Surface Properties of Titanium dioxide and its Structural Modifications by Reactions with Transition Metals

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Surface Properties of Titanium dioxide and its Structural Modifications
by Reactions with Transition Metals

by

Sandamali Halpegamage

A dissertation submitted in partial fulfillment of the requirements for the degree of
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Date of Approval:
November 9, 2016

Keywords: Gas sensing, Photocatalysis, Monolayer mixed oxides, Surfaces and interfaces

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DEDICATION

To the memory of my mother, to my father,

to my husband,

and to my advisor.
ACKNOWLEDGMENTS

As getting closer to the goal of my ‘grad-student’ life, dozens of individuals come to my mind who should be sincerely acknowledged. First and foremost, I thank my advisor Prof. Matthias Batzill for giving me the wonderful opportunity to work in his competitive research group. I thank him for providing me with a research assistantship and for sharing his wisdom in the field over the past few years. I thank him for his long hours of discussing the research topics, improving my writing in the manuscripts and also for giving me the freedom to move on with completing the dissertation when the time was right for graduation. His clear guidance, continuous encouragement and appreciation built up my confidence along the way. The things that I learnt from him were not limited to the research topics; but I also learnt how to keep up the professionalism and how to be considerate and responsible while engaging in research activities with people came from many different countries in the world. Most of all, I admire him for having such a remarkable patience and for forgiving me for my reckless actions which caused sometimes explosions of furnaces and reactors, backstreaming of oil into the chambers and pumping systems and many more mistakes during the time that I was learning to use the equipment in the lab with no prior experience. I truly had the most fulfilling learning experience in his lab and it will keep me moving on to the next step in my career with strong confidence.

Besides my advisor, I would like to extend my gratitude to Prof. Sarath Witanachchi, Prof. Srikanth Hariharan, Prof. Garrett Matthews, Prof. Humberto Gutierrez and Prof. Stephen Saddow for
willingly accepting to be in my graduate committee. Their insightful comments are greatly appreciated. Prof. Sarath Witanachchi, in particular, was the one who granted me the admission to USF opening up the door for all the wonderful opportunities that I came across in USF and I am eternally grateful for him for that.

I am sincerely thankful to Prof. Silvano Lizzit, Dr. Luca Bignardi and Dr. Paolo Lacovig for the late nights they spent helping me with the experiments during my time in SuperESCA beamline in Trieste, Italy. Furthermore, I thank Dr. Xueqing Gong and his group in East China University of Science and Technology, for performing the DFT-based computational simulations and giving more insight into my experimental results.

My deepest thanks go to Dr. Junguang Tao, Dr. Rafik Addou, Dr. Arjun Dahal, Dr. Tim Luttrell, the past member of our lab from whom I learnt a lot; and I also appreciate the great support I received from Dr. James Lallo, Dr. Redhouane Chaghi, Dr. Horacio Coy Dias, Alan Kramer, Yujing Ma, and Manuel Bonilla throughout the past years.

I would also like to extend my gratitude towards the excellent professors I met in the University of Mississippi, Prof. Luca Bombelli and Prof. Richard Raspet, and the professors in the physics department of the University of Peradeniya-Sri Lanka, Dr. Nimal Hettiarachchi, Dr. Upali Karunasiri, Prof. B.S.B. Karunarathne, Dr. Varuni Senewiratne, Dr. V. Sivakumar and Dr. Kalinga Bandara, who taught me and helped me providing with the recommendations. Although not directly supported in the process of higher education, at this moment I would like to mention and thank all the nice teachers I met in Kandy-Girls’ high school and in Nawalapitiya-Junior Girls’ college in Sri Lanka for contributing to my intellectual growth.
I want to thank everyone in the staff of the physics department, specially, Jimmy Suarez, Daisy Matos and Mary Wengyn for taking care of all the bothersome paperwork and things throughout the process.

All the support I received from my Sri Lankan friends scattered all over the world is also unforgettable. I cherish their friendship and thank them all for the fun times we shared. I specially appreciate the unconditional support I received from Chatura, Mahesh and Malinda in difficult times and their true friendship.

Last but not least, I dearly thank my family; my mother and father, in particular, for not just being parents who nourished me but for being my first teachers who laid the foundation for my education, teaching me mathematics, physics, writing essays and all kinds of subjects, through which I was inspired to explore the most interesting aspects of education. My sisters, brother and relatives who have contributed to my success and happiness in many ways should also be greatly acknowledged. Finally, I thank my husband who continued to walk behind me ever since we met; being supportive, loving and caring regardless of how annoying and stubborn I was at times…
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ABSTRACT

Surfaces of metal oxides play a vital role in many technologically important applications. The surfaces of titanium dioxide, in particular, show quite promising properties that can be utilized in solid-state gas sensing and photocatalysis applications. In the first part of this dissertation we investigate these properties of TiO$_2$ surfaces through a vigorous surface scientific approach. In the second part, we investigate the possibilities of modifying the TiO$_2$ surfaces by depositing multi-component transition metal oxide monolayers so that the properties of bare TiO$_2$ surface can be influenced in a beneficial way. For instance, via formation of new surface sites or cations that have different valance states, the chemisorption and catalytic properties can be modified. We use sophisticated experimental surface science techniques that are compatible with ultra-high vacuum technology for surface characterization. All the experimental results, except for the photocatalysis experiments, were compared to and verified by supporting DFT-based theoretical results produced by our theory collaborators.

TiO$_2$ based solid-state gas sensors have been used before for detecting trace amounts of explosives such as 2,4-dinitrooluene (DNT), a toxic decomposition product of the explosive 2,4,6-trinitrotoluene (TNT) that have very low vapor pressure. However, the adsorption, desorption and reaction mechanism were not well understood. Here, we investigate 2,4-DNT adsorption on rutile-TiO$_2$(110) surface in order to gain insight about these mechanisms in an atomistic level and we propose an efficient way of desorbing DNT from the surface through UV-light induced photoreactions.
TiO$_2$ exists in different polymorphs and the photocatalytic activity differs from one polymorph to another. Rutile and anatase are the most famous forms of TiO$_2$ in photocatalysis and anatase is known to show higher activity than rutile. The photoactivity also varies depending on the surface orientation for the same polymorph. So far, a reasonable explanation as to why these differences exist was not reported. In our studies, we used high quality epitaxial rutile and anatase thin films which enabled isolating the surface effects from the bulk effects and show that it is the difference between the charge carrier diffusion lengths that causes this difference in activities. In addition to that, using different surface orientations of rutile-TiO$_2$, we show that the anisotropic bulk charge carrier mobility may contribute to the orientation dependent photoactivity. Moreover, we show that different surface preparation methods also affect the activity of the sample and vacuum reduction results in an enhanced activity.

In an effort to modify the TiO$_2$ surfaces with monolayer/mixed monolayer oxides, we carried out experiments on (011) orientation of single crystal rutile TiO$_2$ with few of the selected transition metal oxides namely Fe, V, Cr and Ni. We found that for specific oxidation conditions a monolayer mixed oxide is formed for all M (M= Fe, V, Cr, Ni), with one common structure with the composition MTi$_2$O$_5$. For small amounts of M the surface segregates into pure TiO$_2$(011)-2×1 and into domains of MTi$_2$O$_5$ indicating that this mixed monolayer oxide is a low energy line phase in a compositional surface phase diagram. The oxygen pressure required for the formation of this unique monolayer structure increases in the order of V<Cr<Fe<Ni in correlation with the enthalpy of formation of oxide for these transition metals. The structure proposed for the stable MTi$_2$O$_5$ mixed monolayer oxide by DFT-based simulations was verified by X-ray photoemission diffraction measurements performed at a synchrotron facility.
CHAPTER 01
INTRODUCTION

Metal oxides are at the heart of technological applications. They cover many aspects of materials science and physics. Among them are insulators (e.g. Al₂O₃, MgO), semiconductors (e.g. TiO₂, Ti₂O₃), metals (e.g. V₂O₃, ReO₃), superconductors (e.g. SrTiO₃), ferroelectrics (e.g. BaTiO₃), antiferroelectrics (e.g. WO₃), ferromagnetics (e.g. CrO₂), antiferromagnetics (e.g. NiO), diamagnetics (e.g. MoO₂) as well as paramagnetics (e.g. RuO₂)[1]. Most of these consist of mixed ionic and covalent bonding[2]. Owing to these fascinating electronic, magnetic, chemical and physical properties, metal oxides extend over a wide range of applications such as heterogeneous catalysis, photocatalysis, solid state gas sensing, fuel cells, paint pigments, non-linear optics, high temperature coatings, medical implants, microelectronics, photovoltaic devices etc.[3].

Almost all metals are oxidized in ambient conditions. The thickness of the oxide layer varies depending on the temperature, oxygen pressure and the time of oxidation. The crystal structures for metal oxides can be quite complex and primarily be found in five forms[1] (see Figure 1.1).

Figure 1.1: Common crystal structures found in metal oxides.
These are: (i) Rocksalt; an fcc lattice with MO composition (M=metal cation; e.g. NiO, MgO, CaO, CoO); (ii) Perovskite; a cubic lattice with ABO$_3$ composition (A,B= metal cations; e.g. SrTiO$_3$, BaTiO$_3$); (iii) Rutile; a tetragonal lattice with MO$_2$ composition (M=metal cation; e.g. TiO$_2$, SnO$_2$, RuO$_2$); (iv) Corundum; a tetragonal lattice with M$_2$O$_3$ composition (M=metal cation; e.g. Al$_2$O$_3$, Cr$_2$O$_3$, V$_2$O$_3$, Ti$_2$O$_3$, α-Fe$_2$O$_3$); close to this is ilmenite which has ABO$_3$ composition; (v) Wurtzite; an hcp stacking of O atoms with metal ions located in tetrahedral interstices (e.g. ZnO).

While the bulk electronic and structural properties are already intensively studied and well understood, studies on oxide surfaces are lacking. At the surface of a crystal, the 3D periodicity of the bulk is broken. The atoms in the top surface layers undergo relaxations, reconstructions and charge redistributions in order to minimize the surface free energy and attain stability. Therefore, the electronic structure and the atomic geometry of the surfaces can be quite different from those in the bulk. These modifications on the surface may lead to formation of new reactive sites and electronic states that exhibit unique chemical functional properties. Metal oxide surfaces and their interfaces are, after all, of key interest in the oxide-based technological device performance. Therefore, both experimental and theoretical surface science studies have been motivated by the desire to gain a deeper understanding of the fundamental electronic, chemical, structural and physical properties of oxide surfaces and their interfaces. In fact, this is where Ultra High Vacuum (UHV) technology and experimental surface science techniques come to play. In understanding the fundamentals, relatively simple well-defined samples are needed. Therefore, while chemists and engineers have done majority of their work on high area powder samples, physicists are drawn to single crystalline samples. Stoichiometric single crystal samples not only simplify the
complexity of real systems but also allow atomistic level investigations to be carried out in a controlled and systematic manner.

The scope of this thesis is centered on surface, interface and chemical properties of titanium dioxide and its role in metal/metal oxide growth. TiO$_2$ is a prototypical transition metal oxide material, which serves as a model system for oxide surface science studies. Therefore, following review focuses on understanding the fundamental structural, electronic and chemical properties of TiO$_2$ and its applications.

### 1.1 Literature Review

TiO$_2$ is one of the first studied and most attractive metal oxides for decades in the field of materials science. It is abundant, inexpensive, nontoxic, environmental friendly and chemically stable; the properties that have contributed to its popularity and technological importance. Ti minerals are mainly found in the form of rutile-TiO$_2$, ilmenite-FeTiO$_3$ and CaTiSiO$_5$[4]. Pure TiO$_2$ is white and odorless. Naturally grown TiO$_2$ contains trace impurities such as Fe, Nb, Ta, Ca, Mg etc.[3, 4] which give rise to the color in the mineral samples (see Figure 1.2). The equilibrium crystal shape of these minerals is determined by the surface free energy in different crystallographic directions. Theoretically this shape can be obtained using the Wulff construction.

A lot of effort has been devoted to exploration of the properties of TiO$_2$ and its applications over the past few decades and the following discussion considers the bulk and surface structures, surface stabilities, relaxations and reconstructions, surface chemical and electronic properties, defects and the applications reported to date.
Figure 1.2: Pure TiO\textsubscript{2} powder and naturally grown TiO\textsubscript{2}. (a) Pure Titanium dioxide. (b) Naturally grown mineral samples of rutile, anatase and brookite phases of titanium dioxide. The color arises due to the impurities and the crystal shape is determined by the Wulff construction.

1.1.1 TiO\textsubscript{2} Bulk and Surface Structures, Stabilities, Reconstructions and Relaxations, Defects, Chemical and Electronic Properties

TiO\textsubscript{2} crystallizes mainly in rutile (tetragonal, a=b=4.584 Å, c=2.953 Å), anatase (tetragonal, a=b=3.782 Å, c=9.502 Å) and brookite (rhombohedrical, a=5.436 Å, b=9.166 Å, c=5.135 Å) phases\cite{3}. Figure 1.3 shows the bulk structures of these three phases of TiO\textsubscript{2}. The basic building unit for all the structures is a slightly distorted octahedral. Rutile is the most stable phase while anatase and brookite phases are metastable and convert into rutile upon annealing to high temperatures (around 700 °C- 800 °C). Although less well-known, TiO\textsubscript{2}-(B); i.e the bronze phase of TiO\textsubscript{2} (monoclinic), is becoming popular in Li-ion batteries and in gas sensing applications \cite{5-7}. Baddeleyite-like (monoclinic) and α-PbO\textsubscript{2}-like (orthorhombic) are two of the recently found high pressure phases of TiO\textsubscript{2}. However, for the most part, only rutile and anatase phases are found to be of technological importance and the single-crystalline rutile TiO\textsubscript{2}, in particular, has been the most investigated surface by experimental surface scientists since it is well-suited for many experimental surface science techniques. Some of the important aspects of surfaces such as stability, relaxations, reconstructions and defects are, therefore, discussed below using the well-understood rutile TiO\textsubscript{2} (110) and (011) surfaces.
Figure 1.3: Ball and stick models of three main TiO$_2$ phases. TiO$_2$ Rutile (a), Anatase (b) and Brookite (c) phases. The basic building unit for all these structures is a slightly distorted octahedral. Shown in bottom left corner is corner sharing octahedral units in rutile TiO$_2$ unit cell.

