

Adsorption-desorption of F₂ diatomic molecule on Ti (100) surface at different coverages

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Abstract

Fluorine molecules and ions are used as an etchant for metal surface processing. The presence of fluorine significantly influences the electrochemical behaviour on a metal surface, which has major relevance for etching, corrosion, electro-catalysis and galvanic deposition processes. Although the fluorine ions play an important role in metal surface etching, the studies remain limited and unclear, especially at the atomistic scale. In this work, density functional theory is used to investigate the structural and electronic properties of F₂ diatomic molecule adsorption on Ti (100) surface at different coverages. Results revealed a dissociative adsorption mechanism of F₂ on the Ti (100) surface. Adsorption energy analysis of F₂ on Ti (100) surface denotes an exothermic process. Moreover, increasing F₂ coverage resulted in the formation of TiF₄ and Ti₂F₆ molecules on the surface. In addition, the calculated heat of formation for TiF₄ was found to be more favourable than Ti₂F₆ species. Calculated desorption energies for TiF₄ and Ti₂F₆ is 11.73 eV/atom and 9.04 eV/atom, suggesting non-spontaneous.

Keywords: Fluorine ion, desorption energy, Ti surface, density functional theory

1. Introduction

Titanium and its alloys components attract lots of attention for usage in various applications such as in the aerospace, medicine as well as automotive industries, due to its high weight-strength ratio (Trevisan et al. 2017). There are several manufacturing techniques for titanium parts such as machining (Campbell 2006), forging (Hu and Dean 2001) and investment casting (Atwood et al. 2005), but investment casting has become one of the most attractive methods. However, during investment casting, titanium reacts with oxygen, nitrogen or intermetallic compounds that result in the formation of the alpha-case layer (Sung et al. 2008). The alpha-case layer makes the surface harder and brittle, which results in cracks manifestation and decreased fatigue life (Lütjering and Williams 2007). Therefore, a post-fabrication process is required such as surface modification and treatment to limit the extent of these problems. Different etching processes are deployed and extensively used for surface modification depending upon the particular materials (Kanarik et al. 2018). The most common etching techniques include wet chemical etching (Pornsirirak et al. 2001), reactive ion etching (Aimi et al. 2004) and plasma etching (Coburn and Winters 1979).

The etching technique is used to remove the top layer from the material through electrochemical reaction (Allongue et al. 1996), corrosion (Tereshchenko et al. 2012) or by breaking the atomic bonds that attaches to the top surface (Kanarik et al. 2017). Recently, acidic etching treatment is the only adopted approach that can modify the overall pore surface structure (Zahran et al. 2016). The etching process plays a crucial role in investment casting, however, the mechanism remains unclear and limited,

especially at the atomistic scale. The etching of metal surface by halogen ions/atoms have originated relevant studies that probe surface structure effects with atomistic scale precision (Aldao and Weaver 2001). Fluorine ion adsorption and interaction with the metal is related to the etching mechanism (Tereshchenko et al. 2012), because the key manner of etching is through ion-metal interaction (Ghosh and Manna 2018). A wide range of media containing F⁻ such as HF (Kim et al. 2021), F₂ (Vitale et al. 2001) and XeF₂ (Williams et al. 2003) ions are commonly used in various industries for material surface etching and corrosion (Wang et al. 2015). Recently, halogen ions were also adsorbed on a Ti (110) surface for etching purposes, owing to the fact that fluorine was reported more thermodynamically stable than other adsorbents (Tshwane et al. 2021).

