covalent interactions existing in TiN. For the metal Ti, however, the calculated OP value is −0.104, which shows no obvious covalent overlap in metal Ti. Thus, as the result of the covalent bonding between Ti and N atoms, TiN exhibits higher melting point and hardness than metal Ti (Table 1). Since the energy bands crossed by E_F, which are derived from the Γ_{25} state, originate mainly from the Ti 3d orbitals (Peak A in Fig. 3), the movement ability of the Ti 3d electrons may play an important role for the metallic conductivity of TiN as well as in metal Ti. Due to this similarity between TiN and metal Ti, no significant difference can be found in their metallic conductivity as shown in Table 1. Furthermore, the bands crossed by E_F are half occupied, so TiN has ability of taking part in chemical reactions and also has the surface activity. For example, some surfaces of TiN are easy to be oxidized.

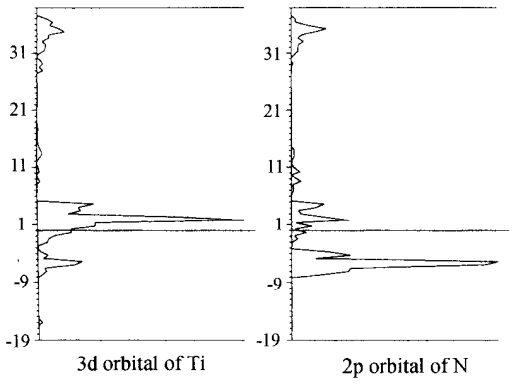


Fig. 4 Some calculated partial DOS for TiN bulk.

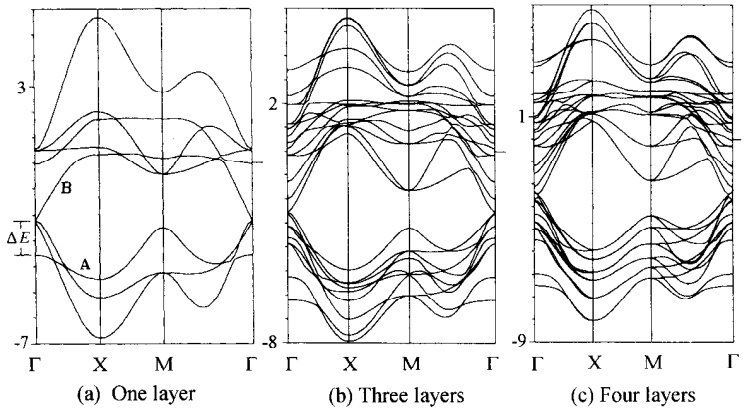


Fig. 5 Band structures for TiN(001) surface.

Electronic structures of TiN(001) *surface*

Comparing with the studies of the TiN bulk, there are few reports on the theoretical studies of the TiN surface, especially the calculations based on the *ab initio* method. Larsson *et al*. have calculated the photoemission spectrum of TiN (001) using the time reversed LEED method,[27] and the surface state on TiN(001) has been discussed in their paper. However, their results were associated with one parameter, surface potential used in calculations, and the band structure of TiN (001) was not presented in their paper.

In this work, we perform band structure calculations on TiN(001) by using the BLYP method. The TiN crystallizes in a rocksalt structure, thus the (001) surface is a neutral surface composed of equal numbers of Ti and N atoms. In the calculations, the crystal is assumed to be constructed by n layers paralleling with the

(001) surface. In such two-dimensional model, the first and the last layers represent the (001) surface, and the other layers can be seen as the bulk of TiN. In Fig. 5 the band structures for $n = 3$ and 4 are shown for comparison. Since no significant differences can be found between the band structures of them, we suppose that $n = 4$ is large enough to describe the electronic structures of TiN(001).

