

# Electronic and Surface Properties of Aluminum (111) Surface Modified by Interstitial and Substitutional Titanium Incorporation

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## Abstract

This study investigates the influence of interstitial and substitutional titanium atoms on the electronic properties of aluminum surfaces using density functional theory (DFT). The study focuses on three variables: the presence and arrangement of Ti interstitials on the aluminum surface, the behavior of Ti substitutional and interstitial impurities, and the energetic stability and structural properties of these systems. Multiple DFT methods are employed to derive conclusions regarding the impact of these variables on the surface properties of aluminum. The study provides valuable insights into how different states of interstitial and substitutional Ti can alter the physical characteristics and performance behaviors of the aluminum surface. The understanding of these effects could enable engineers to design more efficient materials with enhanced properties suitable for various industries.

*Keywords:* Aluminum surface, Density functional theory (DFT), Interstitial, Substitutional, Titanium atoms.

## INTRODUCTION

The understanding of surface property modifications in metals plays a crucial role in enhancing their overall performance, making it a subject of considerable importance.[1,2,3] Particularly, investigating the influence of interstitial and substitutional atoms on the electronic properties of metal surfaces has garnered attention in research. Previous studies have demonstrated the significant impact of interstitial and substitutional titanium atoms on the electronic properties of aluminum surfaces.[4] Interstitial defects, characterized by atoms occupying interstitial spaces, are relatively less stable compared to substitutional doping. Therefore, this study focuses on examining the effects of substituting aluminum atoms with titanium atoms, specifically investigating the alterations in the electronic properties of the aluminum surface. Introducing interstitial and substitutional titanium atoms can induce changes in the material's electronic band structure, charge distribution, chemical reactivity, and adhesion on the surface. [5] Understanding these changes is essential for the development of improved materials and optimizing their performance.

This research article delves into investigating

the influence of interstitial and substitutional titanium (Ti) on the surface properties of an aluminum surface using density functional theory (DFT). The study centers around three variables: the presence and arrangement of Ti interstitials on the aluminum surface, the behavior of Ti substitutional and interstitial impurities, and the energetic stability and structural properties of these systems. To achieve the research objectives, multiple DFT methods are employed, and their outcomes are thoroughly analyzed to derive conclusions regarding the impact of these variables on the surface properties of aluminum. Additionally, the study provides valuable insights into how different states of interstitial and substitutional Ti can alter the physical characteristics and performance behaviors of the aluminum surface. The understanding of these effects could enable engineers to design more efficient materials with enhanced properties suitable for various industries, including aerospace engineering, medical device manufacturing, and beyond. The forthcoming sections present a comprehensive overview and analysis of the research findings.

## Computational Methods

This study employed DFT calculations using the Vienna Ab-initio Simulation Package (VASP) with a

plane-wave-based approach [6, 7, 8, 9]. PAW pseudopotentials [10, 11] were utilized to represent the ionic cores, while a 540 eV electronic kinetic energy cutoff was set for the valence electrons. K-point sampling was performed using a  $6 \times 6 \times 1$  Monkhorst-Pack mesh [12]. The calculations adopted the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [13,14]. Grimme's empirical correction scheme (DFT + D/PBE) was incorporated to account for van der Waals (vdW) interactions [15]. Structural optimization was carried out until the residual forces converged to 0.01 eV/Å. The crystal structures and charge density differences were visualized using VESTA [16]. Bader's Quantum Theory of Atom-in-Molecules approach, known as the Bader charge analysis, was used to study charge transfer [17]. Bonding analysis was conducted using the Crystal Orbital Hamilton Population (pCOHP) technique, a modern descendant of the COHP method [18], which allows for the assessment of bonding, antibonding, and non-bonding interactions through crystal orbital overlap population plots. Net atomic charges (NACs) and bond orders (BO) were computed using the DDEC6 charge density partition scheme developed by Limas and Manz (2016) [19] and Manz and Limas (2016) [20].