The presence of a halogen ion significantly influences the electrochemical behaviour of a metal surface, which is of major relevance for etching and corrosion purposes (Tereshchenko et al. 2012). Work by Fracassi and Dagostino (1992) reported that the fluorine ion treatment makes the Ti atomic surface more reactive towards fluorination and chlorination gases. Selective etching occurred on TiO₂ surfaces by hydrogen fluoride molecule adsorption, it was reported that the HF destroyed the grown (001) faceted surface through the -OH and replace it with TiOF₂ (Wang et al. 2011). Yang et al. (2008) reported that the adsorption of fluoride ions on the surfaces of anatase-TiO₂ makes the (100) surface energetically preferable than (101). HF molecule was adsorbed on the TiO₂ (110) surface and it was seen that the molecule dissociate completely to form Ti-F and H-O species (Tshwane et al. 2019). Chatterjee et al. (2000) found that exposure of Si surface with F₂ at

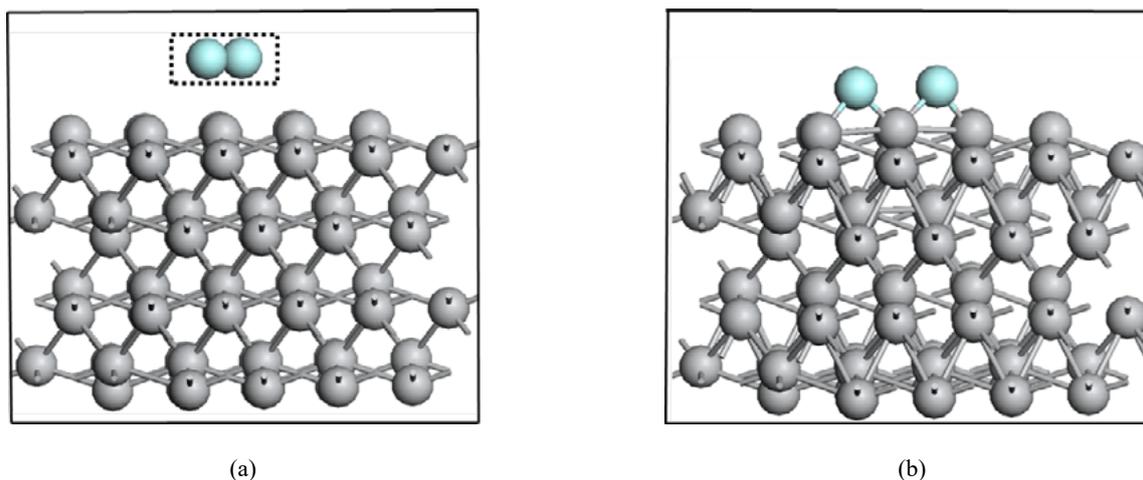


Figure 1: Schematic structure of F_2 molecule adsorption on Ti (100) surface: (a) before and (b) after optimisation

different coverage resulted in forming SiF_2 and SiF_4 species as an etchant product.

Most studies focused mainly on metal oxide surfaces (Quan et al. 2012) and the adsorption mechanism of a single probe molecule (Bouzoubaa et al. 2009). In this work, density functional theory (DFT) was employed to investigate the adsorption mechanism of F_2 molecule on Ti (100) surface at different coverage. This present work provides a fundamental understanding of electronic properties and structural changes on the Ti surface during the F_2 molecule adsorption.

2. Methodology

The study employed DFT to investigate the adsorption behavior of the F_2 molecule on Ti (100) surface using a plane-wave pseudopotential approach as implemented in the Cambridge Serial Total Energy Package (CASTEP) (Segall et al. 2002). The electron-exchange and correlation were described by the Perdew-Burke-Ernzerhof (PBE) functional of the generalised gradient approximation (GGA) (Perdew and Wang 1992). Brillouin-zone integrations using the Monkhorst-Pack approach (Monkhorst and Pack 1976) with k-point sampling grids $4 \times 4 \times 1$ for geometry calculation were employed with cut-off energy of 400 eV. Ti (100) surface was represented by a slab of atomic layers, in which the inner layer was fixed, while the rest of the system was allowed to relax during geometry optimisation. The adsorption energy is defined as:

$$E_{ads} = E_{mol/surf} - (E_{surf} + E_{mol}), \quad (1)$$

where $E_{mol/surf}$ is the total energy of the molecule-surface system, E_{surf} and E_{mol} represent the energy of the pure surface and free molecule, respectively. To calculate the heat of formation of a TiF_x molecule the corresponding equation is:

$$E_{HF} = E_{TiF_x} - (E_{Ti} + \frac{x}{2}E_{F_2}), \quad (2)$$

where E_{TiF_x} , E_{Ti} , and E_{F_2} refers to the energies of TiF_x , Ti and F_2 structures, respectively. The desorption energy of TiF_x species from the Ti (100) surface is defined as:

$$E_{des} = -[E_{a/s} - (E_a + E_s)], \quad (3)$$

in which $E_{a/s}$ is the potential energy of the adsorbate-surface, E_a and E_s represent the potential energies of each adsorbate and the Ti (100) surface separately.

3. Results and discussion

3.1 Structural geometry and adsorption

To analyse the structural adsorption of F_2 molecule on Ti (100) surface, Figure 1 shows the obtained adsorption structure of an F_2 molecule (d_{F-F} 1.409 Å) on a Ti (100) surface, in which Figure 1 (a) present the schematic before optimisation while Figure 1 (b) presents after optimisation. Based on the atomistic model, the adsorption of F_2 molecule on the Ti (100) surface is by a dissociation process that involves a scenario of F-F bond breaking and Ti-F bond forming. Atomic bond breaking and formation are driven by the F ions forming metal halide bonds.

It was seen that the dissociation of a F_2 molecule forms an F-Ti-F interaction with a bond length of (d_{Ti-F}) 2.045 Å and a tilted angle of 98.4°. The interatomic distance ($d_{F...F}$) between the F atoms was found to be 3.098 Å after optimisation. The fact that the F_2 diatomic molecule dissociated leads to the formation of an ionic bond with the positive charge of Ti atoms. Relative final state energy and adsorption energy of a dissociated F_2 molecule on the Ti (100) surface were found to be -0.049 eV/Å² and -10.90 eV, respectively. This suggests that the dissociation of F_2 molecule on the Ti (100) surface is spontaneous due to its negative adsorption energy values.

3.2 Adsorption coverage

Adsorption of the F_2 molecule on the Ti (100) surface at different coverages was studied to investigate the Ti (100) surface changes. Figure 2 shows the atomic configuration of optimised adsorption of F_2 molecule: (a) two F_2 /Ti (100) and (b) three F_2 /Ti (100) surface. We observed that the dissociation of F_2 molecules on the Ti (100) surface resulted in surface structural changes. This leads to the formation of titanium halide (Ti_xF_y) molecules on the surface. In this scenario, the adsorption and dissociation of two F_2 molecules generated a TiF_4 species, while the dissociation of three F_2 molecules resulted in a Ti_2F_6 molecule on the surface.