The stability of an ionic surface, in general, is based on electrostatic considerations[3]. For semiconducting metal oxide surfaces, on the other hand, stability can be achieved via autocompensation; which means that on stable surfaces, the excess charge from cation-derived dangling bonds compensate anion-derived dangling bonds so that the net result in anion-cation-derived dangling bonds is empty or full. This causes a partial covalent character in metal oxides including TiO$_2$. The surfaces of non-polar structures are generally considered as the most stable ones[3, 8]. This can be explained using the lowest energy surface orientation of rutile TiO$_2$(110)-1x1 structure shown in Figure 1.4. As can be seen, the main surface layer has the same number of Ti and O atoms. Ti and O have 4+ and 2- charge states respectively; so the net charge is negative. This layer is sandwiched between two O layers each of which has a net negative charge. Therefore, the total unit does not have a dipole moment and thus results in a stable non-polar surface.
Relaxations and reconstructions are, as mentioned earlier, the mechanisms through which the atoms on surfaces rearrange to reduce the surface free energy in attaining a stable atomic configuration. Even the most stable Rutile TiO$_2$ (110) surface undergoes relaxations and reconstructions in certain UHV conditions\cite{3}. As shown in Figure 1.4, the main surface layer consists of 5 fold coordinated Ti, 3 fold coordinated O and 6 fold coordinated Ti atoms in [001] direction. On top of this layer is 2 fold coordinated O atoms, which are also called the bridging oxygen atoms. Upon relaxation, the in plane O atoms move laterally towards 5 fold Ti atoms while the bridging O atoms and 6 fold Ti atoms move downward and upward respectively leaving the symmetry and the size of the unit cell unchanged. The second layer of this structure also relaxes in the same way but in smaller amounts compared to the first layer relaxations.

TiO$_2$ (011) (equivalent to (101)) is the second most stable orientation of Rutile TiO$_2$ and is well-known for its 2×1 surface reconstruction\cite{9-12}. Figure 1.5 shows the unreconstructed and reconstructed TiO$_2$ (011) surface structures reported in the past. Three of the models proposed for 2×1 reconstruction are titanyl model, microfaceted model and brookite-(001) like model\cite{9}. In titanyl model, upon reconstruction the center TiO$_2$ units have been removed creating deep groves.

**Figure 1.4:** Ball and stick model of rutile TiO$_2$ (110)-1×1 surface. Red balls are O atoms and light blue balls are Ti atoms. Oxygen vacancies are created by removing bridging oxygen atoms on the surface layer.
with oxygen atoms in the sides. This results in Ti=O bonds and thus called titanyl model. Challenging to this, microfaceted-missing row-like model has been proposed later on. Brookite(001)-like model that has even lower energy and good match with the experimental results is the most accepted model to date (see Figure 1.5b). It is also important to point out that the adsorbates on these surfaces can cause re-relaxing and restructuring. For instance, Cu overlayers in TiO$_2$(110) cause Ti atoms at the interface relax back to their original positions [3] while metal oxide overlayers deposited on TiO$_2$(011) cause restructuring of its 2×1 reconstruction [13].

![Figure 1.5: Ball and stick models rutile TiO$_2$(011). (a) Unreconstructed TiO$_2$(011) (bulk terminated-1×1) surface, (b) TiO$_2$(011)-2×1 reconstructed surface for brookite(001) like. Red balls are O atoms and blue balls are Ti atoms.](image)

Commercial Rutile-TiO$_2$ single crystal samples are slightly yellowish and transparent. Before performing surface science experiments in UHV, the surface of the crystal should be cleaned by in-situ by ion sputtering and annealing (this will be further discussed in Chapter 2). After few cycles of sputtering and annealing the crystal becomes dark bluish and opaque. A scanning tunneling microscopy (STM) image of such prepared rutile TiO$_2$(110)-1×1 surface is shown in Figure 1.6. According to the ball and stick model in Figure 1.4, the oxygen atoms protrude above the main surface layer. But in the STM images shown, the Ti atoms appear bright while O atoms appear dark. This contrast is a consequence of STM probing the electronic structure effects of surfaces rather than topographical effects. As can be seen, this surface has wide flat terraces. The
size of the terraces can be varied by annealing at different temperatures. The cleaning procedure also causes removal of oxygen atoms (reduction) and formation of defects on the surface. Defects can exist in the form of point defects (0D-adatoms, vacancies) or line defects (1D-step edges, domain boundaries) and play a predominant role in surface chemical reactions as well as in adsorption and diffusion processes[3]. Ability to control the amount of these defects is one of the advantages in TiO$_2$ single crystal surfaces. The dominant defects in reduced TiO$_2$ are O$^{2-}$ vacancies, Ti$^{3+}$ and Ti$^{4+}$ interstitials. Oxygen vacancy defects migrate via site exchange (vacancy diffusion) mechanism while Ti interstitials migrate as atoms. Atom migration may be faster through open channels in the bulk crystal[3]. Since reduced TiO$_2$ is rich in oxygen vacancies it becomes strongly n-type doped and the conduction band minimum lies very close to the Fermi level in the 3 eV band gap. Therefore the reduced TiO$_2$ surfaces are conductive enough for many experimental surface science techniques where conductive surfaces are essential for avoiding charging effects. The point defects created due to oxygen vacancies in a clean rutile TiO$_2$(110) surface can appear as bright spots as shown in Figure 1.6. Some reports claim that these bright spots are due to H adsorption on the surface. It has been observed that these can be healed by annealing the sample in an oxygen atmosphere. Nevertheless, it has also been shown that the oxygen vacancies can react with residual water, even in UHV conditions, and form hydroxyls, which also appear as bright protrusions in STM images of TiO$_2$. These hydroxyls can react with oxygen and be removed; thus the oxygen treatment is not proving that these bright protrusions are exactly O-vacancies. On the other hand, line defects may appear as stands distributed across terraces on strongly reduced surfaces that sometimes have Ti$_2$O$_3$ composition. Although commercial TiO$_2$ is generally clean it is hard to completely clean off the bulk impurities such as
Fe, Ca, Mg, Al etc. and they can segregate to the surface while annealing. This impurity segregation can also sometimes appear as line defects on the surface.

![Clean TiO$_2$(110) surface](image)

**Figure 1.6:** Scanning tunneling microscopy images of clean rutile TiO$_2$(110)-1×1. Formation of terraces, point defects and line defects are indicated.

TiO$_2$(001) and (100) orientations are less studied compared to (110) and (011) surfaces. However these surfaces play a significant role in orientation dependent photocatalysis studies.

Anatase, the next most attractive phase of TiO$_2$ is the main ingredient (~80-90%) in Degussa-P25 TiO$_2$ powder. (101) is the thermodynamically most stable surface orientation of anatase. According to the past research, anatase phase has been reported as photocatalytically more active than the rutile phase[14]. Atomic scale studies on anatase surfaces are comparably less because of the difficulty in preparing large enough pure anatase single crystals. However, growing well-defined, flat epitaxial single crystalline anatase films is quite well-established by now and a lot of research has been emerged on those films. For instance, (001) orientation of anatase thin films has
been successfully grown on LaAlO$_3$(100) or SrTiO$_3$(001) single crystalline substrates[15] and it exhibits a 4×1 reconstruction as observed in reflection high energy electron diffraction (RHEED) measurements.

TiO$_2$ powder samples rich in Brookite phase of TiO$_2$ is reported to be highly active in photocatalysis[16, 17]. However growth of single crystalline pure Brookite films is not reported to date due to its thermal instability and challenges in finding a suitable substrate with a good lattice match and thus atomic scale investigations of Brookite surfaces do not exist.

In determining electronic structures of TiO$_2$ surfaces, photoemission spectroscopy techniques become handy. A wide variety of theoretical approaches have also been proposed for calculating the electronic structure of TiO$_2$. It is reported that the electronic structure of bulk stoichiometric TiO$_2$ is not too different form that of the surface[3]. The occupied states of the valance band are composed of O 2p while the conduction band is Ti 3d derived. Stoichiometric TiO$_2$ surfaces do not show additional surface states. However, reduced TiO$_2$ exhibits defect states in the band gap region. Reduction of TiO$_2$, i.e. removal of neutral oxygen atoms from the surface, leaves electrons behind that are previously occupied those O 2p states. These electrons move into the conduction band which is composed of Ti 3d states and become unpaired electrons in Ti atoms. Therefore these defect states exhibit Ti3d derived nature. In X-ray photoemission spectroscopy (XPS) the reduced TiO$_2$ shows a shoulder feature which is assigned to Ti$^{3+}$ or lower oxidation states of Ti. Another interesting aspect of TiO$_2$ is interface ‘band bending’. As mentioned earlier the reduced TiO$_2$ acts as an n-doped semiconductor. The electrons left behind become donor-like states and donate electrons to the system. This results in an accumulation layer in the near surface region and downward band bending effect as explained as explained in Figure 1.7.
11.1.2 TiO$_2$ Applications

Due to its outstanding properties, TiO$_2$ spans over a wide variety of applications. A few of the most promising applications are solid state gas sensing, catalysis (photocatalysis and heterogeneous catalysis), as a support for metal/metal oxide growth, as a white pigment, as a self-cleaning material, electrical devices, as gate insulators in SiO$_2$ MOSFET devices[3]. It is also used in the field of biomaterials as a bone implant. Having a high refractive index, TiO$_2$ can strongly absorb UV light and combined with the fact that it is non-toxic and safe, has made it the major ingredient in most of the sunscreen products. This UV resistant property of TiO$_2$ is also used in plastics and other applications. Pure TiO$_2$ is used as a food additive as well as in pharmaceuticals. As emphasized earlier, the performance of devices is largely dependent upon the properties of the surface of the oxide rather than the bulk. This thesis is, therefore, concentrated on applications based on two major aspects of TiO$_2$ surfaces. That is; (i) TiO$_2$ in sensors and catalysis, which are directly connected with the surface chemical and structural properties of TiO$_2$; (ii) metals/ metal oxide growth on TiO$_2$ which of course is the foundation in designing new hetero-structures and interfaces that can be better in sensing and catalysis. Therefore, presented next is a discussion of
the reported work on relevant applications along with fundamental theoretical concepts behind them.

1.1.2.1 TiO$_2$ in Sensing and Catalysis

Adsorption, desorption and reaction of inorganic and organic molecules on TiO$_2$ surface[18] is extensively studied in the field and comprehensive reviews exist [3, 19]. Understanding the fundamentals of these processes provide the basis in designing gas sensors with enhanced performance. (Photo-)catalysis of TiO$_2$, on the other hand, is a broad research topic[20-23] and the most important application of TiO$_2$. Thus, this section has been split into two sub sections: (i) Gas sensing (ii) (Photo-)catalysis and discussed below in detail.

**Gas Sensing:** A good gas sensing material should have; (i) High sensitivity, (ii) Good stability, (iii) Good selectivity, (iv) Fast response and recovery. In addition to these, they should be durable, inexpensive and should be less sensitive to air humidity. Metal oxide gas sensors have advantages of being low in cost and high in sensitivity. However, achieving selectivity and fast response recovery is still under investigation. TiO$_2$ is a wide band gap semiconductor. Semiconducting materials change their conductivity due to adsorption or reaction with the surrounding gas phase molecules. Upon absorption or reaction, charge transfer can occur from or into the surface oxide causing a Fermi level shift within its band gap thereby inducing a band bending effect at the surface. This appears as a change in the electrical conductivity of the oxide material and thus can be used as a gas response signal. It is clear that these reactions and modifications occur at the surface and the interface of the gas sensing material. Therefore, in order to understand the fundamentals of the sensing mechanism, a surface scientific approach is needed. The critical
questions to be answered here are: (i) How do the surface properties of the sensing material (e.g. atomic configurations and crystal orientations) affect the gas sensitivity?, (ii) What are the absorption or reaction sites on the surface?, (iii) What is the detection mechanism and how does the electronic response change at the interface of the absorbed gas/molecules and the metal oxide surface?, (iv) How can the sensitivity and/or the selectivity be enhanced via tuning the surface properties? [24]

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\text{TiO}_2(110) \text{ being the most stable and well-understood surface orientation of Rutile provides an ideal starting point for studying the adsorption and desorption behavior of molecules and thus much of the reported work has been done on this surface. Carboxylic acid (R-COOH) adsorption on Rutile TiO}_2(110) \text{ is one such well-documented system[3]. As discussed above, Rutile TiO}_2(110) \text{ consists of alternating rows of 5 fold coordinated Ti}^{4+} \text{ atoms and 2 fold coordinated O}_2^- \text{ atoms. Thus it exposes both anionic and cationic adsorption sites. The atoms along the rows are separated by } \sim 3 \text{ Å and the rows are separated by } \sim 6.5 \text{ Å. The bond distances in organic molecules is also } \sim 3 \text{ Å. Therefore TiO}_2(110) \text{ surface offer suitable reactive sites for carboxylic to adsorb dissociatively; i.e. by splitting off acetic H and forming chemical bonds between carboxylic oxygen and Ti atom on the surface. This results in acetic acid adsorption on two neighboring 5 fold Ti atoms in a bridge-bidentate fashion. This absorption configuration is better explained in Figure 1.8, which shows the formic acid (CH}_2\text{O}_2^- \text{ absorption on Rutile TiO}_2(110) \text{ surface. Similar adsorption configuration has been reported for catechol[25]. For small carboxylate molecules such as formate or acetate, the surface was observed to be fully covered with a 2×1 superstructure.}
Figure 1.8: Formic acid adsorption on rutile TiO$_2$(110) surface. After dissociation of hydrogen at the surface, formate binds to neighbouring 5 fold Ti atoms in a bidentate fashion.