### Computational Model

The initial phase of our study involved a comprehensive investigation of various facets of aluminum surfaces. Prior to surface calculations, geometry optimization was performed on bulk structures to ensure their stability. Surface modeling was subsequently conducted based on the optimized bulk structures, enabling the calculation of surface energy for different facets of aluminum surfaces. Among the aluminum surface orientations, a specific facet was selected based on its lower surface energy compared to others, indicating easier formation. Furthermore, surface energy serves as an indicator of surface stability, where a lower surface energy corresponds to a more stable surface.

In order to assess the effects of interstitial and substitutional titanium (Ti) atoms on the Al (111) surface, we conducted detailed calculations that involved configuring the interstitial and substitutional Ti atoms within a tetragonal cell. The models employed in our investigation are visually presented in Figure 1. These calculations allowed us to explore the potential impact of Ti atoms in these

different configurations on the Al (111) surface.

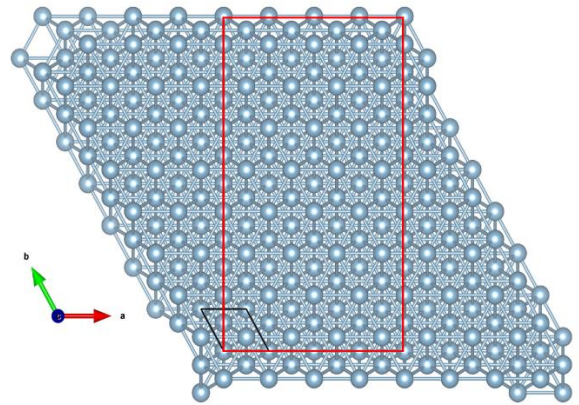


Figure 1. Al (111); Black straight line and red dashed line correspond to rhombohedral and tetragonal unit cell respectively.

To explore the interstitial and substitutional mechanisms and their impacts on the Al (111) surface, we employed specific modeling techniques. For the interstitial mechanism, we simulated an atom exchange process by introducing a titanium (Ti) atom above the Al(111) surface, representing its interstitial position within the lattice. This model, referred to as Al(111)-Ti int, allowed us to investigate the interaction between the introduced Ti atom and the surrounding aluminum lattice, providing insights into phenomena such as atomic diffusion, lattice distortion, and resulting changes in mechanical, thermal, and chemical properties.

In contrast, for the substitutional mechanism, we modeled the replacement of an aluminum (Al) atom on the Al(111) surface with a titanium atom. This model, denoted as Al(111)-Ti subs, enabled us to examine the surface behavior when Ti atoms substitute Al atoms within the crystal lattice.

These mechanisms were accurately captured by adding a titanium atom above the Al(111) surface to represent the interstitial mechanism (hereinafter referred to as Al(111)-Ti int) and substituting an aluminum atom on the Al(111) surface with a titanium atom to represent the substitutional mechanism (hereinafter referred to as Al(111)-Ti subs), as illustrated in Figure 2.

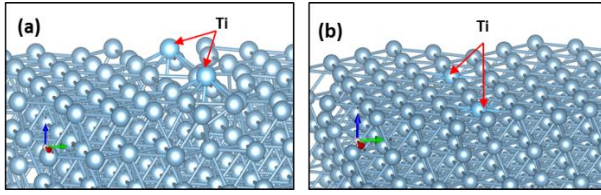


Figure 2 (a) interstitial model and (b) substitutional model of Titanium atom on Al(111) surface.

## RESULTS AND DISCUSSION

### Analysis of Electronic Structure of Aluminum Surfaces

The initial step in our study involved investigating each facet of the Aluminum surface. Prior to conducting surface calculations, we performed geometry optimization on the bulk structures of Aluminum. The bulk structure of Aluminum exhibited face-centered cubic (fcc) symmetry (fm-3m), and the resulting lattice constants were determined to be  $a = b = c = 4.043 \text{ \AA}$ . These values are consistent with experimental measurements reported in the literature as well as those obtained from other computational studies [21].

