

First-principles study of the TiX ($X = \text{B, C, O, N, F}$) surfaces

Kazuaki Kobayashi¹

¹ *National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba-shi, Ibaraki
305-0044, Japan*

Abstract. TiX ($X = \text{B, C, N, O, F}$) bulk and surface systems as a rock salt structure are investigated by using the first-principles molecular dynamics (FPMD) method. The purpose of this study is to investigate a change of the electronic properties in a series of systems for TiX ($X = \text{B, C, N, O, F}$) systematically.

1 Introduction

In this study, bulk and surface systems of TiX ($X = \text{B, C, N, O, F}$) are focused. TiC and TiN are known to be extremely hard and high melting point materials (for example, coating materials). Technologically, they are very important as highly stable field electron emitters and catalysts for various chemical reactions on the surfaces. The TiC and TiN surfaces have been studied [1, 2] for their electronic and structural properties. The purpose of this study is to investigate electronic properties (energy band structure, electron charge density, work function, etc.) of them and an effect due to a difference of anions (B, C, N, O, F). The (001) surfaces of them are non polarized, in which the outermost layer of an ideal (001) surface consists of an equal number of cation (Ti) and anion (B, C, N, O, F) atoms.

2 Method of calculation

The calculation is based on the local density approximation (LDA) in the density functional theory [3, 4, 5]. Troullier and Martins type optimized pseudopotentials [6] with separable forms of Kleinman-Bylander approximation [7] are used in this calculation. A partial core correction (PCC) [8] is considered for Ti pseudopotential. As for Ti, a 3p core state is not considered as a valence state in this study. A supercell model is adopted and a repeated slab geometry is used. The detailed calculation is similar to that of our previous work [1, 2] for the transition metal carbide (TMC) and nitride (TMN) surfaces.

3 Results and discussion

The lattice properties of the bulk are tabulated in Table 1. The lattice properties for TiC and TiN agree with the experimental results [9, 10, 11]. The lattice constant of TiO is larger by 2 % than that of experiment [12]. All electronic structures of bulk are metallic as shown in Fig. 1.

The TiX ($X = \text{B, C, N, O, F}$) ideal surfaces are calculated. Their electronic states are found to be metallic as shown in Fig. 2.

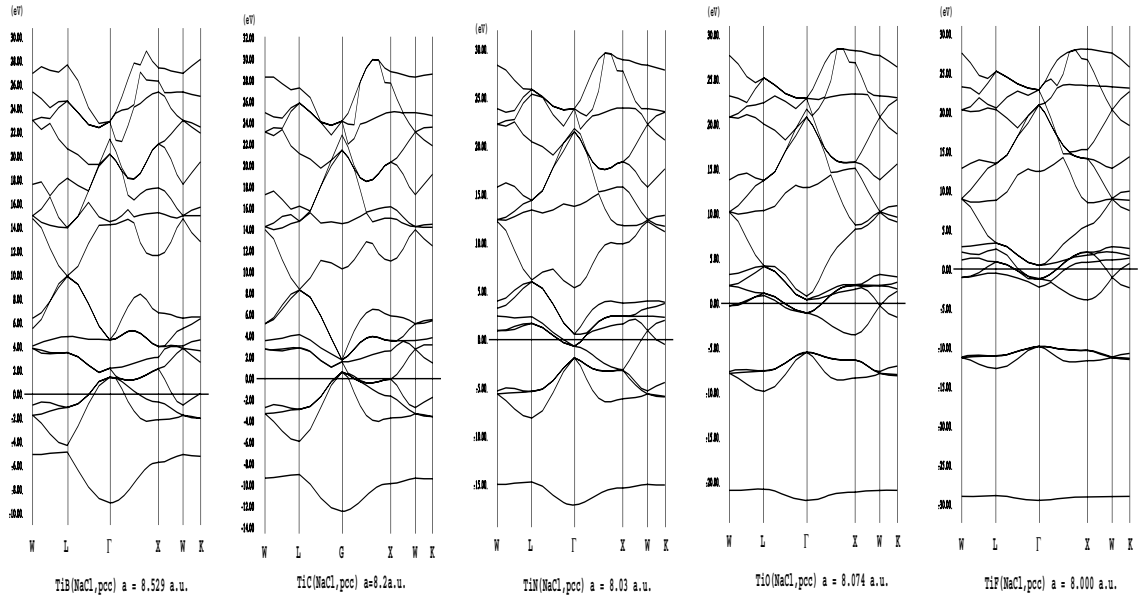


Figure 1: Energy band structures of TiX ($X = \text{B}, \text{C}, \text{N}, \text{O}$ and F) bulk as a rock salt. The Fermi level is indicated by the horizontal line.

Table 1: Calculated bulk properties (equilibrium lattice constants [\AA], bulk moduli [GPa]) and deviation of the present work and experiment for the lattice constant [%].

Bulk	Present work [\AA][GPa]	Exp. [\AA][GPa]	Deviation [%]
TiB	4.50 186		
TiC	4.33 262	4.33 [9]	0.0
TiN	4.25 282	4.238 [10] 288 [11]	+0.2
TiO	4.27 238	4.177 [12]	+2.2
TiF	4.58 103		

The work function for the TiC and TiN surfaces have been studied in the previous work [1, 2] with a structural optimization as shown in Table 2. As for the TiX ($X = \text{B}, \text{C}, \text{N}, \text{O}, \text{F}$) ideal surfaces, it is found as follows.