Generally, SnO$_2$ and ZnO are the most popular gas sensing metal oxide semiconductors[26] whereas TiO$_2$ has attracted more attention as an oxygen sensor. For instance, in early times, TiO$_2$ was used as an O$_2$ gas sensor to control the air/fuel mixture in car engines[3]. It is reported that Pt addition enhances the sensitivity of TiO$_2$ towards O$_2$. Since Ti is a very reactive element, oxygen deficient TiO$_2$ surfaces readily react with O$_2$. The conductivity of the TiO$_2$ decreases upon annealing in oxygen environment due to reoxidation of the crystal while UHV annealing causes the conductivity to increase due to reduction of the crystal as discussed earlier. Therefore, a change in conductivity should be expected in oxygen rich environments. Moreover, Pd-sensitized TiO$_2$ has been used as a hydrogen sensor and it is argued that the oxygen vacancies act as adsorption sites for hydrogen[27]. Another well-known observation is TiO$_2$ reduction upon annealing in H$_2$ environment causing an increase in the conductivity. It also shows good sensing properties towards CO, ethanol, methanol etc. One of the disadvantages in TiO$_2$-based gas sensors is their inability to distinguish between gases; in other words the selectivity of TiO$_2$ gas sensors is poor. Attempts have been made to improve this selectivity; for e.g. via introducing dopants. Nano sensors obtained
from TiO$_2$:Cr nano powders have been reported to show promising dynamic response characteristics towards hydrogen. It is reported that the sensitivity of TiO$_2$ towards various gases can also depend on the surface orientation; one example being that the Rutile TiO$_2$ (001) oriented films show the highest selectivity towards H$_2$ against CO. Studies on Anatase phase of TiO$_2$ have also been performed on mineral samples or on epitaxial thin films grown on STO or LAO substrates[28]. Anatase thin films deposited by pulsed DC magnetron reactive sputtering method on glass, sapphire(0001) and Si(100) substrates have successfully been used as CO sensors and a large decrease in the resistance has been measured for film thickness of ~100 nm at elevated temperatures (~ 300 C) for CO concentrations of 20-100 ppm(parts per million). The decrease in the resistance has been attributed to CO interaction with the surface oxygen or with the Ti-O in the bulk. More importantly, the films have been completely regenerated just by turning off CO without exposing to oxygen or air and the response/recovery time is reported to be 1-2 minutes. It has been discovered recently that the TiO$_2$-(B) nanowires synthesized with a hydrothermal method act as a chemiresistive sensor and exhibit large and reversible change in the conductivity upon exposure to traces of nitroaromatic and nitroamine explosive vapors along with a high sensitivity and a fast response time[29]. Nitroaromatic and nitroamine explosive compounds not only own high electronegativity due to strong oxidizing chemical groups but also have strong tendency to adsorb on the surfaces of objects exposed to their vapor. TiO$_2$-(B) nanostructures, on the other hand, owning a high surface-to-volume ratio as well as a large surface area for the molecules to adsorb, facilitate the surface charge transfer interaction with the molecules. In fact, TiO$_2$-(B) nanowires have higher charge transfer ability than anatase TiO$_2$ because of their less compact structure and higher levels of oxygen vacancies that come from Ti$^{4+}$ ions. These Ti$^{4+}$ ions, which can be coordinated by hydroxyl groups create a hydroxyl terminated surface which traps electrons
and facilitates adsorption of nitro groups in the above mentioned explosive compounds. This in turn results in an increase in resistance upon exposure to vapors of explosives and decrease in resistance while returning to fresh air. Importantly, TiO$_2$-(B) offers a good stability which is also a must requirement for being an efficient gas sensor.

**Photocatalysis:** For a material to be a photocatalyst, four basic requirements must be fulfilled[30]; (i) Absorption of photons with energy larger than the band gap and create bound electron-hole pairs(i.e. excitons), (ii) Separation of these electrons and holes in the space-charge region, (iii) Diffusion of the charge carriers to the surface without getting recombined or trapped at the defect states, (iv) Resulting in charge carries possessing sufficient oxidation (holes/ h+) and reduction (electrons/e-) potentials in order to perform redox reactions at the surface. Hence, an efficient photocatalyst must be able to maximize the potential charge carrier generation and transfer into the adsorbed molecules while minimizing their recombination. A simple schematic representation of the photocatalytic process is shown in Figure 1.9.

Photocatalysis is by far the most discussed application of TiO$_2$. Since Fujishima and Honda first discovered the capability of TiO$_2$ electrodes to produce hydrogen by photolysis of water in early 1970’s[31], it has been an ever growing field of research for the past few decades. TiO$_2$ fulfills many of the above mentioned basic requirements a photocatalyst should have; i.e. when TiO$_2$ surface is irradiated with near-UV light (<~400 nm) electrons get excited from the valance band to the conduction band creating electron- hole pairs. These electron-hole pairs, if not recombined in the bulk, can diffuse to the surface and perform redox reactions. In particular, the holes (h+) produced in the process have strong oxidation power and cause complete destruction of organic pollutants into CO$_2$ and H$_2$O. This makes it a perfect candidate in the applications developed for
air and water purification and people started coating the walls in hospital operating theaters and car parks with TiO₂ in order to keep the environment clean.

Figure 1.9: The basic processes involved in photocatalysis. Upon absorbing photon an exciton is created and the separated. Some charge carriers recombine in the bulk or at the surface. The charges that are successfully reached the surface can participate in reduction and oxidation reactions. Shown in the right is photocatalytic water splitting and hydrogen production on TiO₂.

Degussa-P25 is the most common commercial TiO₂ powder-photocatalyst, which consists of anatase-TiO₂ and rutile-TiO₂ phases. As mentioned before, studies show that anatase-TiO₂ phase, in general, is more active than rutile-TiO₂ phase. The efficiency of photochemical reactions performed by TiO₂ may differ from one polymorph to another due to various reasons; the most common reason is the differences in their band gap energies. The oxidation/reduction potential of the charge carriers, charge carrier life time, charge carrier diffusion and polaron effective mass, surface properties in transferring charges between the adsorbed molecules are the other possible reasons. The surface properties not only vary between different polymorphs but also depend largely on the crystalline orientation for the same polymorph [32-37]. Therefore, efforts have been
made to study the surface orientation dependence of photocatalytic activity of TiO$_2$ and to explain the surface scientific reasoning behind it. A couple of fundamental reasons for the surface-orientation dependence are; (i) directional electron and hole diffusion that arises from band structure and the nature of band bending near the surface, (ii) surface reconstructions that induce band gap states and enable charge transfer and electron trapping due to the modifications in the surface crystal field interactions with the adsorbents[30].

Traditionally, the photocatalytic activity of TiO$_2$ is measured either by observing the rate of decomposition(decoloration) of dye molecules or by observing the rate of Ag (or Pb) deposition on TiO$_2$ dipped in a Ag$^+$ (or Pb$^{2+}$) solution upon irradiation of the surface with UV-light. Studies done using Ag$^+$ deposition on oriented Rutile-TiO$_2$ showed that (101), (111) and (001) have higher Ag deposition rate than (100) and (110). Moreover, according to some recent work, there is little orientation dependence for as-polished crystal samples while the photo-reactivity of ultra-smooth samples exhibit strong orientation dependence. Although the redox reaction is efficient, TiO$_2$ is only able to absorb about 3% of the solar power due to its wide band gap (~3.0-3.2 eV) and its inability to absorb visible light. Therefore, efforts have been made to extend its light absorption range to visible light. Some of the attempts include; TiO$_2$ doping with metal/non-metal impurities, coupling TiO$_2$ with narrow-band gap semiconductors, preparing oxygen deficient TiO$_2$ surfaces and exploring new phases of TiO$_2$ with lower band gap energies. For instance; doping with Fe, N, C, S, F, B, P etc. is reported to help shifting the light absorption threshold of TiO$_2$ to visible light[22]. Vacuum reduction and preparation of oxygen deficient surfaces is a simple and an efficient way of making TiO$_2$ visible light active[38, 39]. It is reported that the Ti$^{3+}$ interstitial sites and oxygen vacancies created through vacuum reduction are the major contributors that make TiO$_2$ sensitive to visible light.
1.1.2.2 Metal/Metal Oxide Growth on TiO$_2$

Metal/metal oxide growth on a second oxide support material is an ever growing area of research. Surface modifications and interface charge redistributions associated with metal/metal oxide heterojunctions sensitively affect the functionality of many devices and applications[40]. One such device is Metal-Oxide-Semiconductor-Field-Effect-Transistor or a MOSFET, where there is a thin dielectric oxide layer sandwiched between a metal electrode and a semiconducting substrate. Since the length scale of these devices are in nanometer regime, the materials and interfaces inside should only be a few atomic layers thick so that a careful surface and interface study in an atomistic-level becomes crucial. Another application where interface properties strongly affect to the functionality is heterogeneous catalysis. The phenomenon of SMSI—i.e. strong metal support interactions was first introduced by Tauster who observed metal catalysts supported on certain reducible oxides suppressing the H$_2$ and CO adsorption[3]. In other reactions, for instance, methane production from CO and H$_2$ has been enhanced by SMSI systems[8]. Therefore, SMSI has attracted great interest in designing new materials with unique functional properties including selective heterogeneous catalysts and nanocatalysts. Growth behaviour of almost all the metals across the periodic table have been tested on TiO$_2$(110) (and in a few cases on TiO$_2$(011)) in the past[41-43]. Discussed below are only the elements that are relevant to the current study and an overview of the growth modes, growth kinetics associated with these systems.

In a simplified approach, growth mode or morphology can be divided into three groups considering that systems are in thermodynamic equilibrium: (i) Cluster growth (Volmer-Weber growth), (ii) Layer-by-layer growth (Frank-van der Merwe growth), (iii) Layer plus cluster growth (Stranski-Krasternov growth). This distinction has been made based on the surface free energy of the
overlayer metal/vacuum interface \((\gamma_{v,m})\) support oxide/vacuum interface \((\gamma_{v,s})\) and the metal/support oxide interface \((\gamma_{m,s})\). Consider the simple expression given in Figure 1.10 below.

\[
\gamma_{m,s} = \gamma_{v,s} - \gamma_{v,m}
\]

**Figure 1.10:** Schematic of a metal film island on a substrate. \(\gamma\) is the surface free energy (or the surface tension).

When the left side of the above equation is greater, cluster growth takes place. When it is less, layer-by-layer growth can be expected. For thicker films, as in epitaxial film growth, when the epitaxial strain increases the overlayer can break up and start forming clusters. However, it is important to point out that, in this simplified explanation, many other important factors that affect the growth behavior have been neglected. Some of these factors are growth kinetics, role of the defects on the surface on nucleation of islands, intermixing of metal atoms at the interface, change in stoichiometry of the substrate upon metal deposition, background pressure and temperature conditions etc. Therefore, all these factors should be taken into account in order to gain an in-depth understanding of the growth behavior of metal/oxide systems.

Physical vapor deposition via molecular beam epitaxy (MBE) is the most common technique employed so far for the metal deposition on oxide supports. The growth mode of the system, as discussed earlier, can primarily depend on the surface/interface free energy. Also, it strongly depends on the reactivity of the metal atoms towards the surface of the substrate. In thermodynamic point of view it is closely related to the heat of formation of oxide of the metal being deposited and the heat of formation of lower oxides of the substrate. Mid or late transition metals, for
instance, have lower affinity for oxygen and have least stable oxides; therefore no significant reduction of the support metal oxide was observed after deposition in UHV and 3D cluster growth is more likely to occur. In contrast, the early transition metals and alkali metals are less stable and have high affinity for oxygen thereby reduce the oxide support while deposition in UHV and wetting of the support oxide can be expected. Those metals which prefer wetting the surface may grow in a layer by layer fashion. Ion scattering spectroscopy (ISS, which is also called low energy ion scattering spectroscopy or LEIS) is a useful technique for studying the growth behavior. ISS is sensitive to the top most surface layer and thus in layer-by-layer growth, the signal from the substrate should eventually vanish upon completion of a monolayer. In contrast, in 3D cluster growth, the intensity of the substrate signal decreases but does not completely vanish. Figure 1.11 explains the three main growth modes and the corresponding intensity (measured by Auger spectroscopy) of the film and the substrate.

Many of the mid to late transition metals are tempting to form 3D clusters on low energy TiO$_2$(110) surface. Nevertheless, mid to late transition metals have also exhibited quasi-layer-by-layer growth at low enough temperatures or at room temperature. Sometimes the disordered clusters may align with the substrate and form thermodynamically preferable ordered structures during annealing as the thermal energy can help overcome the activation barriers associated with the redox reactions or diffusions. Although wetting is not thermodynamically favoured for mid to late transition metals, getting ordered monolayers may still be possible with the right choice of the substrate and controlled growth conditions such as temperature, growth rate and background pressure. The presence of gases, such as O$_2$ and CO, may also influence the wetting thermodynamics and kinetics as they can modify the surface free energy.
Figure 1.11: Schematic representation of the three main growth modes. The schematic plots in the last row show the corresponding intensity attenuation (measured by Auger spectroscopy) versus the coverage of the film.

Oxygen background pressure, of course, plays a vital role in producing ordered structures and some LEED (Low Energy Electron Diffraction) data reported has helped determining the specific site occupation and how well the metal structures match with the substrate.

STM is always an excellent tool for observing the morphology of these overlayers in an atomic-scale. On the other hand, XPS (X ray Photoemission Spectroscopy) and AES (Auger Electron Spectroscopy) gives useful information about the oxidation states of the deposited metal and the substrate and in most cases peak shifts have been observed indicating interface band bending effects associated with the metal deposition. The oxidation state of the deposited metal/metal oxide also changes with the coverage which is evident from AES and XPS measurements. Late transition
metals, for instance, are ionic on oxide surfaces when they are isolated but having more metal atoms close by make them neutral due to the lateral metal-metal bond formation.

The kinetics and energetics associated with metal adatom migration across the surface of the oxide and on the existing metal particles as well as with the stepping up and stepping down from the edges of the metal islands are important to understand in order to control the growth mode and the film morphology. Figure 1.12 explains some of these important processes schematically. The two essential features that cause layer-by-layer growth mode are: (i) strong attraction to the edge of an island which arises from metal-metal bonding and (ii) smaller energy difference between adsorption energies of metal to metal adsorption site and metal to oxide adsorption site. Also, the 2D islands can spread when there is smaller activation barrier for stepping down from the existing islands compared to thermal energy. On the other hand the 3D island formation is prevented when the activation barrier for stepping up is larger compared to the thermal energy. In terms of applications, supported 3D clusters have also shown interesting chemical properties. For instance, Cu/TiO$_2$(110)-1×1 system, which exhibited uniformly distributed growth of clusters with self-limiting size, has been a good candidate for ‘flat model catalysts’.

