First principle study of HF molecule adsorption on TiO$_2$ (110) surface

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Abstract. Titanium and its alloy components are one of the most important technological materials, which has found extensive application in various industries. However, surface defects play a key role in the mechanical properties of these components. Currently, wet chemical etching is one of the most important procedure for surface processing due to the presence of HF since it can etch metal oxide. Therefore, there still a need to investigate the etching mechanism. In this work, adsorption of HF on TiO$_2$ (110) surface has been studied using density functional theory to investigate the fundamental process of etching. HF molecule is adsorbed on the TiO$_2$ surface by dissociation to form Ti-F and O-H species. The interaction between HF and TiO$_2$ surface become more favorable at high HF coverage. The pre-adsorbed of water molecule is favorable for HF adsorption process, which is in good agreement with experimental results. Fluorination processes show the formation and desorption of water intermediate at 0.50 ML coverage. We also investigated the relation between the work function and Mulliken charge for HF adsorption. The results indicate that the interaction of F on the surface attracts electrons due to its higher electronegativity than oxygen. Our results suggest that adsorption of HF is considered chemisorption process.

1. Introduction
Titanium and its alloys are one of the most important materials used in various industries such as aerospace, biomedical and automotive [1]. During the investment casting, oxygen is absorbed from the ceramic mould, which results in the formation of an alpha case layer and is very brittle [2]. Formation of this alpha case layer causes deterioration of mechanical properties that result in material micro-failure [3]. Surface modification is required due to spontaneously growth of a native oxide layer. Recently, wet chemical/ion etching process has been widely employed as a surface modification using hydrogen fluoride (HF) as an etchant, to remove alpha case layer and improve the surface quality [4, 5]. Metal surface etching by HF is one of the most important material tailoring techniques in the manufacturing of metal-based alloyed components. The main purpose of chemical etching is to remove alpha case layer by breaking down titanium oxide layer [6]. The presence of fluorine ion significantly influences the electrochemical behaviour of a metal surface, which is a major relevance for etching and corrosion [7]. There are many theoretical and experimental studies on surface etching but the mechanism of hydrogen fluoride etching process is still not well-understood [8]. In order to get a better understanding of atomic
etching mechanism, a density functional theory (DFT) approach has become an attractive theoretical method to provide chemical bonding, atomic interaction and hybridisation [9]. Recently, research interest has emerged driven by the demand of a new method that is capable of etching metal surface oxides. However, previous studies focused mainly on the Al2O3 surface [10] and the adsorption behaviour on a single atom or probe molecules on metal oxides [11]. Wang et al., [12] investigated the selective etching phenomenon on anatase-TiO2 surfaces. Their results demonstrated that the etching processes is energetically preferable and merely occur on the (100) surface under high HF concentrations. Recently, work done by Yang et al [13] demonstrated that the adsorption of fluorine (F) ion on the surfaces of anatase-TiO2 makes (100) surface energetically preferable to (101) surface.

To investigate deeply on the fluorination process of titanium or metal oxides surface, in this work DFT is employed to study the adsorption behavior of HF on rutile TiO2 (110) surface. These present work greatly improve our understanding on electronic properties of titanium dioxide and reaction behavior of HF. The structure of HF on TiO2 (110) surface with and without pre-adsorbed water at different coverage were systematically investigated. The adsorption energies, the relative energy, Mulliken charge analysis and work function of the systems were calculated. The main goal of the study is to identify the key steps to remove oxygen atoms from the metal oxide surface.

2. Methodology
The study employed DFT to investigate adsorption behavior of HF on TiO2 surface using plane-wave/pseudopotential approach as implemented in Cambridge Serial Total Energy Package (CASTEP) [14]. The electron-exchange and correlation were described by the Perdew-Burke-Ernzerh functional of the generalized gradient approximation (GGA) [15]. The GGA-PBE functional underestimate the band gap, which reduces photo-induced electron transfer during reactions [16]. In order to correct the strong electronic correlation problem, DFT+U method is utilized with a U parameter of 5.0 eV for Ti in TiO2 that was first proposed by Dudarev et al [17]. The Brillouin-zone integrations are using the Monkhorst-Pack approach [18] with K-point sampling grids 4x4x1 for geometry calculation with cut-off energy of 400 eV. The adsorption energy is defined as:

\[ E_{\text{ads}} = E_{HF/\text{slab}} - [E_{\text{slab}} + E_{HF}] \]  

(1)

Where \( E_{HF/\text{slab}} \) is the total energy of the molecule-surface system, \( E_{\text{slab}} \) and \( E_{HF} \) represent the energy of the pure surface and free HF molecule, respectively. A \( E_{\text{ads}} \) is negative for exothermic adsorption process and positive for endothermic.