Subsequently, surface modeling was conducted based on the optimized bulk structures. The surface energies of various Aluminum surface facets were then calculated using the following formula, as previously described by Iddir et al. [22] and Sun and Ceder [23]:

$$\gamma = \frac{E_{slab} - E_{bulk}}{2A} \quad (1)$$

where  $\gamma$  is surface energy,  $A$  is the surface area,  $E_{slab}$  is the total energy of the slab,  $E_{bulk}$  is the total energy of the corresponding bulk, and the factor 1/2 in Equation 1 is owing to two equivalent surfaces in the slab. The surface energy of Aluminium surfaces were calculated via Equation 1, the computation results are listed in the Table 1.

Table 1. Surface energy of Aluminium surfaces.

Miller Indices (hkl)	Surface Energy (eV/Å <sup>2</sup> )
(111)	0.05

(322)	0.06
(332)	0.06
(100)	0.06
(221)	0.06
(331)	0.06
(321)	0.06
(311)	0.06
(110)	0.06
(211)	0.06
(310)	0.06
(320)	0.06
(210)	0.06

Our results show that Al (111) has lower surface energy compare to other aluminium surface orientation it means that this surface orientation is easier to formed. Moreover, the surface energy can be a measure of the stability of the surface—a lower surface energy indicates a more stable surface; therefore Al (111) surface orientation will be use in this paper.

The work function of the Al (111) surface can be calculated using following equation [24]

$$\Phi = V_{vac} - E_f \quad (2)$$

Where  $\Phi$  is the work function,  $V_{vac}$  is the vacuum level in the vacuum region, and  $E_f$  stands for the Fermi energy of the slab. The work function of Al(111) were calculated to be 4.02 eV. The derived work functions are consistent with values in other calculation [25] and experiment[26].

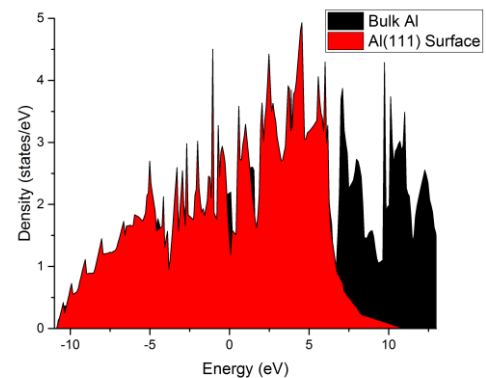


Figure 3. Density of states (DOS) of Al Bulk and (111) surface

Investigating the electronic structures of Aluminium bulk and (111) surface is crucial for understanding the material's properties and potential applications. In Figure 3, we present a comparison of the total density of states (DOS) between Aluminium in the bulk and at the (111) surface.

From Figure 3, several key observations can be made. Firstly, the bandwidths of the DOS for surface atoms are narrower compared to those of the bulk atoms. This suggests that the electronic states near the surface are more localized and confined compared to the more delocalized states in the bulk. Secondly, the DOS of the surface atoms exhibit higher values around the Fermi level compared to the bulk atoms. This indicates a higher density of electronic states available for interaction and bonding at the surface. These findings provide insights into the electronic structure differences between the Aluminium bulk and (111) surface, shedding light on their distinct behaviors and potential reactivity. Further analysis and interpretation of these results will contribute to a comprehensive understanding of Aluminium's electronic properties.

The Aluminium surface was modeled using a slab comprising six Al layers with a 20 Å vacuum region within a tetragonal cell. To investigate the interface, we placed the Ti atom above the Al (111) unit cells, which have dimensions of  $a=8.58$  Å and  $b=19.81$  Å, as depicted in Figure 1. The DDEC6 net atomic charges analysis of the topmost layer of Al (111) surface, presented in Figure 4 (a), reveals several significant findings. Firstly, the topmost layer of Al (111) exhibits negative net atomic charges. Specifically, each aluminum atom in the topmost layer carries an average net atomic charge of approximately -0.040. This indicates an excess of electrons in this layer.