**Figure 1.12:** Processes taking place during metal/oxide growth on a support oxide. Adsorption, re-evaporation, step-down, step-up, surface diffusion, island nucleation and interdiffusion are indicated.
Sticking probability (i.e. the fraction of metal atoms that stick to the surface when they hit with the surface) and the number density of nuclei are two important factors to be considered in discussing homogeneous nucleation versus heterogeneous nucleation. For most of the transition metals the sticking probability is considered to be equal to 1 at room temperature or below. But it is subjected to change with the temperature and usually decreases with increasing temperature as the rate of desorption or re-evaporation of the atoms that are diffusing along the surface may increase with the temperature. Turning into homogeneous and heterogeneous nucleation; in homogeneous nucleation formation of a nucleus starts when two adatoms being deposited meet together while they diffuse along a defect free surface. In contrast, in heterogeneous nucleation two diffusing adatoms meet together and start nucleation in defect sites. Therefore, in homogeneous nucleation one can expect the islands to be evenly spread while in heterogeneous nucleation they are not. Surface defects has a significant impact towards the number density of islands. Diffusing metal adatoms are strongly attracted to surface defects (step edges, vacancies, impurities etc) and they tend to stay longer in these defect sites. So two diffusing adatoms have higher probability of starting a new island nucleation site when they meet at a surface defect site. Therefore, high defect density may increase the number density of islands. In TiO$_2$, however, the metal/substrate interaction is vigorous; thus the diffusion length of metal adatoms on the surface is very small. As a result, the defects on TiO$_2$ surface becomes comparably less important in island nucleation.

The 2D island density and the critical island size determine the critical coverage which is defined as the maximum coverage a film can have before it starts to form a 2$^{nd}$ layer. Defect dominated nucleation increases the critical coverage. Therefore, slightly reduced surfaces are expected to give more flat surfaces than stoicheometric surfaces. For example, sputtered and incompletely annealed
surfaces have produced better films (high critical coverage) than fully annealed and improved surfaces. Temperature, coadsorbed gases and the choice of the substrate/metal system are the other factors that influence the critical coverage. Coadsorbed gases, in particular, change the free energy of the surface, for e.g. CO increases the critical coverage of Pt on TiO$_2$(110) and an efficient Pd coverage on NiAl(110) has been observed in the presence of CO. Therefore it further confirms that the background gases can support layer like growth. Moreover, these gases can also influence the diffusion barriers, upstepping/downstepping energies etc. and thus change the thickening kinetics. In many cases, the oxide of the metal has been able to wet the support than the pure metal. For e.g. PdO wets Al$_2$O$_3$ TiO$_2$, MgO and LAO while FeO do not agglomerate as bad as pure Fe on Al$_2$O$_3$ and TiO$_2$(110).

‘Encapsulation’ is a common phenomena often appears for group-VIIIB metals such as Fe, Co, Rh, Ir, Ni, Pd and Pt. It has been reported that, for Fe/TiO$_2$(110) system, after annealing for several hours at 500-700 °C, Fe gets covered by Ti-suboxides and remains in metallic state; and re-emerge after ion sputtering[3].

The modifications of surface chemisorption and catalytic properties of metal thin films on oxide supports can also depend on the film thickness and the coverage; i.e. in one atom thick islands the chemisorption sites are mostly offered by the metal atoms that are bonded with the oxide lattice while in thicker films the sites offered can be metal atoms bonded with other metal atoms. The following paragraph describes how the CO adsorption has been influenced by the Fe coverage on TiO$_2$(110)[44].

Fe/TiO$_2$(110) system has been studied and characterized by AES, LEED, ISS, UPS (UV Photoemission Spectroscopy) and HREELS (High Resolution Electron Energy Loss Spectroscopy) by Junzhuo Deng and co-workers. In this study, the Fe overlayer was found to
grow in a layer by layer fashion while oxygen migrated from the substrate to deposited Fe. The oxidation state of Fe, in fact, depends on the coverage and the oxidation state of the substrate. If the substrate was reduced metallic Fe (or Fe$^0$) formed. Upon exposure to CO, Fe$^0$ has been observed to be forming from Fe$^{3+}$. So, the question arose where these electrons came from to perform this reduction reaction. It was concluded that these electrons could only come from oxygen that is bound to Fe$^{3+}$ while CO became CO$_2$ leaving electrons to Fe$^{3+}$. Interestingly, the CO adsorption has remarkably varied with the Fe coverage. To understand the mechanism behind this they carried out HREELS and UPS measurements and found out that, for low Fe coverages (~0.2 ML) CO stretching frequency (observed in HREELS) shows no change from that of the gas phase of CO while for high Fe coverages (~2 ML) the stretching frequency was significantly lower. It is known that 5-sigma orbital of CO shifts towards 1-pi orbital when CO adsorbs on most of the group-VIII metals. It is also known that the separation of 4-sigma and 1-pi orbitals reflects the tendency of dissociation of adsorbed CO. So the argument is, larger the separation-longer the C-O bond and higher the tendency for dissociation. UPS measurements revealed that for low Fe coverages the peak positions for 5-sigma, 4-sigma and 1-pi molecular orbitals remain almost the same as in the gas phase of CO; resulting weak chemisorption. But for high Fe coverages, 5-sigma peak shifted towards 1-pi peak, while the distance between 4-sigma and 1-pi bonds increased; resulting strong chemisorption. It has also been observed that the stretching frequency of CO adsorbed on low Fe coverage was equal to that of a monolayer metal-carboxylic; e.g. Fe(CO)$_5$; implying that the structural requirement might not be satisfied for strong chemisorption of CO because the Fe atoms may be regarded as isolated individuals on the surface; and for high Fe coverage, on the other hand, many nearest neighbours and next nearest neighbours exist to facile electron transfer for strong chemisorption. This concludes that the chemisorption state of CO is
related to the structural characteristics of deposited Fe which in fact varies with the Fe coverage as discussed earlier.

Vanadium oxide on oxide supports is another system that has attracted enormous interest due to its high reactivity and selectivity towards many industrial applications[45-47]. Vanadium, being an early transition metal, reacts vigorously with the oxide support while deposition. For instance, in $V/TiO_2(110)$, $Ti^{3+}$ appears while Vanadium overlayer oxidizes itself, possibly forming $V^{3+}$. However, thicker films and the films deposited on reduced oxide supports have exhibited metallic Vanadium. Electron diffraction experiments have revealed that, for low coverage of V, the preferred adsorption sites are at the position of six-fold Ti atoms underneath the bridging oxygen atoms; and for high coverage of V, islands with bcc(100) structure form and no long range order has been observed. Upon exposure to oxygen, these islands may oxidize possibly forming $V_2O_3$. Metallic Vanadium is only stable up to ~500 K and diffuses into the bulk at ~600 K. However, oxidized V layers are more stable than metallic V. While depositing V with oxygen the substrate (in this case-Ti) has remained fully oxidized and annealing at ~1100 K has resulted structural re-arrangements with formation of large Vanadia particles and/or formation of interface layers presumably having $VTiO_3$ structure; no diffusion into the substrate has been observed in this case.

One of the interesting observations that has been made was, $TiO_2(110)$ supported Vanadium oxide monolayers being able to oxidize methanol into formaldehyde whereas clean $TiO_2(110)$ or multilayer Vanadia were inactive for the reaction[3].

$TiO_2(110)$ substrate has also been used for growth of Ni. Although an S-K growth mode was theoretically postulated, experimental STM studies has revealed 3D cluster formation of Ni preferentially nucleating at the step edges of the substrate. Ni/$TiO_2$ systems have exhibited tendency to adsorb CO at all coverages as well as enhanced catalytic properties[3].
A series of papers has reported the growth behavior, film structure and stabilities of Cr on TiO$_2$(110). Being in the category of early transition metals, Cr wets the support oxide forming an oxidized Cr overlayer. Reduction of the substrate has been observed in XPS. Having a rutile-structure, CrO$_2$ has been able to grow epitaxially on TiO$_2$(110) surface[3]. These CrO$_2$ films have important applications in spintronic devices.

1.2 Research Goals

Based on the background information all three topics on TiO$_2$; i.e. Gas sensing, (photo-)catalysis and metal/oxide growth on TiO$_2$ are equally exciting and motivating. The available facilities and the limited time frame imposed constraints on what systems to be studied under each topic. The selected systems in fact, provided a solid foundation and a thorough knowledge of each field that enabled one to answer the two questions; (i) How do the fundamental surface properties (chemical, structural and electronic) of TiO$_2$ affect the sensing and (photo-)catalysis?, (ii) What role does TiO$_2$ surfaces play in metal/oxide growth and what properties of these new systems are beneficial in enhancing the sensing and catalysis.

1.2.1 Surface Properties of TiO$_2$ in Sensing and Catalysis

Sensing and catalytic properties of the TiO$_2$ surface have been investigated through the following systems.

1.2.1.1 Molecular Scale Investigation of TiO$_2$ Gas Sensing

TiO$_2$, as discussed earlier, acts as an intrinsic n-type semiconductor due to the Ti interstitials and oxygen vacancies in the bulk. Therefore, a charge transfer can take place upon adsorption and
desorption of electronegative molecules causing modifications in the depletion layer in the space charge region at the interface which in turn results in a change of the conductivity of the TiO$_2$ substrate. Here we investigate the adsorption and desorption behavior of DNT (Figure 1.13) on TiO$_2$-rutile (110).

![2,4-Dinitrotoluene](image)

**Figure 1.13:** 2,4-Dinitrotoluene (DNT). DNT is a pale yellow solid powder at room temperature. The chemical formula for the molecule is shown in the right.

DNT, i.e. 2,4-Dinitrotoluene, is a toxic organic compound (Threshold Limit Value [TLV] of 1.5 mg/m$^3$) which is mainly being used in the military industry in making explosives. It is not an explosive by itself but it can be converted into TNT (2,4,6-trinitrotoluene), one of the well-known explosive compounds. DNT is a hazardous waste as well as a carcinogen and known to be causing various other health complications including fatigue, anxiety, depression and a disease called ‘Methemoglobinemia’; in which it converts hemoglobin to methemoglobin and reduces the ability to release oxygen into tissues. Therefore, it is highly important to have devices to detect such harmful compounds in order to ensure the environmental safety. However, the low vapor pressure (<100ppb) of these explosives has made it very difficult to be detected. Research shows that TiO$_2$ nanostructures, TiO$_2$-(B) nanowires in particular, are sensitive to low vapor pressures and exhibit significant change in the conductivity upon exposure to DNT vapors. But, to date, studies have not been reported in a molecular level. Understanding the adsorption and desorption behavior in a
molecular level is crucial in order to know how efficient TiO$_2$ can be as a gas sensor and to know in what ways performance of the sensing devices be enhanced. This motivated us to carry out investigations on DNT/TiO$_2$-rutile (110) system in a molecular level. Since a lot of work is done on the most stable TiO$_2$(110) single crystal, its surface geometrical structure is already well-understood. As discussed before, surface structure of TiO$_2$(110) supports carboxylic acid adsorption in a bridge-bidentate fashion. In DNT, there are two O-terminated nitro-groups of DNT (see Figure 1.13) but there is no acidic H to dissociate. Thus some uncertainty remains whether it is possible to observe non-dissociative bridge bidentate adsorption via coordination through the two oxygen atoms, since the nitro-oxygen atoms in this case are not under-coordinated like the oxygen at the carboxylic group after H-dissociation. Moreover, DNT seems more ‘bulky’ than simple carboxylic acids such as formic or acetic and thus steric hindrance may be expected upon dense packing. A complete coverage may still be possible via C-N bond. In addition to exploring adsorption mechanism, the thermal stability and desorption mechanisms were also to be determined since recovering time is also an essential property of in a gas sensing device. We also collaborate with a theoretical group (Xue-Qing Gong, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China) in order to gain more insight about the growth mechanism, thermal stability and interfacial properties of these systems.

### 1.2.1.2 Crystallographic Properties of TiO$_2$ in Photocatalysis

Decomposition of pollutants via Photo-induced redox reactions is a remarkable aspect of TiO$_2$ as already discussed. The challenge still remains to make it a more efficient catalyst. The two phases of TiO$_2$ considered in the study was Rutile and Anatase. The fact that Anatase phase is
photocatalytically more active than Rutile phase is well-known. Investigation of phase dependence and orientation dependence of photoactivity of TiO$_2$ has already been done by many groups. However, the reasons as to why these differences exist are not fully understood. This is because most of the photocatalytic experiments have been carried out using powder samples. Due to the differences in the morphology in the two phases in common powder samples, a clear explanation for the differences may not be postulated. Another issue of using these systems is the difficulty in isolating the surface effects from bulk effects.

Growth of high quality (atomically smooth terraces with well-defined monatomic steps) anatase TiO$_2$(001) epitaxial thin films on LaAlO$_3$(001) [with crystallographic relationship (001)[-110]$_{\text{anatase}}//$(001)[110]$_{\text{LAO}}$] and rutile TiO$_2$(001) epitaxial thin films on r-cut Al$_2$O$_3$(-1102) [with crystallographic relationship (101)[-111]$_{\text{rutile}}//(-1102)[20-2-1]_{\text{sapphire}}$] using molecular beam epitaxy (MBE) or pulsed laser deposition (PLD) is successfully done in the past. These planar epitaxial thin films, in contrast to powder samples, may allow isolation of surface effects from bulk effects as well as exclude the differences arise from morphological differences in the two phases.

The main objectives of this study are: (i) growth of high quality TiO$_2$ anatase(001) and rutile(011) thin films, (ii) measure the photoactivity by varying only the thickness of the films, (iii) measure the effect of post-growth annealing for anatase and rutile films (iv) measure the effect of vacuum reduction for rutile single crystals, (v) measure the differences in photocatalytic activity as a function of orientation for rutile TiO$_2$.

This series of experiments would simplify the complexity of the real systems (e.g. powder photocatalysis) and allow making a reliable comparison between the activities in the two phases.
and the activities for different crystalline orientations for the same phase; thereby allowing one to present an acceptable explanation for the observed differences in a surface scientific point of view.

1.2.2. Monolayer Mixed Oxide Growth on TiO₂

The general motivation for synthesizing oxide heterostructures is their novel chemical functional properties that can be utilized in enhancing the performance of oxide-based technological applications including sensing and catalysis. The fast-growing advancements of experimental and theoretical surface science tools have enabled the investigation of even more complex multi-component oxide structures and interfaces. Therefore, deviating from the common or traditional studies of oxides supported on another oxide, this study focuses on synthesizing only a single atomic-layer thick ordered multi-component oxide layers on a second oxide and characterizing them in an atomistic-level as these surfaces and interfaces may possess unique functional properties and be potential candidates for novel nanotechnological devices and applications.

The two classes of multi-component oxide systems that have been targeted here are: (i) Monolayer metal oxides which exist at the interface of a second metal oxide, (ii) Surface mixed oxides where the metal atoms intermixes with the substrate metal atoms and stabilize within the surface lattice positions of the substrate (see Figure 1.14 for clarification).