3. Results and discussion
3.1 Structural geometry and adsorption energy
Surface model is an essential basis precision for adsorption calculations. In figure 1, the optimized structure of TiO2 (110) surface is presented wherein figure 1 (a) shows the side-view and figure 1 (b) top-view. The TiO2 (110) surface consist of three-fold oxygen atoms (O3c), five- and six-fold titanium atoms (Ti5c and Ti6c, respectively). The resulting of geometry of the surface slabs are relaxed to obtain energetic minima. The surface energies of the two slabs with four and six layers relaxed are 1.39 and 1.93 Jm⁻², which were found to be in good agreement with the results obtained Idriss et al [19]. The surface energy depends on the atomic number of layers; 7-layer slab was found to be more stable with lower surface energy than 13-layer. Therefore, 7-layer slab model was selected to describe the adsorption of HF molecule on TiO2 (110) surface.
Table 1 presents the adsorption energies and geometric parameters of HF interacting with TiO$_2$ (110) surface. Firstly, HF molecule was placed on Ti5c and Ti6c site as shown in figure 1 (b) and the systems were relaxed to determine their adsorption energy. Comparing the ir adsorption energies, it was found that HF molecule thermodynamically favors adsorption site of Ti5c (-4.36 eV) interaction than that of Ti6c (-4.16 eV) on the TiO$_2$ (110) surface. This clearly reveals that bonding is crucial for HF to react with TiO$_2$ surface and that could drive HF dissociation. The adsorption energy values are negative, entailing that initial fluorination process of TiO$_2$ (110) surface is energetically favorable.

| Surface site | E$_{ads}$ (eV) | d$_{Ti-F}$ (Å) | O-H (Å) |
|--------------|----------------|----------------|---------|
| Ti5c         | -4.36          | 1.94           | 1.03    |
| Ti6c         | -4.16          | 1.97           | 1.01    |

In order to understand adsorption energy trends, the HF molecules are adsorbed at different coverages and their corresponding adsorption energies, geometric parameters and Mulliken charges are shown in table 2. For all the HF coverage considered, their adsorption energy become more stable with an increasing HF coverage. According to Mulliken charge analysis, Ti atoms gained some positive charge from F-ion surrounding. This suggest that Ti surface atoms loses electrons to F atoms during the interaction.

| Coverage (ML) | E$_{ads}$ (eV) | Mulliken charge | Bond length (Å) | Angle H-O-H (°) |
|---------------|----------------|-----------------|-----------------|-----------------|
|               |                |                 | Ti5c-F          | Ti6c-F          | H-O-H           |
| 0.25          | -4.36          | 1.13            | 1.94            | -               | 1.01            | -               |
| 0.50          | -5.40          | 1.15            | 1.93            | 1.97            | 1.04,1.02       | 104.1           |
| 0.75          | -8.16          | 1.22            | 1.95            | 2.01            | 1.11,1.10       | 107.9           |
| 1.0           | -9.19          | 1.34            | 1.95            | 2.05            | 1.00,1.13       | 107.2,110.4     |

Coverage: number of molecules (ML) adsorbed per adsorption site.

It was found that the Mulliken charge increases with HF coverage. This suggest that exposing TiO$_2$ surface to various HF molecules results in surface saturation. Figure 2(a-d) shows the optimized structure of HF adsorption at different coverage. When placing single HF molecule on the surface slab corresponding to 0.25 ML coverage as shown in figure 2(a), the H-F bond raptures to form Ti-F bond with bond length of 1.94 Å. Hydrogen ion chemically bonds to a neighbour oxygen to form hydroxyl with bond length of 1.01 Å. However, Ti-O bond elongate from the initial bond of 2.01 Å to 2.32 Å. When the second HF molecule is introduced, as shown in figure 2(b), the HF molecule dissociate to form new bond of Ti-F2 with bond length of 1.97 Å. Interestingly, for 0.25 to 0.75 ML coverage, the
oxygen (O3c) atom is pulled out of the surface forming H₂O molecule as shown in figure 2 (b) and (d). This suggests a stronger chemical interaction of HF and TiO₂ (110) surface. The maximum number of HF molecule coverage was four. Similar adsorption mechanism was observed for all HF coverage and this suggests that HF molecules dissociate completely to the TiO₂ (110) surface.

![Figure 2](image)

**Figure 2.** (a)-(d) Adsorption structures of HF on the TiO₂ (110) surface at different coverage.

### 3.2 Relative Energy

To further understand the fluorination process of titanium dioxide, the successive relative energy of two dissociated HF molecules in the TiO₂ (110) surface are also calculated and their results are shown in figure 3. The total relative energies of the systems for the water formation and desorption were found to be 2.371 eV and 0.291 eV, respectively; which suggest that the reaction is not spontaneous. It appears that two HF molecules dissociate completely to the TiO₂ (110) surface and the two hydrogen atoms are transferred to the neighbouring oxygen to form intermediate water molecule. This shows a stronger chemical interaction of O-H bonding. Therefore, the intermediate water desorbed from the surface to become a free molecule suggest that the oxide layer can be removed as the water intermediate from the surface.
3.3 Co-adsorption of H₂O and HF on the TiO₂ (110) surface