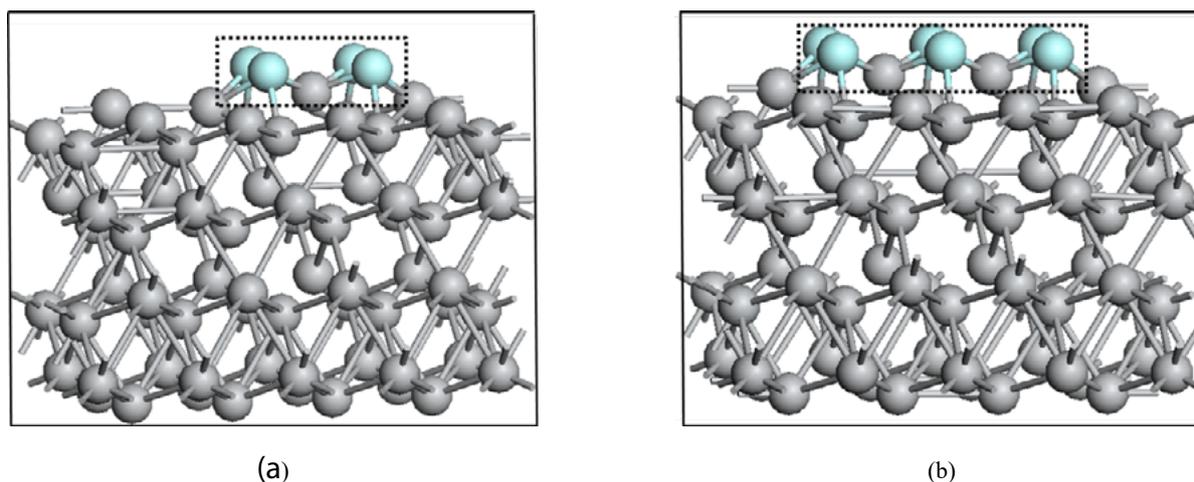


Figure 2: Atomic configuration of optimised adsorption of F_2 molecule at different coverage: (a) two F_2/Ti (100) and (b) three F_2/Ti (100) surface

The formation of Ti_xF_y species was observed which could be pulled upwards, becoming an isolated molecule that is desorbed from the Ti (100) surface. This implies that the F ion is first adsorbed on the surface and then the formation of the Ti_xF_y etch product occurs at high coverage. However, since the molecules are still attached to the Ti surface in Figure 2, both the formation and desorption energies are calculated in the next section. Similar work was done on the exposure of F_2 molecule on metal Si (100) surface where the relative primary etching product such as SiF_2 and SiF_4 molecules were observed (Chatterjee et al. 2000).

3.3 Formation and desorption energy of Ti_xF_y molecules

In order to obtain the chemical trend of these Ti_xF_y species, the heat of formation and desorption energy were calculated and are presented in Table 1. Heat of formation (E_{HF}) of the compound inherently reflects the stability while the desorption energy is the desorption potential for a molecule to be detached from the surface. It was found that all Ti_xF_y species possess negative E_{HF} denoting that the formation process of Ti_xF_y molecules is exothermic. TiF_4 molecule was found to be the most stable with a lower formation energy of -6.13 eV/atom than TiF_6 with E_{HF} of -6.08 eV/atom. Moreover, the desorption energy values were found to be positive indicating that the desorption process of Ti_xF_y molecules is by non-spontaneous reaction. It was found that the desorption energy value of Ti_2F_6 molecule is lower than that of TiF_4 implying that the double Ti_2F_6 molecule has a lower desorption barrier as compared to a single TiF_4 species. This has clearly shows that the etching mechanism of the titanium surface is based on the formation and desorption of Ti_xF_y molecule and the amount of material removed is etching per Ti_xF_y formed.

Table 1: Calculated heat of formation (E_F (eV/atom)) and desorption energies (E_{des} (eV/atom)) for Ti_xF_y molecules

Molecule	E_F (eV/atom)	E_{des} (eV/atom)	$d_{(Ti-F)}$ (Å)	F-Ti-F
TiF_4	-6.13	11.73	2.973	93.2°
Ti_2F_6	-6.08	9.04	2.944	93.2°

3.4 Density of states

To investigate the electronic interaction between fluorine ion and Ti (100) surface, the partial density of states (PDOS) curves were analysed. The PDOS plots present the number of orbital states per unit energy. Figure 3(a) presents the PDOS curves of the free TiF_4 crystal structure (top panel), clean Ti (100) surface (middle panel) and TiF_4 molecule formed on the Ti (100) surface (bottom panel). Electronic peaks for free crystal TiF_4 (Figure 3(a) top panel) consists of s-, p- and d- with only p- orbital contributing more at the Fermi level (E_F). We observed pronounced electronic peaks at around -3 eV that correspond to p- and d- orbitals for F and Ti atoms, this also indicates the p-d hybridisation for Ti-F interaction.

In addition, the PDOS plots for clean surface (Figure 3(a) middle panel) showed the Ti d- band contributing more to the Fermi level (E_F) and minimum contributions from both s- and p- orbitals. Slight changes were observed on PDOS plots for TiF_4 formed molecule (Figure 3(a) bottom panel) as compared to the clean Ti surface (middle panel). New electronic peaks emerged between -10 to -5 eV (see bottom panel), which correspond to the p- electrons from the F atoms. Furthermore, we noticed a slight decrease in the magnitude of the electronic peak for the formed TiF_4 formed molecule as compared to the pure surface.