![Figure 1.14: Ball models for metal overlayer formation. (a) A traditional metal catalyst supported on another oxide. (b) Monolayer oxide on oxide support. (c) Mixed surface oxide monolayer.](image-url)
Metal atoms tend to form 3D clusters on oxide supports since, in a simple thermodynamic point of view, the oxide has lower surface free energy than many metals. Thus, the questions which we are aiming to find the answers are: (i) Is it possible to achieve a wetting behavior via controlling the oxygen partial pressure and temperature?, (ii) What are the suitable support oxide materials which could facilitate wetting behavior?, (iii) What metal elements would be more suitable in attempting mixed monolayer formation on the support?.

Some of the reported monolayer oxide catalysts supported on a second oxide are $\text{V}_2\text{O}_5/\text{TiO}_2$, MoO$_3$/Al$_2$O$_3$, CrO$_3$/Al$_2$O$_3$, WO$_3$/Al$_2$O$_3$, Re$_2$O$_7$/Al$_2$O$_3$, TiO$_2$/SiO$_2$, Fe$_2$O$_3$/SiO$_2$, NiO/ZrO$_2$ and WO$_3$/ZrO$_2$. Pd/CeO$_2$(110) system is an example for a mixed monolayer oxide reported in the past. CeO$_2$(110) in this case, is a high surface energy orientation which may have led to the formation of PdCeO$_x$ mixed oxide surface phase. So far, reports on synthesizing well-defined ordered monolayer oxides or mixed monolayer oxides are rare as it is quite challenging and requires surface sensitive characterization techniques.

As an initial system for this study we select Fe/TiO$_2$(011). Single crystalline TiO$_2$ (011) is a high energy surface orientation which exhibits energy lowering surface reconstructions; in other words (011) orientation of TiO$_2$ is less stable compared to stable (110) orientation TiO$_2$. Therefore, unlike TiO$_2$ (110) on which cluster growth of metals was favored in many cases, TiO$_2$ (011) may be a better candidate in stabilizing ordered surface covering monolayers or mixed monolayers. Fe, on the other hand, known to form stable bulk mixed oxide phases with TiO$_2$ for e.g. FeTiO$_3$ –ilmenite, and thus may be capable of mixing with surface atoms as well. We extend this study to a few of the other transition metals as well, namely V, Cr, and Ni, in an attempt to examine if there is a generality for the formation of intermixed oxides. All these transition metals crystallize as sesquioxides with the corundum structure. As mentioned earlier, FeTiO$_3$, i.e. ilmenite structure, is
close to corundum structure with ordered Fe- and Ti- sublattices. Due to the similarities in the bulk oxide structures of these transition metals we speculate that it may be possible that they all are capable of forming similar intermixed oxide surfaces.

Once we are able to discover the growth conditions to stabilize these metal oxide overlayers or surface mixed oxides on TiO$_2$ (011), we characterize them with surface sensitive techniques to explore the chemical and structural information, thermal stability and catalytic properties. The theoretical group that we are collaborating with (Xue-Qing Gong, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China) provides us with possible structural models for these systems based on DFT- based computational approaches.

1.3 Outline of the Dissertation

Having reviewed the relevant background information the research goals have been set in section 1.1 and 1.2 of this first chapter. In the chapter 2, the experimental and theoretical methods that have been utilized for the study are explained. This includes a brief introduction of UHV technology and the basic theory behind all the surface scientific instrumentation followed by a comprehensive discussion of surface analysis techniques. This would allow the reader to be familiar with the nomenclature used throughout this document. In chapter 3, the results are presented along with a discussion. This will include all the theoretical and experimental findings and discussion of results. The last chapter, i.e. chapter 4 will give a summary of the results and future outlook.
Atomic scale investigations of surfaces require the samples to be clean and well-defined. Also, the surface cleanliness and composition should remain unchanged throughout the duration of the experiment. Therefore, the rate of arrival of gas phase reactants towards the sample surface should be minimized. These requirements can only be achieved via conducting experiments in ultra-high vacuum (UHV) conditions.\(^1\)

### 2.1 Introduction to UHV Systems

A UHV system consists of special sets of instrumentation including roughing pumps, turbomolecular pumps, ion pumps, ionization gauges, gate valves, precision leak valves, load locks, sample manipulators, heaters, ion guns, residual gas analyzers (RGA), deposition techniques and analysis techniques. The materials used in UHV systems should have low vapor pressure and should preferably be non-magnetic since many of the surface analysis techniques involve electron beams or ions that are deflected by magnetic fields. Most suited UHV material is stainless steel, while tantalum, molybdenum, tungsten, aluminum and copper are also commonly used. Especially, Ta, Mo and W are refractory (i.e. resistant to heat and wear) metals and used for construction of evaporators and sample holders. The pumping system is collectively able to bring

\(^1\) Surface Science by K.Oura, V.G. Lifshits, A.A. Saranin, A.V.Zotov and M.Katayama has been referred to while composing this chapter.
the pressure inside the chamber down to $\sim 10^{-10}$ Torr; i.e. about 12 orders of magnitude below the atmospheric pressure which is 760 Torr. The principle of operation of these pumps is discussed next (see Figure 2.1 for illustration).

Roughing pumps: These are also called ‘rotary’ pumps and usually employed as backing pumps for turbomolecular pumps. Rotary pumps can bring the pressure in the chamber down to $\sim 10^{-3}$ Torr. A schematic diagram of the cross section of a rotary pump is shown in Figure 2.1a. As can be seen, the gas enters and get trapped in the volume between the rotor vanes and the stator. While the clockwise rotation of the rotor, this volume of gas become compressed and then expelled into the atmosphere through the outlet. The oil inside the pump acts as a lubricant and a sealant. For preventing backstreaming of oil into the chamber liquid nitrogen trap (oil trap) is often used at the inlet.

![Figure 2.1: Schematic diagrams that illustrate the principle of operation of different pumps used in UHV. (a) Roughing pump, (b) Turbomolecular pump, (c) Ion pump.](image)

Turbomolecular pumps: Figure 2.1b shows a cross sectional view of a turbomolecular pump. The stack of rotors with slightly angled multiple blades rotates at a speed as high as 50,000-100,000
rpm, and sweeps the gas molecules towards the exhaust. Turbo pumps efficiently pump down most of the gases and bring the pressure in the chamber down to $\sim 10^{-9} - 10^{-10}$ Torr. One disadvantage of turbo pumps is the vibrations that it causes which results in noise in microscopic imaging techniques used in surface analysis.

Ion pumps: Ion pumps are the most popular in UHV systems due to their vibration-free operation and ability to reach $\sim 10^{-11}$ Torr pressure. As shown in Figure 2.1c, ion pumps consist of a set of short stainless steel tubes (anode) mounted in between two Ti plates (cathode). A strong magnetic field is applied parallel to the axis of the tubes so that the electrons emitted from the cathode can move in helical trajectories inside the tube. This motion of electrons results in ionization of the gas molecules inside the tubes. The ionized gas molecules are then accelerated by the electric field, strike the Ti coated cathode plates and get buried which is the mechanism of pumping. While striking the plates these ions can sputter Ti causing the walls of the tubes, cathode and the pump coated with Ti.

Although not essential, titanium sublimation pumps (TSP pumps) are also used in many UHV systems in order to maintain a good vacuum. TSP is made up of a Ti coated filament which can be heated directly by passing an electric current through it. While heating, Ti sublimate from the hot filament and covers the walls of the chamber with a fresh Ti film which reacts readily with active gases such as $\text{N}_2$, $\text{H}_2$ and $\text{O}_2$ forming non-volatile compounds.

Ionization gauge is an essential component in UHV systems that enables one to read the pressure. A schematic diagram of an ion gauge which uses thermionic emission of electrons for the operation is shown in Figure 2.2. When the electrons from the hot filament accelerated towards the grid, which is held at high potential, the atoms and molecules get ionized. These ions are attracted to the collector, i.e. a grounded wire, and then converted to a pressure reading.
Figure 2.2: Schematic diagram of the operation principle of an ion gauge. The electrons from the hot filament accelerate towards the grid. The atoms or molecules then get ionized and directed towards the collector where this ion current was converted to a pressure reading.

A properly evacuated UHV system only contain a mixture of H$_2$, CO$_2$, CO, N$_2$ and small amount of H$_2$O in gas phase. If the interior of a UHV chamber is exposed to air, it should be wrapped up with heating tapes and baked properly while pumping down, in order to desorb all the water vapor covering the chamber walls. Residual gas analyzers can be used to record the mass spectrum of the elements or molecules present inside the UHV chambers and detect any unwanted gases that may have entered through air leaks. A He gas flow can be used to locate the leaks in the systems. Figure 2.3 shows few of the UHV systems in ISSL (Interface and Surface Science Laboratory) where the current experiments have been performed.

2.2 Sample Cleaning

Preparation of a clean sample surface is the first thing to do before every experiment in UHV. In general, sonicating the samples in organic solvents (acetone, ethanol) in ultrasonic bath followed by rinsing in deionized water before introducing them into UHV system is recommended. Atomically clean surfaces can only be obtained via in-situ cleaning of the sample. Ion sputtering and annealing (heating) are the in-situ cleaning methods that have been employed in the current systems.
Figure 2.3: Photographs of UHV systems in ISSL (Interface and Surface Science Laboratory) in USF. Few of the important components are as labeled in each system.
The heating can be done by passing an electrical current through the sample, radiatively heat the sample by bringing a hot filament or BN-heating element in close proximity to the backside of the sample, or by bombarding the back of the sample plate with energetic electrons usually accelerated by applying a high voltage of ~1 kV between an electron emitting filament and the sample or sample holder. The adsorbed species can then be evaporated from the sample surface at temperatures below the melting point of the material under investigation. Impurity segregation and/or formation of strongly bound compounds (e.g. C) while annealing are couple of shortcomings in this cleaning method. Therefore, this should almost always be followed by ion sputtering which is discussed next.

![Figure 2.4: Schematic diagram of an ion sputter gun. In addition to cleaning samples, this can also be used in mass spectrometry and ion scattering spectroscopy methods.](image)

Bombardment of the sample surface by noble gas ions (e.g. Ar⁺) is called ion sputtering. The contaminants can be effectively removed or sputtered off together with the top layer of the surface using this method. Ar gas can be admitted into the UHV chamber through a precision leak valve and ionize in the ion gun. Figure 2.4 shows a schematic diagram of the operation principle of an ion gun. Electrons emitted from the cathode collide with Ar gas atoms resulting in Ar⁺. The ions
are then extracted from the ionizer and accelerated towards the sample with the desired energy (0.5-5 keV). While this is an efficient cleaning technique, the drawback is the degradation of the surface atomic structure. In order to recover the stoichiometry and crystalline order of the sample surface and to remove the embedded Ar atoms, subsequent annealing is essential. Few cycles of ion sputtering and annealing are in general required to obtain an atomically clean and well-defined sample surface that is free of contaminants.

2.3 Deposition Techniques

Different deposition methods are employed in different experiments. Most common method compatible with UHV is physical vapor deposition (PVD). In this method, the material to grow the film is delivered as beams of atoms or molecules which can be generated using electron beam evaporators or pulsed laser deposition (PLD) techniques. In electron beam evaporators, the solid material in the form of powders or rods is heated by a high current electron beam that is generated by thermionic emission of electrons from a hot filament. In large electron beam evaporators these electrons can be focused on the material to be evaporated using permanent magnets which causes local melting and formation of a pool of liquid of the evaporated material. This is not the case for mini-electron beam evaporators in which only a high voltage applied between the filament and the evaporant is used for focusing the electron beam. In pulsed laser deposition, the beam of atoms or molecules is generated by pulsing a laser on a target that is made up of the material to grow the film. One advantage of PLD is that the target can be made by mixing several different materials to a desired ratio so that films with complex multicomponent structures can be grown. In the case of oxide film growth, oxygen is introduced into the chamber via precision leak valves in order to provide sufficient oxygen to form the film. In most cases, the substrate is held at an elevated
temperature while deposition, to ensure that the atoms have sufficient energy to migrate over the surface to lattice sites and form ordered crystalline structures. However this temperature should be carefully selected and controlled in order to avoid unwanted diffusion of atoms from the bulk, intermixing and roughing of the film. Materials that have sufficient vapor pressure well below the melting point (e.g. Fe, Si) can be sublimated via directly heating a wire or a rod of the particular material by passing an electric current through it.

2.4 Surface Analysis Techniques

Sample surfaces can be analyzed with microscopy techniques, spectroscopy techniques and diffraction techniques that are compatible with UHV. Discussed below are the techniques that have been utilized in the current work.

2.4.1 Microscopy Techniques

Microscopy techniques, in general, produce a direct real space magnified image of the surface under investigation. The techniques used in surface scientific analysis, in particular, are able to produce atomically resolved images thereby providing information about the surface crystallography, surface morphology and surface composition. Principle of operation for the different microscopy techniques employed in the current work is discussed next.

2.4.1.1 Scanning Tunneling Microscopy (STM)

Tunneling is a quantum mechanical phenomenon where electrons from one conductor penetrate to another conductor (or a semiconductor) through a classically forbidden potential barrier. The
potential barrier in this case is vacuum and the two conductors are an atomically sharp metal tip and the sample surface. Figure 2.5 shows the main components in an STM system.

Atomically sharp STM tips can be made by electrochemical etching of W, Pt-Ir or Au wires with desirable diameters followed by in-situ annealing. The tip is fixed in a Au coated tip holder which is then places on another holder made of piezoelectric ceramic material. This piezoelectric ceramic holder acts as an electromechanical transducer that converts electric signals into mechanical deformations in the range of ~1mV to 1kV and helps fine control of the tip movement when it is close to the sample surface.

![Figure 2.5](image_url)

Figure 2.5: Schematic diagram of the main components used in STM. The tunneling current I between the sample and the tip is indicated in the zoomed area. Red balls indicate atoms of the tip and yellow balls indicate atoms from the sample.

When the atomically sharp tip is close the surface of the sample the wave function of the tip atoms and the surface atoms leak out into the vacuum and overlap with each other within the forbidden gap. At this point the distance between the tip and the sample \(d\) is only ~5-10 Å. If the bias
voltage applied between the sample and the tip is $V$, the tunnel current $I_T$ flows through the gap can be expressed by:

$$I_T = \frac{V}{d} e^{-Ad\sqrt{\Phi_B}}$$

where, $A$ is a constant and $\Phi_B$ is the effective barrier height or the work function (see Figure 2.6).

**Figure 2.6:** Energy diagram illustrating the tunneling effect in STM. The sample is biased positively with voltage $V$. Electrons tunnel from the filled states in the tip to the empty states in the sample. $\Phi_1$ and $\Phi_2$ are the work functions for the sample and for the tip. $\Phi_B$ is the effective barrier height. $d$ is the effective tunneling gap. $E_{F1}$ and $E_{F2}$ are the Fermi levels for the sample and the tip respectively.