Previous result revealed that etching titanium oxide surfaces through a wet fluorination process is more favourable than dry etching [20], whereby the existence of water plays a crucial role. One-way to establish this theory, co-adsorption behaviour of H₂O and HF on the TiO₂ (110) surface was also investigated. The same technique was done by Quan et al [10] on aluminium oxide surfaces. Figure 4 present the co-adsorption of H₂O-HF molecules on TiO₂ (110) surface. When the water molecule is adsorbed on the TiO₂ (110) surface, a Ti-O bond formed with the bond length of 1.906 Å. The calculated adsorption energy of -4.83 eV was found, this is in good agreement with the value of -4.796 eV found by Dai et al [21]. When HF molecule is adsorbed on the TiO₂ (110) surface with the present of H₂O molecule, HF dissociate completely to form Ti-F and O-H with the bond length of 1.989 Å and 1.001 Å, respectively. Adsorption energy of HF with pre-adsorbed H₂O (-6.02 eV) is more stable than the adsorption energy (-4.36 eV) without pre-adsorbed water molecule. When the second HF molecule is introduced on the surface, the adsorption energy is (-7.28 eV) more favourable than the adsorption energy without H₂O molecule. This suggest that the pre-adsorption of water or wet HF is favourable for fluorination of TiO₂ surface than adsorption of HF gas. This correspond with the experimental observation of dry and wet etching on TiO₂ and SiO₂ surfaces [22].

**Figure 3.** Relative energy of HF on TiO₂ (110) surface.
3.4 Work function and Mulliken charge

Etching mechanism is often electrochemical in nature and this concept arises from corrosion [23]. The process involves electron charge transfer hence Mulliken charge analysis were calculated and summarized in table 3. The trend seen is that the Mulliken charge increases with an increasing HF molecules which implies that more charges are depleted from the surface upon the Ti-F interaction. The changes in surface charge shown to affect surface work function. When a single HF molecule is adsorbed, the work function slightly increases from 2.651-2.815 eV. It was also found that the work function is coverage depended as shown in table 3. The work function offers a good measure of how prone is the corrosion of a certain material [24].

| Coverage (ML) | Work function | Mulliken charge |e|
|--------------|--------------|-----------------|
| 0.25         | 2.815        | 1.13            |
| 0.50         | 3.392        | 1.15            |
| 0.75         | 3.237        | 1.22            |
| 1.00         | 3.682        | 1.34            |

In this study change in the work function has been found to be coverage depended see figure 5. The large relative increase in work function with increasing HF coverage is due to the high electronegativity of fluorine atoms. However, for 0.75 ML coverage the work function decreases as shown in figure 5 due to the repulsive interaction between closed adsorbed fluorine-ion. Different changes in the work function are cause by charge transferred associated with fluorine ion.
In figure 6 the electrostatic potential is shown where (a) is pure surface slab and (b) the highest coverage (1 ML). The electrostatic potential of the pure surface tends to be flat in the vacuum region, while after the adsorption of HF there is a potential step in the vacuum region for all coverage. The potential step in the middle of the vacuum is due to the dipole introduced by the fluorine-ion, which result in two surfaces - upper and lower. The upper surface ($\Phi_1$) consist of Ti-F with the higher value of the work function while lower surface ($\Phi_2$) consist of Ti-O layer with the lowest value of work function. The decrease of lower work function ($\Phi_2$) shows that the surface lost electrons during adsorption, which implies the manifestation of surface corrosion.

**Figure 5.** Change in the work function as a function of coverage.

**Figure 6.** Electrostatic potential: (a) clean surface and (b) 1ML coverage.
4. Conclusion

The adsorption characteristic of HF molecule on TiO$_2$ (110) surface at different coverage was investigated using DFT approach. The explicit surface slab calculations were conducted to study the adsorption of HF molecules per cell on a rutile TiO$_2$ (110) surface. HF molecule dissociate completely upon adsorption on the TiO$_2$ surface, to form Ti-F bond while the hydrogen ion is chemically bonded to the nearest oxygen to form hydroxyl. The adsorption stability of HF molecule increases with an increasing HF coverage. Interestingly for all coverages their adsorption energies are negative, this implies that adsorption process is exothermic and etching mechanism is energetically permitted at high coverage. In addition, the pre-adsorption of water molecule was investigated on TiO$_2$ surface and it was found to be more favourable for HF adsorption. The total energy of the two dissociated HF molecules on the TiO$_2$ surface were found to be 2.371 and 0.291 eV for the formation and desorption of water intermediate. This preliminary reaction suggests that etching of TiO$_2$ (110) surface occurs at high temperature. Furthermore, reaction showed intermediate water desorbed from the surface, which mimic one of several possible cases when the oxide layer is suddenly destroyed by etching mechanisms. The study revealed a significant increase in the work function at different coverage due to the high electronegativity of the fluorine atom. Furthermore, Mulliken charge analysis showed a positive charge increase with an increase in HF adsorption molecule. Since during adsorption, fluorine atom withdraws electrons from Ti atoms

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