- (1) The values of the work function for the TiB, TiC and TiN ideal surfaces are decreasing in order of $\text{B} \rightarrow \text{C} \rightarrow \text{N}$.
- (2) The values of the work function for the TiN, TiO and TiF ideal surfaces are increasing in order of $\text{N} \rightarrow \text{O} \rightarrow \text{F}$.
- (3) The value of the work function for the TiN ideal surface is lowest in those for the TiX ($X = \text{B}, \text{C}, \text{N}, \text{O}, \text{F}$) ideal surfaces.

Energy band structures of the TiX ($X = \text{B}, \text{C}, \text{N}, \text{O}, \text{F}$)(001)- 1×1 ideal surfaces as shown in Fig. 2. A position of the Fermi energy for the TiN surface as indicated by a horizontal line in Fig. 2 is the highest in the three energy band structures for TiB, TiC and TiN. The value of the work function is determined as an energy difference between a vacuum level and the Fermi energy. A decrease in the value of the work function from TiB to TiN is caused by the position of the Fermi energy as schematically shown in Fig. 2, although the actual vacuum levels of the above three surfaces are not equal to each other. It is not clear the reason why the values of the work function from the TiN to TiF increase.

Table 2: Calculated work function [eV] for the TiX ($X = \text{B, C, N, O, F}$) ideal surfaces. A value of 3.86 eV [14] in the parentheses is for the unrelaxed surface.

	Relaxed	Unrelaxed	Theory	Exp.
TiB		4.93		
TiC	4.62	4.19	4.7 [13]	3.8 [15]
TiN	3.25	3.03		2.92 [16]
TiO		3.27		
TiF		3.35		
TaC	4.16	3.85	4.24(3.86) [14]	4.3 [17]
TaN	3.45	3.79		4.0 [16]
HfC	4.28	3.86		4.5 [17]
HfN	2.79	3.13		3.85 - 3.90 [16]
NbC	4.26	3.85		4.2 [17]
NbN	3.33	3.59		3.92 [16]
ZrC	4.30	3.94		4.0 [17]
ZrN	2.79	2.84		2.92 [16]

4 Summary

The electronic properties for TiX ($X = \text{B, C, N, O, F}$) bulk and ideal surface systems are calculated by the FPMD method. It may be not enough to explain the work function change of them in this study. It needs more detailed analysis of the electronic properties (charge densities and energy band structures, etc.). In this study, the surface structures for TiB, TiO and TiF are not optimized by using the FPMD method. It is very important to investigate the work function change due to a structural optimization in a future next task.

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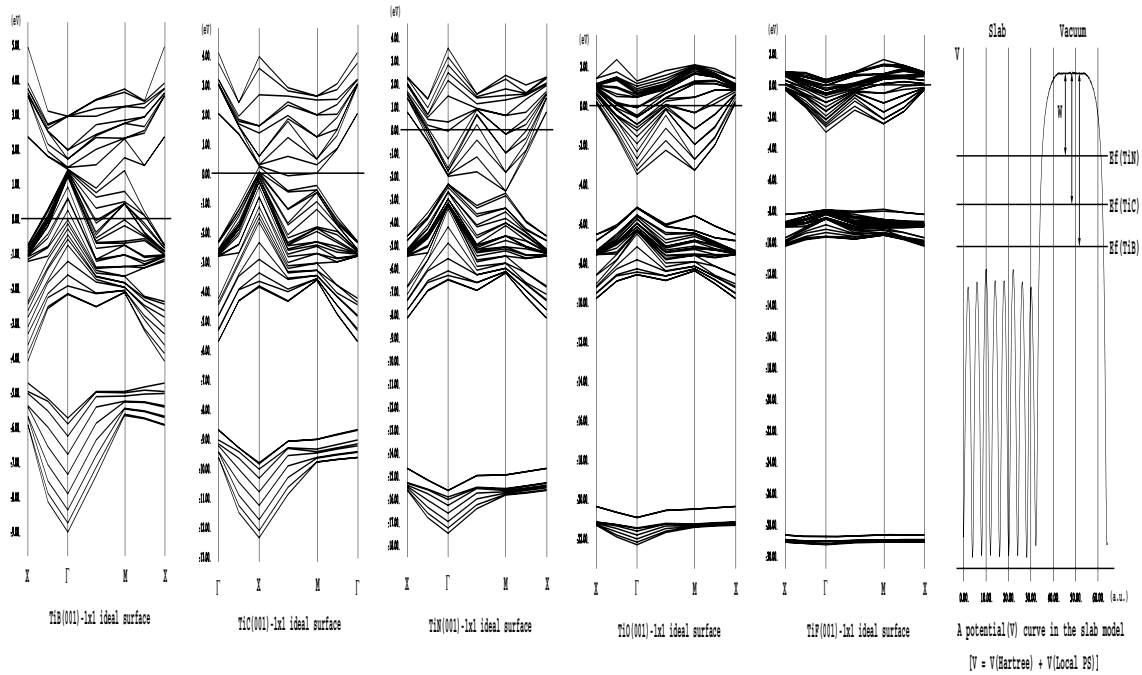


Figure 2: Energy band structures of the TiX ($X = B, C, N, O, F$) ideal surfaces and schematic view of the potential curve for Hartree + local pseudopotential terms for the TiB, TiC and TiN surfaces. A number of k-points is 16 in the whole surface Brillouin zone. The Fermi level is indicated by the horizontal line. $E_f(TiB)$, $E_f(TiC)$ and $E_f(TiN)$ is the Fermi energies of the TiB, TiC and TiN surfaces, respectively. “W” is the work function.

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