It is important to point out that STM is sensitive to local density of electronic states in the surface rather than the topographical effects. Depending on positive or negative bias voltage applied to the tip with respect to the sample, electrons flow from the sample to the tip or from the tip to the sample respectively. Therefore, for positive sample bias voltages, a map of empty electronic states of the surface is observed in STM. In contrast, for negative sample bias voltages, a map of filled electronic states of the surface is obtained. Depending on the information to be known, STM can be operated in three modes: (i) constant current mode, (ii) constant height mode, (iii) STS (i.e.
scanning tunneling spectroscopy) mode. Figure 2.7 illustrates STM used in constant current mode and constant height mode.

Figure 2.7: Schematic illustration of STM used in two modes. (a) Constant current mode, (b) Constant height mode.

In constant current mode, the bias voltage and the tunnel current are kept at constant values as the tip scans over the surface. In order to keep the current constant, the vertical position of the tip has to be adjusted by varying the feedback voltage $V_z$ on the Z-piezoelectric driver. This results in a topographical map of the surface as a function of tip position. In constant height mode, the tunnel current is allowed to change while maintaining a constant vertical distance between the sample and the tip. In this case, the bias voltage is fixed and the feedback loop is turned off so that the variation of tunnel current as a function of tip position is mapped. In STS, the tunnel current is recorded for various bias voltages at constant tip-sample separation and the information about the local density of states as a function of energy can be obtained. From this I-V curve, the sample density of states, which is defined as $(dI/dV)/(I/V)$ can be calculated and the spatial distribution of
particular surface states can be mapped. STS is a successful probe of a very local (as small as a single adatom at the surface) electronic properties at the surface.

2.4.1.2 Atomic Force Microscopy (AFM)

AFM senses the force between the tip and the sample under investigation and thus, unlike in STM, AFM can be used to image all types of samples that are either conductive, semiconductive or insulating. The principle of operation of AFM is explained in Figure 2.8. A sharp tip is attached to the free end of a cantilever. When the tip is close to the sample surface the interatomic force between the two causes the cantilever to deflect. This deflection is monitored using the deflection of a reflected laser beam that strikes the cantilever from behind. It is said that a typical sensor is able to detect deflections as small as ~ 0.01 Å. Surface topography can be mapped by measuring this deflection while the tip scans over the sample surface.

![Figure 2.8: Schematic illustration of AFM operational principle that uses laser beam deflection.](image)

Tip-sample interaction force curve is shown in Figure 2.9. When the separation between the sample and the tip is large, a weak attractive force occurs between the two. While decreasing of
this distance, the attractive force increases and at some point the electron cloud of the tip and the sample overlap and start to develop a repulsive force. The occurrence of repulsion can be better explained as a consequence of wave function overlapping and Pauli exclusion principle, which causes promotion of electrons to higher energy levels. At the point where force goes to zero the distance between the sample and the tip is only a few Å, and when the distance is closer, the repulsive force dominates.

**Figure 2.9:** The Van der Waals force between two atoms versus the separation (distance) between the two atoms. The regions highlighted with red indicate the tip-sample separation in AFM contact mode and non-contact modes.

AFM can be operated in three modes: (i) contact mode, (ii) non-contact mode, and (iii) tapping mode. In contact mode, the separation between the tip and the sample is only a few Å and the force between the two is repulsive. An image of the topography of the sample is generated due to the tip-sample interaction. Here, similar to STM, the topographic images can be acquired in two modes: constant height mode; where the scanner height is constant and the deflection of the cantilever is recorded to produce the image, and constant force mode; where the cantilever
deflection is fixed by keeping the net force applied to the cantilever a constant. This is the most widely used mode in AFM as the net force can be easily controlled and the data can be easily interpreted. In non-contact mode of AFM, the separation between the tip and the sample is in the range of \( \sim 10-100 \, \text{Å} \). Therefore, the force between the two is weakly attractive. In this case, the cantilever keeps vibrating at its resonance frequency typically in the range of \( \sim 100-400 \, \text{kHz} \) with an amplitude of few tens of Å. Due to the tip-sample interaction, the resonance frequency \( \nu \) modifies according to: \( \nu \propto (c - F')^{1/2} \), where \( c \) is the spring constant of the cantilever and \( F' \) is the force gradient. For keeping the resonance frequency a constant, the scanner height is controlled by the feedback system, generating the image. Tapping mode AFM is similar to non-contact mode AFM but the difference is that the cantilever tip in this case barely touches the sample surface at the minima of its oscillations. Although this mode of AFM does not produce atomic resolution images, it can be successfully used for imaging rough surfaces.

2.4.2 Spectroscopy Techniques

Spectroscopy techniques are essential in analyzing electronic and chemical properties of surfaces. The techniques employed in the current experiments can be subdivided into two categories: (i) secondary electron spectroscopy and (ii) ion scattering spectroscopy. The two techniques are discussed separately below in detail.

2.4.2.1 Secondary Electron Spectroscopy

The electronic structure of surfaces can be studied through analyzing the secondary electrons emitted from the surfaces (or from near surface regions) while bombarding them with electrons or with photons and this is called electron spectroscopy. The fact that secondary electrons with energy
ranging from 5-2000 eV strongly scatter from solids can be used to achieve surface sensitivity. The intensity decay in secondary electrons can be expressed by $I_s=I_0 \exp\left(-\frac{d}{\lambda_{\text{IMFP}}}\right)$; where $I_s$ and $I_0$ are final and initial intensities, $\lambda_{\text{IMFP}}$ is the inelastic mean free path (IMFP) and $d$ is the distance travelled by secondary electrons. IMFP is defined as the distance travelled by an electron before its intensity decays $1/e$ of the initial intensity. Figure 2.10 shows IMFP for secondary electrons as a function of their kinetic energy. IMFP is a material property; however, it follows a universal curve the shape of which is given by figure 2.10 and as can be seen, for the energy range 20-200 eV, IMFP is only a few Å.

![Figure 2.10: Inelastic mean free path of secondary electrons as a function of their kinetic energy.](image)

**Photoelectron Spectroscopy (PES):** Photoelectron spectroscopy (PES) is one of the most common electron spectroscopy methods that can be used to identify the elements, composition, and charge states (chemical states) and valance band structures at surfaces or near surface regions. In this method, secondary electrons are generated via bombarding the sample surface with photons.
and analyzed using electron energy analyzers. The technique is based on photoelectric effect where an electron occupied in a state in the solid with binding energy $E_{BE}$ absorbs a photon with energy $h\nu$ and escapes from the solid with a kinetic energy that is given by:

$$E_{kin} = h\nu - E_{BE} - \phi_s$$

where $\phi_s$ is the work function of the material ($\phi_s = E_{vac} - E_{fermi}$). Therefore, if the photon energy $h\nu \geq E_{BE} + \phi_s$ the electron escape from the solid. In order for it to be detected in the vacuum, its velocity should be directed towards the surface and it should not loose energy due to collisions with other electrons on the way. Figure 2.11 explains the photoemission process on a metal.

![Figure 2.11: Schematic representation of the photoemission process on a metal surface. Sharp peaks in the spectrum is caused by core-level emission. The background is due to the inelastically scattered electrons.](image)

$$\text{Valence bands}$$

$$\text{Core levels}$$
It should be pointed out that when calculating the kinetic energy measured at the analyzer, the work function of the material should be replaced with the work function of the analyzer. This is illustrated in Figure 2.12. Since the analyzer and the sample is in electrical contact the Fermi-level of the sample and the analyzer align with each other which results in a contact potential which is given by $\Delta \Phi = \Phi_S - \Phi_A$. So, the kinetic energy measured $E_{\text{kin}} = h\nu - E_{\text{BE}} - \Phi_S - \Delta \Phi$, which results in $E_{\text{kin}} = h\nu - E_{\text{BE}} - \Phi_A$.

![Figure 2.12: Schematic representation of the energy band alignment between the sample and the analyzer in XPS.](image)

Depending on the wavelength or the energy of the photons, PES can be subdivided into two categories; i.e. X-ray photoemission spectroscopy (XPS) that uses x-ray radiation with energy $\sim 100$-10000 eV ($\lambda \sim 1$-100 Å) and Ultraviolet photoelectron spectroscopy (UPS) that uses photons (can be from a separate UV source or from soft x-rays) with energy $\sim 10$-50 eV ($\lambda \sim 1000$-250 Å). PES experimental set-up consists of a monochromatic photon source, the sample under investigation and an electron energy analyzer to record the photo-emitted electron spectra (see
Figure 2.13). Various types of analyzers have been used in analyzing the photoemitted electrons in PES experiments. Generally, the analyzers record the number of emitted electrons versus energy. Figure 2.13 shows a hemispherical analyzer often used in many laboratories. The electrons with a definite energy (called pass energy) are directed towards the detector by applying a desired voltage to the electrodes of the analyzer. In general, the ordinary laboratory sources are specific for XPS and UPS, while the whole photoemission energy range is achieved in synchrotron radiation sources.

In lab-XPS sources, the x-ray flux is created by bombarding Mg or Al target with high energy electrons generated by accelerating electrons from a heated filament (cathode) over ~5-20 keV. This causes creation of core-level holes in the target material which are subsequently filled by transition of electrons from higher energy levels (e.g. $2p_{3/2}$ to 1s, $2p_{1/2}$ to 1s). The resulting emission spectra for Mg and Al is dominated by Mg-K$_\alpha$ (at 1253.6 eV) and Al-K$_\alpha$ (at 1486.6 eV) radiation, the line width of which is ~700 meV. The sampling depth, that is, the depth from which 95% of secondary electrons are scattered by the time they reach the sample, is approximately given by $3\lambda_{\text{IMFP}}$. For Al-K$_\alpha$ radiation, the sampling depth is ~1-10 nm, however, it should be pointed out that the probing depth does not directly depend on the photon energy but only on the kinetic energy of the emitted electrons, which of course, for a given binding energy, can be influenced by photon energy of the radiation.

Lab-UPS sources use discharge lamps filled with inert gases (e.g. He). In He discharge lamps, depending on the gas pressure and discharge current, characteristic lines with photon energies 21.2 eV (He-I; line width ~ 3 meV) or 40.8 eV (He-II; line width~ 17 meV) are generated.
More sophisticated photon sources are available in synchrotron facilities. The energy of synchrotron radiation vary from a few electron volts to kilo electron volts and by using a monochromator, photons with desired energy can be filtered for different experimental purposes. Being stable and polarized are the other advantages of high intensity synchrotron radiation which make it a powerful probe in surface analysis. Figure 2.14 shows a photograph of a synchrotron radiation laboratory and a schematic of its main components. A brief description of how it works follows.

Synchrotron radiation is created when electrons moving at relativistic velocities are accelerated. Accelerated electrons or charged particles always radiate however for generating X-rays, the speed should be relativistic.
Figure 2.14: Synchrotron radiation facility. (a) Photograph of Elettra synchrotron at Trieste, Italy. (b) Schematic diagram that shows the major compartments found in the synchrotron laboratory. (c) Photograph of the top view of a model end station at Elettra.

Electron injector, linear accelerator, booster ring, storage ring, beamline and end station are the main compartments found in a synchrotron radiation laboratory. The electron injector is located in the first part of the ‘booster’ ring. The principle of generation of charged particles here is similar to that in a cathode ray tube. These particles (electrons) are guided through a high vacuum steel tube, i.e. through the booster ring, where they are accelerated to gain an energy of about 2.5 billion electron volts upon subjected to intense electromagnetic fields. These high energy electrons are then shoot into the storage ring where they circulate at a speed close to the speed of light with a constant energy. Synchrotron radiation is generated in the storage ring. The ring is composed of alternating straight and curved sections. In the curved sections there are powerful magnets which deviate the electron path guiding them along the circular path. During this deviation of its path,
electrons emit energy in the form of light beams tangent to the storage ring. These light beams, called beamlines, are directed to separate end stations where they are filtered, monochromatized and focused before entering the chambers in which the experiments are performed and analyzed. By making the electrons in the storage ring oscillating, brighter radiation can be generated. For this purpose the electrons are subjected to an alternating magnetic field created using Undulators, i.e. a collection of alternating north and south pole magnets.

**XPS Analysis:** As can be seen in Figure 2.11, the spectrum recorded in XPS corresponds to the density of occupied states in the sample under investigation. In a typical XPS spectra, the core levels appear as sharp peaks at specific binding energy positions which are characteristic to element or atom species. The background seen in the spectrum is formed by the inelastically scattered secondary electrons. The shape of the spectrum is affected by the different cross-sections of excitations for different electron levels. The valance band features in XPS spectrum are very weak due to very low photoelectric cross-section for valance band states at X-ray energies. When the X-ray photon energy is close to electron binding energies of the particular element under investigation, the core-level peaks with maximum intensity are observed while exceedingly high photon energies cause this intensity to drop. Therefore, XPS is well-suited as a core-level probe. Fine structures of core-levels; e.g. spin-orbit splitting, are also observed in high resolution XPS. Chemical shifts (from ~1-10 eV) occur in core-level peak positions in XPS spectra due to varying chemical environment around the atom species that the sample is composed of. This phenomenon gives it the ability to distinguish the bonding state or the charge state of elements in addition to identifying the composition. Therefore, XPS is also called ESCA which means electron spectroscopy for chemical analysis. The chemical shifting phenomenon can be explained as
follows: The binding energy of electrons is defined by their Coulomb attractive force with the nucleus. Upon formation of chemical bonds electron transfer between the atom species occur resulting in changes in the initial charge density around the atoms. This in turn modifies the binding energy of the electrons with the nucleus. In general, when the electrons transfer from the atoms, the electron screening around the atom weakens and enhances the bond strength which causes the binding energy peak to shift to higher values (oxidation). In contrast, when electrons transfer into the atoms, the screening effect enhances and the bonding between the electrons and the nucleus gets weakened causing the binding energy peak to shift to lower values (reduction).

Quantitative analysis (concentration of atomic species etc.) can be carried out in XPS by calculating the intensity of the peaks of atom species using the simplified expression given below.

\[
I_s = I_0 \sigma_s \int_0^d \exp\left(-\frac{x}{\lambda_{IMFP}}\right) \, dx
\]

Here, \(I_s\) is the measured peak intensity (given by the area of the peak) for a particular atom species, \(I_0\) is the initial intensity of the photoemitted electron, \(\sigma_s\) is the photoionization cross-section, \(\lambda_{IMFP}\) is the IMFP and \(d\) is the distance travelled by the photoemitted electron.