Now we focus our attention on the band structure of TiN(001). To compare with the TiN bulk and exclude the bands derived from the bulk for simplicity, we also calculated the band structure for $n = 1$ (Fig. 5(a)), which has two atoms in the unit cell as well as in the bulk. Like the band structure of the TiN bulk (Fig. 2), the bands designated as the interaction between surface Ti 3d and N 2p orbitals still appear at energy region -7—-3 eV, and the bands crossed by E_F are originated mainly from Ti 3d orbitals. Two special energy bands labeled A and B in Fig. 5(a) must be paid more attention. In the ARPES spectrum of $TiN_{0.83}$ crystal along the direction Γ-Δ-X, a feature which is non-dispersive in photoemission at 2.9 eV below E_F cannot be identified with a bulk band.[10] Several possible explanations have been considered for this band. In our calculated band structure of TiN(001), this band, labeled A in Fig. 5(a) is well reproduced. Our result gives direct support for the explanation thatthis band corresponds to a surface state of TiN(001). Since the TiN studied in this work is stoichiometric, it is impossible that this band is produced by bulk vacancies of the specimen. The calculations of LEED scheme also draw the same conclusion.[27] The more detail discussions about this surface state are presented below.

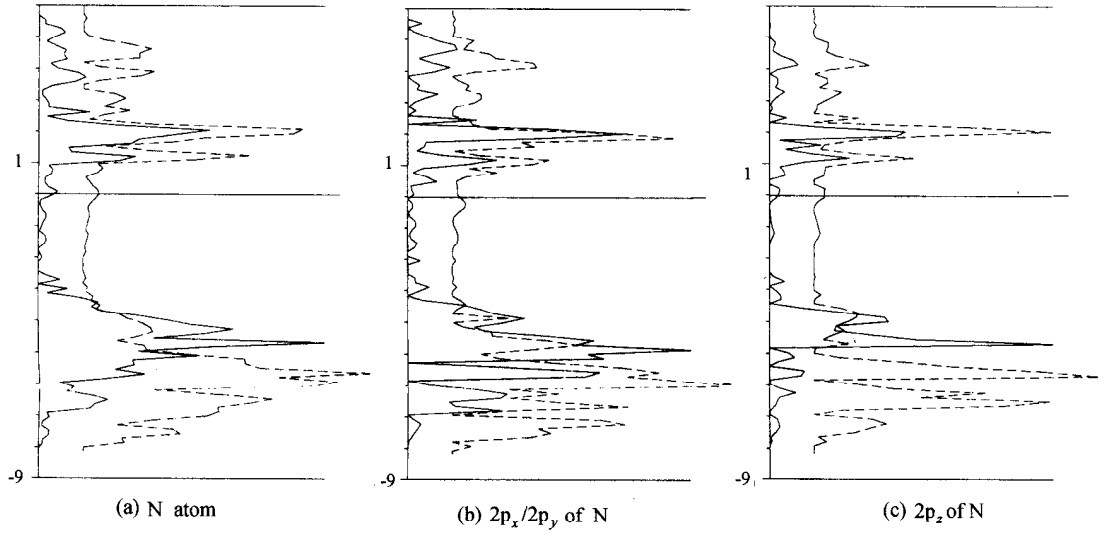
Some partial DOSs of the surface and the bulk atoms for TiN(001) three layers are shown in Fig. 6 to identify the occurrence and components of the surface state observed in ARPES. The DOS of the surface Ti and the bulk Ti atoms nearly coincide with each other. In contrast, great difference can be found between the DOSs of the surface N(N_S) and the bulk N(N_B) atoms (Fig.6 (a)). The bands consisting of orbitals of N_S are mainly located in the region about -5.0—-3.5 eV. However, the bands of N_B show a shift to lower energy and appear at the region of -7.0—-5.0 eV. Hence, it can be concluded that the states derived from (001) surface atoms are mainly centered at 3.5—5.0 eV below E_F, which is in agreement with the experimental results although the actual peak position of the surface state is located at about -2.9 eV relative to E_F. Some partial DOSs of the 2p orbitals of N_S are presented in Fig. 6 (b) and (c). It is indicated that the above mentioned difference can be attributed to the different energy ranges of the 2p orbitals located for N_S and N_B atoms, especially for the $2p_z$ orbitals. The peaks of $2p_z$ orbital of N_S are found to lie closer to E_F than the corresponding peaks of N_B, as well as for the features of $2p_x/2p_y$ orbitals. Thus the surface state observed in ARPES consists essentially of $2p_z$ orbital of N_S, and also exhibits some contributions of the N_S $2p_x/2p_y$ orbitals. Our results indicate that such surface state is mainly originated from the different chemical bonding around N_S and N_B atoms. The reason why this surface state also consists of $2p_x/2p_y$ orbitals of N_S has been explained by Larsson *et al*. They pointed out that, as TiN is somewhat ionic, this surface state could be induced by a change in the electrostatic potential at surface. In their LEED calculations, when the potential applied for N_S is shifted $+0.4$ eV relative to the bulk potential, the calculated results are seen to be in accord with the experimental results, and they obtained a surface state at about 2.0 eV below E_F. In our band structure of one TiN(001) layer (Fig. 5(a)), at Γ point, the N 2p orbitals are splitted into two groups, $2p_x/2p_y$ and $2p_z$ because of the lower symmetry, and they are separated by an energy gap of about 1.0 eV (labeled ΔE in Fig. 5(a)). This energy gap decreases with the number of the layer chosen in the calculations, and a gap of about 0.6 eV is obtained for four TiN(001) layers (Fig. 5(b)), which is close to the value 0.4 eV used in the LEED calculations.