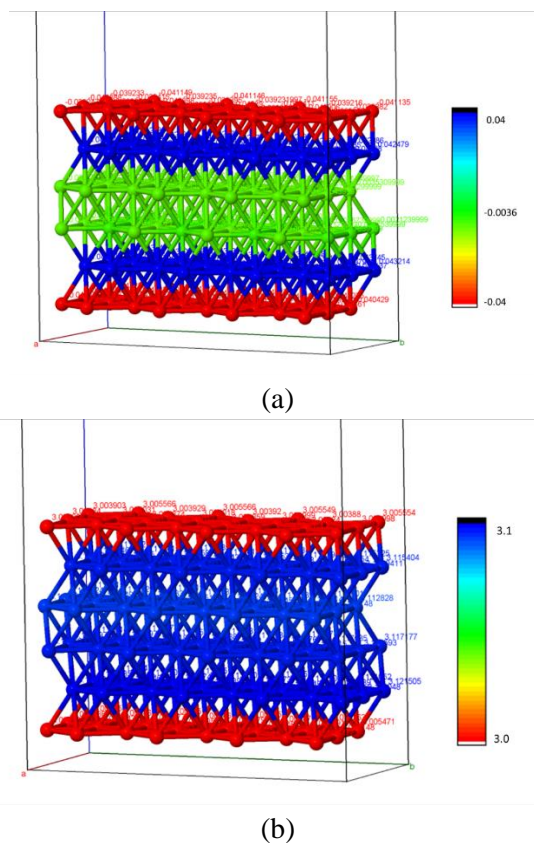


Figure 4 (a) Net atomic charges and (b) sum of bond order distribution of Al(111) surface

The DDEC6 net atomic charges analysis of the topmost layer of Al (111) surface, presented in Figure 4 (a), reveals several significant findings. Firstly, the topmost layer of Al (111) exhibits negative net atomic charges. Specifically, each aluminum atom in the topmost layer carries an average net atomic charge of approximately -0.040. This indicates an excess of electrons in this layer.

Furthermore, the analysis of bond orders between the Al atoms within this surface indicates values ranging from 0.25 to 0.30. These bond orders signify a moderate degree of bonding between the aluminum atoms in the topmost layer. Additionally, the sum of bond orders for each atom in this layer falls within the range of 3 to 3.1, indicating a reasonable level of stability in the bonding interactions. These findings provide valuable insights into the electronic characteristics and bonding behavior of the topmost layer of Al (111) surface. The negative net atomic charges and the bond order values contribute to our



understanding of the surface's reactivity and its potential interactions with other atoms or molecules.

### Analysis of Electronic Structure of Interstitial and Substitutional Ti Atom On Al (111) Surface

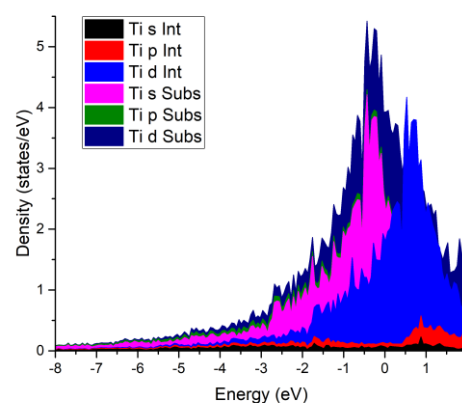
The results indicate that the most stable adsorption position of Ti on the Al (111) surface is observed at the hollow site between Al-Ti bond atoms. The Ti atom is located at a distance of approximately 2.9-3.0 Å from the nearest Al atom. In the substitutional mechanism model, one Al atom is replaced by a Ti atom, resulting in Al-Ti bond lengths of 2.82 and 2.84 Å after energy minimization.

The work function values of the Al (111)-Ti Int and Al-Ti subs systems are determined to be 3.87 eV and 4.02 eV, respectively. These values are slightly smaller or equal to the work function of the clean Al (111) surface.

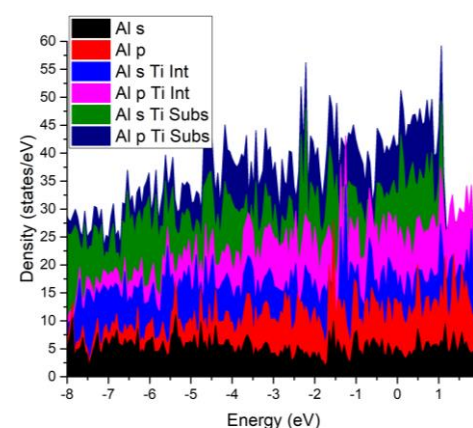
The introduction of titanium atoms through both interstitial and substitutional mechanisms leads to a reconstruction of the surface morphology, thereby impacting the electronic properties of the surface as a whole. To analyze the effect of the titanium atom on the surface, the projected density of states (pDOS) of the surface was calculated. Figure 5 illustrates the comparison of the pDOS for both interstitial and substitutional Ti atoms and their interaction with the neighboring Al atoms.