In order to achieve surface sensitivity in XPS, grazing incidence of radiation and grazing angle detection of photoemitted electrons can be employed in addition to tuning the photon energy that gives the lowest IMFP; the latter is however, is only possible in synchrotron radiation sources.

**UPS Analysis:** Since UPS uses low energy photons, only the electrons occupied in higher lying valance band states can be excited into vacuum during the photoemission process and the valance band spectra can be observed for sample surfaces. In addition to that, these states are the filled
bonding orbitals for adsorbates; so, the modifications in the valance band structure can be used in studying surface chemical reactions as well.

UPS can be used in two regimes namely, angle-integrated UPS and angle-resolved UPS (ARUPS). In angle-integrated UPS, the photoemitted electrons are collected over the entire half-space of the sample surface and the density of states within the valance band of the surface is observed. In ARUPS, the photoemitted electrons are collected in a selected grazing angle so that the wave vector of the emitted electrons can also be known in addition to the energy. With this information, the dispersion of surface states can be determined. For further understanding of this, consider the following expression for the photoemitted electron kinetic energy;

\[ E_{\text{kin}} = \frac{\hbar^2 (k_{\perp}^2 + k_{\parallel}^2)}{2m} \]

where, \( k_{\perp} \) and \( k_{\parallel} \) are perpendicular and parallel components of wave vector \( k \) with respect to the surface. Here, the electron wave vectors that have already escaped into the vacuum region are considered. If a given \( k \) makes an angle \( \theta \) with respect to the surface normal, the parallel component \( k_{\parallel} \) can be written as,

\[ k_{\parallel} = \sqrt{2mE_{\text{kin}} \frac{\hbar^2}{\text{sin} \theta}} \]

For 2D surfaces, only the parallel component of the wave vector is conserved which implies that the parallel component of the internal wave vector is equal to that of external wave vector. By plotting \( k_{\parallel}\) (internal) versus the binding energy (as measured by \( E_{\text{kin}} = \hbar\omega - E_i - \phi_{\text{analyzer}} \)), energy dispersion of surface states can be determined.

It is important to point out that, although UPS is a surface sensitive technique, additional measurements may require in distinguishing surface and bulk contributions of energy states to the spectrum. For instance, the surface state dispersion curve can be measured for different photon
energies, and if it is a real surface state, the dispersion curve should remain the same for different photon energies, since for surfaces, only the parallel component of the wave vector is considered to be conserved which of course does not hold for bulk states.

### 2.4.2.2 Ion Scattering Spectroscopy (ISS)

In this technique, elastically scattered ions from a sample surface are analyzed. Depending on the energy range that have been utilized, this can be subdivided into low-energy ion scattering (1-20 keV), medium-energy ion scattering (20-200 keV) and high-energy ion scattering (200 keV-2 MeV; this is also called the Rutherford backscattering spectroscopy) spectroscopy. The fundamentals of Low energy ion scattering (LEIS or ISS) technique is discussed here as the energy of the ions used in the current studies was ~ 1000 eV. ISS is mainly employed in determining surface composition of samples. This can be understood by considering simple classical binary collisions of particles and conservation laws of energy and momentum. Figure 2.15 shows a schematic diagram of a binary collision of an incident ion with a surface atom.

---

**Figure 2.15:** Schematic diagram of a binary elastic collision of an incident ion with a surface atom.

- $m_i = \text{mass of ion}$
- $m_t = \text{mass of target atom}$
- $E_i = \text{Energy of ion after collision}$
- $E_{i0} = \text{Energy of incident ion}$
- $E_r = \text{Energy of the recoiling target atom}$
Applying the laws of conservation of momentum and energy for this collision gives:

\[
\frac{E_I}{E_{I,0}} = \frac{\cos \theta + \sqrt{\frac{m_T^2}{m_i^2} - \sin^2 \theta}}{1 + \frac{m_T}{m_i}}
\]

Here, the scattering angle \( \theta \) can be determined by the angle between the ion source and the analyzer, which is fixed by the experimental set-up. The energy of the scattered ion which can be measured at the detector, only depends on the mass of the target atom. In other words, if the primary energy of the incident ion is known, the mass of the target atom can be determined and thus the information about the atomic composition of surfaces can be obtained. The resolution (i.e. the ability to separate signals from different target atoms) of the technique depends on monoenergicity and collimation of the incident ions and the angular acceptance of the detector analyzer. Acceptance angle is generally a few degrees and if it is larger more ions can be accepted resulting in low signal to noise ratio; however the broader peaks may reduce the resolution. The extreme surface sensitivity in this technique stems from ion neutralization. Incident ions that may penetrate into the surface may be neutralized by the free charges from the bulk and thus will not be detected in the analyzer which only detects ions. One disadvantage of this method is that the unknown neutralization cross sections from different elements can leave uncertainties in determination of the exact ratio of atoms in surfaces.

### 2.4.3 Diffraction Techniques

Electrons or x-ray photons diffracted or scattered by atoms in a solid surface carry information about its crystal structure or the atomic arrangement within the unit cell. Analyzing the intensity or the pattern produced by the diffracted beam, the crystal lattice can be determined. The concept
of reciprocal lattice becomes useful for this analysis and the following discussion provides the basics about a 2-dimentional (2D) lattice in real space and reciprocal space.

Surfaces and interfaces are generally considered as 2D objects and the surface lattice can be described by the lattice vector; \( \mathbf{r} = p \mathbf{a} + q \mathbf{b} \) (\( p, q \) are integers) with two translation vectors \( \mathbf{a} \) and \( \mathbf{b} \) in real space. Then in the reciprocal space, the reciprocal lattice vector becomes \( \mathbf{G} = h \mathbf{a}^* + k \mathbf{b}^* \) (\( h, k \) are integers) with \( \mathbf{a}^* \) and \( \mathbf{b}^* \) vectors defined as;

\[
\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{n}}{|\mathbf{a} \times \mathbf{b}|}\\
\mathbf{b}^* = 2\pi \frac{\mathbf{n} \times \mathbf{a}}{|\mathbf{a} \times \mathbf{b}|}
\]

where \( \mathbf{n} \) is the unit vector normal to the surface.

The diffraction pattern is directly related to the crystal lattice in reciprocal space by the condition;

\[
\mathbf{k} - \mathbf{k}_0 = \mathbf{G}_{hk}
\]

where \( \mathbf{k}_0 \) is the incident wave vector, \( \mathbf{k} \) is the scattered wave vector, \( \mathbf{G}_{hk} \) is the reciprocal lattice vector. For elastic scattering, \( |\mathbf{k}_0| = |\mathbf{k}| \) by the law of conservation of momentum. For representing the diffraction pattern one can do the Ewald construction as illustrated in Figure 2.16a. The steps to follow are; (i) Construct the reciprocal lattice for the given crystal, (ii) Draw \( \mathbf{k}_0 \) vector with respect to an origin chosen such that \( \mathbf{k}_0 \) terminates at a reciprocal lattice point, (iii) Draw a sphere of radius \( k = 2\pi/\lambda \) with respect to the chosen origin, (iv) Draw \( \mathbf{k} \) vector to the reciprocal lattice points that lie on the surface of the sphere. Now, it satisfies the conditions \( \mathbf{k}_0 - \mathbf{k} = \mathbf{G}_{hk} \) and \( |\mathbf{k}| = |\mathbf{k}_0| \) which are the necessary conditions to get a diffraction pattern.
2.4.3.1 Low Energy Electron Diffraction (LEED)

LEED is a surface sensitive technique that provides surface structural information. The electron energy used in LEED is ~30-200 eV and thus the wavelength of electrons are only ~1-2 Å which satisfies the condition for atomic diffraction (from de Broglie wavelength, \( \lambda = \frac{\hbar}{2mE}^{1/2} \)). Also, the mean free path of the low energy electrons is very short (order of a few atomic layers), so that only the atoms in the top layers are able to contribute to elastic scattering.

It should be noted that, for 2D lattices, the periodicity normal to the surface is considered infinite which leads the reciprocal lattice vector normal to the surface go to zero; i.e. the reciprocal lattice points normal to the surface are infinitely dense and considered as rods. Then the Ewald construction in LEED can be explained as in Figure 2.16b. Here, only the parallel component of the wave vector to the surface is conserved; i.e. \( k_0^\parallel - k^\parallel = G_{hk} \). In this case, the incident wave vector terminates at a reciprocal lattice rod and the intercepts of the rods with the Ewald sphere give \( k \) vectors for diffracted beams.

The LEED experimental set up shown in Figure 2.17 consists of three main components; an electron gun to produce low energy electrons, sample holder with the sample, a hemispherical fluorescent screen to observe the diffraction pattern of the elastically scattered electrons.
In this set up, the cathode is at \(-V\). Last aperture of the lens, sample and the first grid are grounded. Electrons from the cathode accelerate towards the sample with an energy \(eV\) and scatter from the sample to the field free space. Inelastically scattered electrons are rejected by the second and third grids. The second and third grids are at close to cathode potential but somewhat lower than that. If \(\Delta V\) is larger, then the LEED pattern is brighter but the background intensity is also higher. Therefore in order to get a better contrast in the LEED pattern, the retarded potential should be tuned. The fourth grid is grounded and the fluorescent screen is at high potential \(\sim 5 \text{ kV}\). Therefore, the diffracted electrons that are elastically scattered get reaccelerated towards the screen and produce the diffraction pattern. This pattern can be viewed by placing a viewport in front of the back side of the sample or through a view port placed behind the transmission phosphorescent screen.
Figure 2.18: Schematic diagram of a LEED diffraction pattern. This illustrates the labelling style of diffraction spots in the pattern.

Figure 2.18 shows a schematic of a typical LEED pattern for normal incidence of a primary electron beam. The diffraction pattern that have been observed is the surface lattice in the reciprocal space. The number of spots seen in the pattern can be changed by changing the electron energy, which changes the radius of the Ewald sphere. A well-ordered crystalline surface produces a pattern with bright sharp spots on the screen. Surfaces with defects and imperfections cause weakening and broadening of the spots. Disordered or amorphous surfaces and fine polycrystalline samples do not produce diffraction patterns in LEED. Bulk terminated surfaces would produce 1×1 LEED patterns. When the surfaces have superstructures formed on top, due to reconstructions of the surface layers or due to new structures formed after depositing a new material, then
additional LEED spots or the so-called ‘superspots’ are developed. If, in real space, the superstructure has doubled the periodicity with respect to the bulk unit cell, then in the diffraction pattern in the reciprocal space would exhibit half-order spots.

Although the LEED diffraction pattern is able to give information about the symmetry and the periodicity of the surface unit cell compared with the bulk crystal structure, it does not give information about the atom positions or structural information of the surface. Therefore, in order to get the structural information, LEED I-V analysis, i.e the intensity of the spots with the electron energy should be recorded. These I-V curves are compared with the simulated I-V curves that have been obtained for a predicted structure. Comparison done by visual inspection of the two I-V patterns is subjective and not reliable. Therefore, a quantitative criterion should be employed for proper comparison between the model and experiment. Calculating the reliability factor (R-factor) is a method proposed in the past for this purpose. More details of R-factor calculation may be found in the references [48-51]. Generally, R≤0.2 implies good agreement, R~0.35 implies moderate agreement and R~0.5 implies bad agreement. Determination of the structure this way is quite time consuming since it may require a lot of computational effort and structure modifications in order to get the best match (minimum R-factor) between theory and experiment.

2.4.3.2 Reflection High-Energy Electron Diffraction (RHEED)

This is also a widely used technique in UHV systems, especially in determining the crystallinity of surface structures. In contrast to LEED, RHEED utilizes high-energy electrons incident on the sample at a grazing angle and the scattered electrons are detected at a grazing angle through which the surface sensitivity was achieved. The Ewald sphere construction for RHEED is shown in Figure 2.19a. In this case, the Ewald sphere is larger than the spacing between the reciprocal space
lattice rods and intersects these rods at grazing angles. Streakiness in the RHEED patterns are commonly observed due to finite thickness of Ewald sphere and the reciprocal rods. Figure 2.19b shows the experimental set up used in RHEED. The electron energy used here ranges from 5-20 keV and the grazing angle is \( \sim 1-5^\circ \) with respect to the sample surface. Unlike in LEED, no additional acceleration of the scattered electrons is needed as the primary electron energy is high enough to produce intense fluorescence on the screen.

![Ewald construction in RHEED and RHEED experimental set up.](image)

**Figure 2.19:** Ewald construction in RHEED and RHEED experimental set up. (a) Ewald construction, (b) RHEED set-up.

The basic structural information gained in RHEED is very similar to that in LEED. However, RHEED provides a couple of additional interesting information as well. One of them is that, it can identify the presence of 3D crystalline islands on the surface by producing transmission electron diffraction spots (see Figure 2.20b). The other one is, by measuring the RHEED intensity during growth, the film thickness can be monitored and controlled; only when the films grow layer-by-layer fashion. A typical shape of a RHEED intensity profile recorded during film growth is shown in Figure 2.20c. As can be seen, the intensity demonstrates well-defined oscillations the period of
which corresponds to the time taken for completion of a monolayer. The intensity maxima occur upon completion of an atomically smooth surface monolayer while the minima correspond to most disordered surface or small 2D islands of about half a monolayer coverage. Measuring the intensity oscillations with time provide information about the growth rate and thus this is widely used in MBE film growth.

**Figure 2.20:** Additional information gained in RHEED. (a) Surface scattering from flat surface, (b) Transmission diffraction in 3D crystalline islands. (c) Intensity oscillations observed in layer-by-layer film growth.

### 2.4.3.3 X-ray Photoelectron Diffraction (XPD)

X-ray photon induced photoelectron diffraction is a powerful method for investigating the surface atomic structures. A comprehensive review on XPD is given in [52]. In particular, this method is useful in probing local atomic structures at and below surfaces and thus in studying interface layers. In this method, the core-level electrons are generated by X-rays and these photoemitted electrons act as a localized monochromatic electron wave, the amplitude of which is inversely proportional to the distance of the electrons from the emitting atom, propagating from the center of the atomic potential. This technique is therefore element specific; i.e. the energy and the angular distribution of the photo-emitted electrons carry information about the local atomic structures around a specific emitter atom and in most cases, diffraction processes up to 5th order or less is sufficient for detailed analysis. The probing range is limited by the mean free escape depth of
photoelectrons. Collecting the photoelectron intensities by varying the angle (angle-resolved) or by varying the energy (energy-resolved) allows the determination of crystal structures of the samples in XPD.