Except for the state derived from band A in Fig. 5 (a), another state associated with the band B can be found in our calculated results. Actually, the states that we are concerned are those which exhibit the chemical activity when the surface reactions, such as for example the surface adsorption, take place. In general, mainly the orbitals of the surface atoms which are perpendicular to the surface (σ type) can take part in the reactions happening on the surface, for example in present case, the N_S $2p_z$ orbital and the surface Ti 3d orbitals which contain the components of z direction (d_{z^2}, d_{xz} and d_{yz}). Just for this reason, the surface state associated with band A is a σ type surface state because it consists mainly of N_S $2p_z$ orbital, and the $2p_x/2p_y$ components of this band can mainly provide electrostatic influences

or π type weak interactions during the surface reactions. The band B in our calculated band structure (Fig. 5 (a)) has not been observed experimentally. One possible reason is that this band is easy to be overwhelmed by the transitions in the bulk, and in calculated DOS, no significant peaks associated with this band are observed. However, band B consists essentially of 3d orbitals of the surface Ti, and in details, it contains a significant contribution of $3d_{z^2}$ orbital of the surface Ti atom. Therefore, the state associated with this band is also a σ type surface state, and it may play an important role when the surface reactions happen on the surface Ti atoms.

Elastic constants of TiN

Ahuja *et al*. calculated the elastic constants of TiN,[14] achieved by use of the LMTO method. The results from their study are in good agreement with the experimental ones although one constant, C_{12} differs significantly. Table 3 presents the results of our BLYP calculation for the elastic constants and the bulk module of TiN, which agree much better with the experimental values[28] than the results obtained by the LMTO method. Our results indicate that the BLYP method is not only a good method to study the electronic structures but also a possible way to investigate other properties of compounds.



(a) N atom (b) $2p_x/2p_y$ of N (c) $2p_z$ of N

(—) surface N; (---) bulk N

Fig. 6 Some partial DOS for TiN(001) four layers.

Table 3 Calculated and experimental elastic constants (Mbar) and bulk modulus (Mbar)[a]

Method	C_{11}	C_{12}	C_{44}	Bulk modulus	References
BLYP	6.42	1.48	1.59	3.13	this work
LMTO /LDA	7.35	0.93	2.5	4.56	14
LMTO/GGA	6.10	1.00	1.68	2.70	14
Experimental	6.25	1.65	1.63	3.18	28

[a] The bulk modulus is calculated by $(C_{11}+2C_{12})/3$.

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