The introduction of interstitial and substitutional titanium atoms in the Al (111) surface leads to changes in the projected density of states (PDOS) for the Al-s and -p orbitals compared to the clean Al (111) surface. The density near the Fermi level is observed to be higher than that of the clean surface. Additionally, energy shifts are observed, with the substitutional mechanism resulting in a shift to lower energy levels and the interstitial mechanism leading to a shift to higher energy levels.

In the case of the substitutional mechanism, the Ti-s, -p, and -d orbitals exhibit higher density above the Fermi level compared to the interstitial mechanism. This indicates a larger fraction of empty states, allowing the surface to readily accept electrons and form hybridized molecular orbitals with other atoms.



(a)



(b)

Figure 5 (a) pDOS of Ti atom on Interstitial and Substitutional mechanism (b) pDOS of Al atom in clean Al (111) surface, Al (111)-Ti Int Surface and Al (111)-Ti Subs surface.

The DDEC6 analysis reveals notable changes in the net atomic charge distribution and bonding characteristics of the Al (111)-Ti surfaces, as illustrated in Figure 6. The color representation in Figure 6 (a) indicates that the yellow regions correspond to net atomic charges ranging from -0.03 to -0.045, the orange regions represent charges between -0.11 and -0.18, while the blue color represents the Ti atom with a charge of 0.4. It is worth noting that some Al atoms in the vicinity of the Ti atom exhibit positive net atomic charges, suggesting electron loss as they form bonds with the Ti atom.

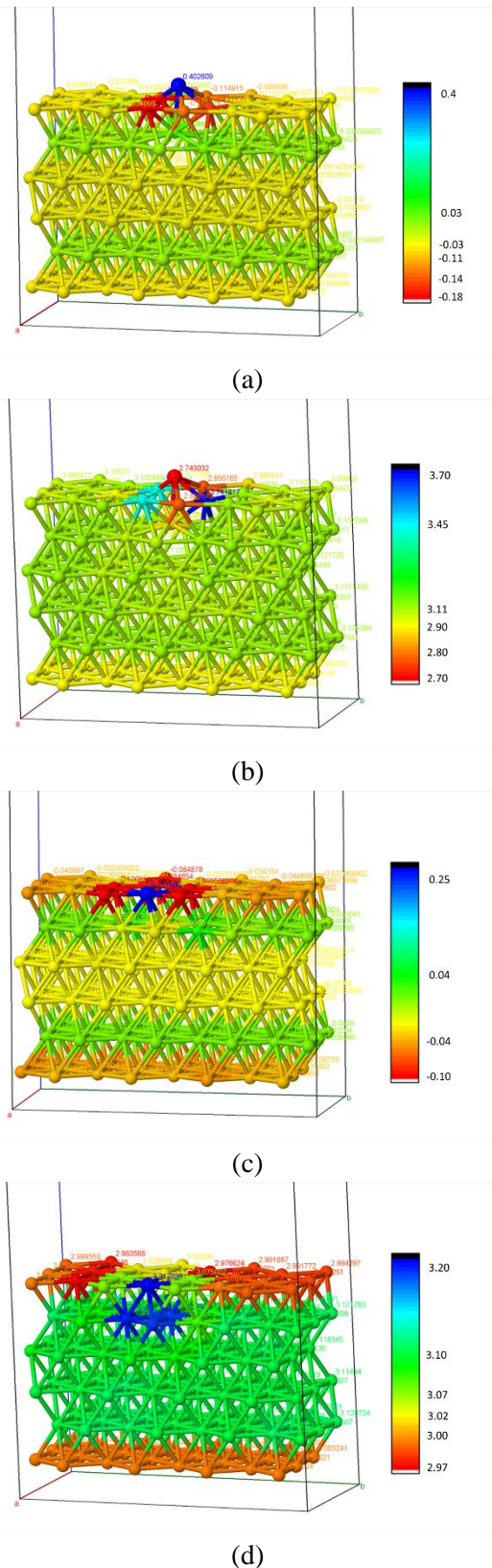


Figure 6 Net atomic charge and sum of bond orders distribution of (a) and (b) Al (111)-Ti Int surface (c) and (d) Al (111)-Ti subs surface