Figure 3(b) presents the PDOS profiles of the free Ti_2F_6 crystal structure (top panel), clean Ti (100) surface (middle panel) and Ti_2F_6 molecule formed on the Ti (100) surface (bottom panel). PDOS curves for a free Ti_2F_6 crystal (top panel) consist mainly of s-, p- with electronic peaks around -7 to -8 eV and d- orbital states dominating more at the Fermi level (E_F). We observed a similar electronic peak for the formed Ti_2F_6 molecule (see Figure 3(b) bottom panel) corresponding to the p- orbital from the F atom. However, the PDOS peak for the Ti_2F_6 free crystal molecule possesses a higher peak intensity than the TiF_4 plots. Moreover, there is no significant difference between the form TiF_4 and Ti_2F_6 molecules, except for the higher magnitude of the electronic peaks.

3.5 Charge Density Difference

Additionally, the iso-surface contour of charge density, which clearly depicts the electronic interaction between Ti and F atoms.

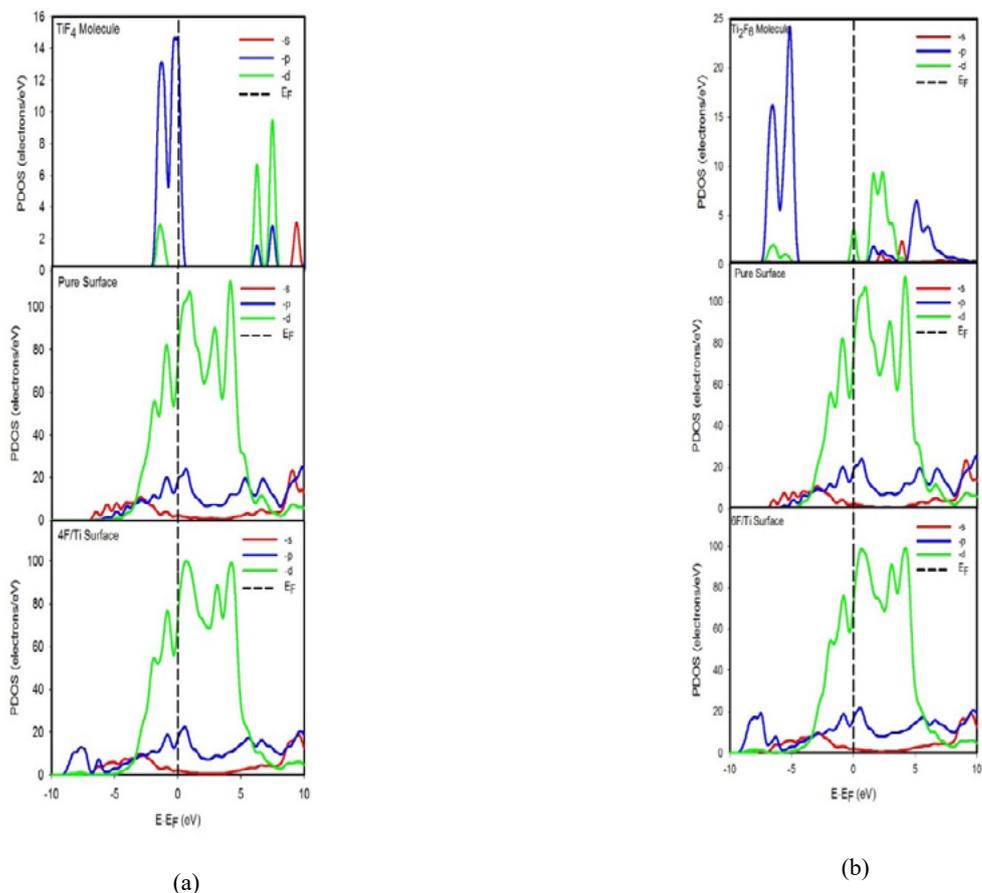


Figure 3: Partial density of states plots for adsorbed F_2 molecules on Ti (100) surface at different coverages: (a) two F_2 /Ti (100) and (b) three F_2 /Ti (100) surface