These alterations in net atomic charge are a result of surface reconstruction and atomic rearrangement caused by the introduction of Ti atoms. Notably, the region surrounding the Ti atom, as depicted in Figure V.14c, exhibits a more negative net atomic charge. These observations from the PDOS and DDEC6 results indicate that the substitutional mechanism is more likely to facilitate stronger interactions with the adsorbate.

The presence of interstitial and substitutional Ti atoms induces changes in the charge distribution of the aluminum surface. This redistribution of electronic charge density, stemming from the incorporation of interstitial and substitutional titanium atoms, leads to a shift of charge from aluminum lattice atoms to the interstitial or substitutional sites. Consequently, these charge density redistributions can influence the surface's electrical conductivity and electronic behavior. Moreover, the presence of interstitial and substitutional Ti atoms on the aluminum surface can impact its chemical reactivity, altering its ability to interact with other substances or undergo chemical reactions. These changes in chemical reactivity can be attributed to the interactions between the interstitial and substitutional Ti atoms and the surrounding aluminum lattice. Additionally, the incorporation of interstitial and substitutional Ti atoms may influence the adhesion properties of the material, potentially weakening the chemical bonds between the aluminum surface and other materials and resulting in reduced adhesive properties. Overall, the addition of interstitial and substitutional Ti atoms on the aluminum surface can significantly impact its electronic properties and chemical reactivity.

## CONCLUSION

The findings of this study yield several important conclusions. Firstly, the investigation of different surface facets revealed that the Al (111) orientation exhibits a lower surface energy, indicating its enhanced stability and ease of formation compared to other orientations. Consequently, the Al (111) surface was selected for further analysis in this study.

The calculated work function of the Al (111) surface, at 4.02 eV, aligns with previous calculations and experimental values. This work function value reflects the energy required to remove an electron

from the surface, suggesting improved electron emission characteristics.

Analysis of the electronic structures of both Aluminum bulk and the (111) surface revealed distinctive features. The surface atoms exhibited narrower bandwidths and higher density of states (DOS) around the Fermi level in comparison to the bulk atoms. This discrepancy indicates surface-induced electronic effects and signifies a deviation in electronic properties between the surface and bulk regions.

The adsorption behavior of titanium (Ti) on the Al (111) surface was examined using interstitial and substitutional mechanisms. The most stable adsorption position was determined to be the hollow site between Al-Ti bond atoms. Both interstitial and substitutional Ti incorporation models were considered, and their resulting Al (111)-Ti Int and Al (111)-Ti Subs surfaces exhibited work functions of 3.87 eV and 4.02 eV, respectively. Notably, these values were lower than the work function of the clean Al (111) surface.

The introduction of Ti atoms through interstitial and substitutional mechanisms induced changes in the projected density of states (PDOS) for Al-s and -p orbitals. The density near the Fermi level increased in comparison to the clean surface, indicating modified electronic properties. Particularly, the substitutional mechanism demonstrated higher density above the Fermi level for Ti orbitals, suggesting a stronger interaction with the adsorbate.

The incorporation of interstitial and substitutional Ti atoms resulted in a redistribution of electronic charge density, leading to alterations in net atomic charges and bond orders. The substitutional Ti atoms exhibited a more pronounced interaction with the surface and induced a more negative charge distribution in the surrounding region.

In summary, the presence of interstitial and substitutional Ti atoms on the Al (111) surface had notable effects on its electronic properties, charge distribution, and bonding behavior. These changes can impact the material's electrical conductivity, chemical reactivity, and adhesion properties, presenting implications for a variety of applications.

#### ACKNOWLEDGMENT

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