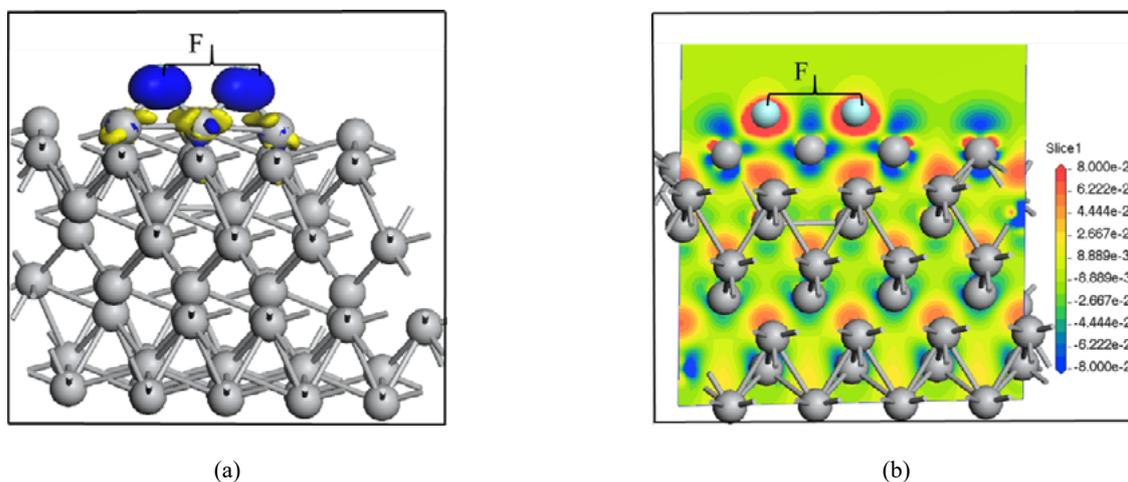


Figure 4: Charge density difference for F_2 molecule adsorption on a Ti (100) surface: (a) charge density and (b) 2D electron density distribution

Figure 4 presents the charge density difference for the F_2 molecule adsorbed on the Ti (100) surface. Charge density plots clearly show charge redistribution among the F and Ti atoms during bonding. The magnitude of the charge is shown by a different colour, whereby, the blue and yellow indicate electron depletion and accumulation as shown in Figure 4 (a), respectively. We observed that the charges are depleted from the Ti atoms and accumulated by F atoms. Therefore, the electrons around the F atoms are uniform indicating their ionic character (see Figure 4 b), this suggests the

valence electrons of Ti atoms are strongly pulled toward the F and Ti atoms and become more positively charged represented by the yellow iso-surface region.

4. Conclusion

The adsorption mechanism of F_2 diatomic molecule on Ti (100) surface at different coverage was successfully studied using the DFT simulation approach. It was found that the adsorption of the F_2 molecule is through a dissociation process resulting in Ti-F

interaction. Upon increasing the coverage adsorbates resulted in structural changes by forming TiF_4 and Ti_2F_6 molecules with tilted angle and bond length (Ti-F) of 98° and 2.045 \AA . In addition, the heat of formation energies for Ti_xF_y molecules possess a negative value, which denotes an exothermic process. Moreover, the Ti_xF_y molecules were observed to desorb away from the Ti (100) surface indicating the manifestation of the etching process. The calculated desorption energies for probable desorption products (TiF_4 and Ti_2F_6) is non-spontaneous. It was found that Ti_2F_6 molecule is more likely to desorb from Ti (100) surface than a single TiF_4 molecule, thereby indicating that to etch Ti surface is through desorption of a Ti_xF_y molecule. Furthermore, the charge density difference of the Ti_xF_y molecule shows a spherical charge distribution implying ionic bonding between Ti-F interactions.

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