As illustrates in Figure 2.21, the basic processes involved in XPD are: (i) Generation of localized core-level photoelectron by an X-ray photon, (ii) Propagation of photoelectron as a spherical wave around the emitter atom, (iii) Scattering of the wave by nearest neighbor atoms and generating secondary waves originating from neighbor atoms, (iii) Propagation and interference of direct wave and the elastically scattered part of the waves from neighbor atoms (both of these waves have same λ and constant relative phase), (iv) Recording the interference pattern at the detector as a function of emission angle or as a function of electron kinetic energy. This interference pattern is a result of single or multiple-scattering processes and path length differences of the direct and scattered electron waves.

Figure 2.21: Schematic diagram of the processes involved in XPD. A core-level photoelectron propagates and scatter from a neighboring atom environment. The interference pattern of the direct wave and the scattered wave is recorded at the analyzer.
Intensity measured at the detector is given by;

\[ I(k) = |\psi(k)|^2 \]

where, \( \psi(k) \) is the final state wave function which includes directly emitted wave, scattered waves from all the neighbor atoms and also the multiple scattering effects. Considering only the single-scattering for simplicity;

\[ I(k) = |\psi_0(k) + \sum_l \psi_l(k)|^2 \]

where, \( \psi_0(k) \) is the direct wave from the emitter atom and \( \psi_l(k) \) is the single scattered wave function for the \( l^{th} \) atom. This term contains factors describing incoming polarization of the x-ray photon beam, mean free path of electrons, geometric path lengths as well as material properties such as scattering amplitude and phases which are functions of scattering angle. Specifically, the geometric phase difference \( \exp[ikr(1-\cos \theta)] \) which introduces the path length differences, is a function of scattering angle and the outgoing wave vector. Dependence of this exponential term on \( k \) and \( \theta_l \) can be used for structural analysis. For instance, the intensity of the diffracted electrons can be recorded at a fixed angle for varying \( k \) values, i.e. as a function of kinetic energy for the photoelectrons. For this, a tunable energy X-ray source is needed which, in general, is found in synchrotron storage rings. On the other hand, keeping the X-ray photon energy constant, one can record the intensity of the photoelectrons by varying \( \theta_i \), which can be achieved by varying the polar and azimuthal angles of emission via rotating the sample with respect to the source and the detector or via rotating the detector with respect to the source and the sample. This can be done using ordinary X-ray sources and does not necessarily require synchrotron radiation. The first method of recording data for varying \( k \) is generally called ‘energy-scanned XPD’ while the second method is called ‘angle-scanned XPD’.
Figure 2.22 illustrates occurrence of photoelectron diffraction in a simple and an ideal situation where there are two propagating spherical waves, one from an emitter atom and the other from a scatterer with zero scattering phase shift, interact and form an interference pattern. As can be seen, the most intense 0th order intensity maximum occurs when the kinetic energy of the photo-emitted electrons is large. The reason for this is large scattering amplitude and small scattering phase shifts in the forward direction of the emitter towards the detector. This phenomenon is called ‘forward scattering’ or ‘forward focusing’. At small kinetic energies, the scattering amplitude and the phase shifts sensitively depend on the changes in kinetic energies even by a few electron volts. It is also clear from Figure 2.22 that when the photoemission intensity is measured for varying θ, an interference pattern that is unique to the local atomic arrangement of the crystal can be recorded.

Figure 2.22: Interference pattern produced by two ideal spherical waves from an emitter and a scatterer. Scattering phase shift is equal to zero. Zeroth order peak is the strongest for high kinetic energy regime. Higher order peaks become stronger for low kinetic energies.
Recalling the behavior of inelastic mean free path (IMFP) of electrons with the kinetic energy is important at this point, in order to determine the probing depth. According to the universal curve for IMFP versus electron kinetic energy, the IMFP is as low as ~1-2 Å for electron kinetic energies of ~ 100 eV. [For $E_{\text{kin}} > 150$ eV, IMFP can be calculated using $\text{IMFP} \approx 0.522(E_{\text{kin}})^{1/2}$ which is valid to a reasonable degree.]

Therefore, by tuning the X-ray photon energies such that the kinetic energy of the photoemitted electron is ~ 100 eV, this method becomes extremely surface sensitive and can be used to determine surface structures and sub-surface structures accurately. Distinguishing between surface, sub-surface (or bulk) components is trivial as these components exhibit core-level shifts in the peak position due to structural changes or due to different chemical environments. By recording the angular dependence (polar/azimuthal) of each component, the structures for the surfaces and for the buried surfaces can be identified. However, an energy source with resolution better than 0.3 eV is needed in order to effectively resolve the small shifts in the peak positions.

Experimental set-up for XPD measurements see Figure 2.23) consists of an electron energy analyzer, an excitation source and a sample clamped in holder that can be rotated over polar and azimuthal angles. Here, the intensity of the photoemitted electrons is recorded as a function of the emission angle over the full solid angle above the sample surface. The angle $\alpha$ indicated in the figure is the angle between the source and the analyzer and is generally fixed at $\sim 45^\circ$-$70^\circ$. The polar/azimuthal angle increment can be $\sim 2^\circ$-$4^\circ$ and at least 1000 photoemission spectra have to be recorded for producing a single diffraction pattern. The typical scan period for one data point can ~ 20 sec, depending on the energy window and the peak intensity. This process can be quite time consuming and thus high flux excitation sources, automated computer controlled data acquisition
and high speed electron detection systems are invaluable in reducing the time span of the experiment. Therefore, these experiments are performed in synchrotron radiation facilities.

![Figure 2.23: Experimental set-up used in XPD and EDAC cluster. (a) Schematic diagram of the general geometry of a XPD experimental set-up. (b) An atomic cluster shape used in EDAC simulations.](image)

As discussed in LEED, in determining the correct structure of the surfaces (or sub-surfaces), qualitative and quantitative (R-factor analysis) comparison of the experimental diffraction pattern to a simulated diffraction pattern of a predicted structural model is customary in XPD as well. In the experiments performed in the present work, these simulations were carried out using EDAC (Electron Scattering in Atomic Clusters) package for DFT (Density Functional Theory) based predicted structural models. EDAC cluster-model approach that implements multiple scattering of electrons in solids and molecules is a computer code developed by F.J. Garcia De Abajo and co-workers. A comprehensive description of this is given in reference [53]. Briefly, the clusters for the structural models predicted for the samples under investigation have been constructed by defining the coordinates of the atoms in the unit cell layer by layer fashion starting from the topmost surface layer with respect to a reference point. Figure 2.23 shows a simple schematic
representation of a cluster. The size and the scattering volume of the cluster are defined by $R_{\text{max}}$. The computation time strongly depends on $R_{\text{max}}$. Apart from the cluster coordinates, the emission energy (i.e. kinetic energy of the photo-emitted electrons KE), inner potential ($V_0$), IMFP, maximum orbital quantum number ($l_{\text{max}}$), emitters, scattering order and Debye temperature ($\theta_D$) are few of the important parameters to be chosen carefully so that the simulated data produces a diffraction pattern that is well-matched with the experimental XPD pattern. An example of a complete input file is given in Appendix II. Quantitative comparison can then be carried out using R-factor analysis and, as mentioned, for good theory-experiment agreement, the expected R-factor is $\sim 0.2$. 


CHAPTER 03
RESULTS AND DISCUSSION

Experimental and theoretical results are presented under two main sub topics; (i) Surface properties of TiO₂ in sensing and catalysis, (ii) Monolayer/mixed oxide growth on TiO₂. Sensing and catalysis are two major aspects through which the surface properties of TiO₂ could be properly understood. Monolayer metal/metal oxide growth on TiO₂, which could result in structural and compositional modifications of the surface, may lead formation of novel functional materials that could be more efficient in sensing and catalysis applications. The experimental results that have been presented here are performed at ISSL (Interface and Surface Science Laboratory) in our home institution University of South Florida and at SuperESCA beamline in Elettra synchrotron laboratory in Trieste, Italy. Theoretical results have been carried out by our collaborators at Key Laboratory of Chemical Engineering, Centre for Computational Chemistry and Research Institute of Industrial Catalysis in East China University of Science and Technology, China.

3.1 Surface Properties of TiO₂ in Sensing and Catalysis

In order to understand the sensing and catalytic properties of TiO₂ surface we carried out experiments for few of the selected systems and the results are discussed below under the sub topics: (i) Molecular scale investigation of TiO₂ gas sensing (ii) Crystallographic properties of TiO₂ in photocatalysis.
The results of the gas sensing studies have been published in Journal of Physical Chemistry C-with the title “Combined Surface Science and DFT study of the adsorption of Dinitrotoluene (2,4-DNT) on Rutile-TiO₂(110): Molecular scale insight into Sensing of explosives”[54].

TiO₂ photocatalysis results are published in Scientific Reports-with the title “Why is anatase a better photocatalyst than rutile?”[14], and in Thin Solid Films- with the title “Photocatalytic activity of anatase and rutile TiO₂ epitaxial thin films grown by pulsed laser deposition” [15].

3.1.1 Molecular Scale Investigation of TiO₂ Gas Sensing

In this study, using a combined STM and DFT-based calculations, we investigate the adsorption and desorption behavior of DNT on Rutile-TiO₂(110) in an atomistic level. In addition to that, we test the thermal stability and reactions of the adsorbed DNT molecules and finally investigate the possibilities of recovering the surface via UV light irradiation.

Figure 3.1: Schematic diagrams of the two UHV systems in which the experiments have been performed. One system is equipped with XPS and the other one has STM. The main components used in each chamber are as labeled.
3.1.1.1 Experimental and Computational Methods

**Experimental Methods:** The experiments were performed in two UHV chambers equipped with STM and XPS respectively (Figure 3.1). The base pressure of the chambers were $\sim 2 \times 10^{-10}$ Torr. The STM system consists of a room temperature Omicron VT-STM and the XPS uses a non-monochromatized Al-anode x-ray source and a five-channel hemispherical energy analyzer. Empty state STM images were recorded with electrochemically etched tungsten tips cleaned via in-situ voltage pulsing. The rutile-TiO$_2$(110) single crystalline surface preparation and DNT adsorption and desorption procedures were identical for both UHV systems. Briefly, the commercially available rutile-TiO$_2$(110) crystal (MTI-corporation) was prepared by multiple cycles of Ar$^+$ sputtering at room temperature (1 kV, 5 $\mu$A, 40 min), followed by annealing at 600 °C for 20 min. This cleaning procedure, as discussed earlier, causes bulk reduction of TiO$_2$ and formation of O$^2-$ vacancies and Ti$^{3+}$ interstitials which become mobile at low temperatures and are able to react with the adsorbed molecules. The sample cleanliness was checked by STM or XPS measurements. DNT dosing was done in each UHV system through precision leak valves with their open ends connected to directed stainless-steel tubes. The distance between the sample surface and the tube end was as close as ~4 cm. At room temperature, DNT is a pale yellow solid powder and has a low vapor pressure. This solid DNT powder was filled into a CF-flanged glass-test tube and connected to the precision leak valve with stainless steel tubing. This dosing assembly was evacuated via a turbo pump. In order to increase the vapor pressure, the stainless steel tubing was brought into ~80 °C by wrapping it up with heating tapes and the solid DNT powder was brought to melting point by dipping CF-flanged glass test tube in boiling water. For measuring the UV reactions, the DNT adsorbed TiO$_2$ surface was illuminated with UV light by using a 100 W
Hg-arc lamp coupled into the chamber through a UV fiber optic feedthrough made up of 0.6 mm fused silica optical fiber. This was brought as close as ~1 cm to the sample surface during illumination. In this process any additional heating of the sample due to the infrared radiation from the emitted UV light has been avoided by using a water filter.

**Computational Methods:** First-principles DFT based calculations were done within the generalized gradient approximation (GGA). The PWScf code included in the Quantum-Espresso package was used. Electron-ion interactions for C, N, O 2s, 2p, and Ti 3s, 3p, 3d, 4s shells were described by ultrasoft pseudopotentials. For the smooth part of the wave functions, the plane-wave basis set cut-offs were 25 and the augmented density was 200 Ry. Periodic slab model with three O-Ti-O tri layers was used for rutile TiO$_2$(110) surface. The vacuum between the slabs was greater than 10 Å. 4×2 surface cell the size of which is 11.796×12.971 Å$^2$ and corresponding 1×1×1 $k$-point mesh were used. The adsorption was modeled on one side of the slab. During optimizations, all the atoms, except those in the bottom TiO$_2$ tri-layer of the slab, were allowed to move with a force threshold of 0.05 eV/Å. Following expression was used for calculating the average adsorption energy $E_{ad}$ of DNT:

$$E_{ad} = -\frac{1}{n} \left( E_{DNT/TiO_2} - nE_{DNT} - E_{TiO_2} \right)$$

Where; $E_{DNT/TiO_2}$ is the total energy of the system with n DNT and TiO$_2$ support in a surface cell, $E_{TiO_2}$ is the total energy of the TiO$_2$ slab, $E_{DNT}$ is the total energy of a single DNT molecule in gas-phase. To estimate the van der Waals (vdW) interactions between co-adsorbed DNT molecules London dispersion corrections of the Grimme DFT-D type were included in the calculations. Tersoff-Hamann’s approach in the constant-current mode was used for simulating the STM
images. For plotting the isosurface of the electronic density at $2 \times 10^{-5}$ e/bohr$^3$ an empty-state window of 1.0 eV above the edge of the conduction band was employed.

### 3.1.1.2 Experimental and Computational Results and Discussion

The results and discussion of this study are presented in two sub sections; (i) Experimental studies of room temperature adsorption of DNT on TiO$_2$(110) supported with DFT simulations, (ii) Thermal stability, reactions and UV-light induced desorption of DNT.

**Room Temperature DNT Adsorption on TiO$_2$(110):** Figure 3.2c shows an STM image of a clean TiO$_2$(110) surface that has Ti$^{4+}$ and bridging O$^2-$ sites along bright and dark rows respectively. Figures 3.2d, 3.2e and 3.2f shows STM images for sub-monolayer coverages of DNT after dosing at room temperature. As can be seen, DNT molecules appear as bright protrusions on terraces and no significant adsorption on step edges was observed. This may imply that either the DNT molecules are not mobile enough at room temperature to reach step edges or the step edges in this surface do not offer strong adsorption sites. Also, in subsequent STM images the DNT molecules were imaged in the same position which supports the fact that they are immobile at room temperature. It is important to point out that this behavior of DNT molecules is different from carboxylic acids or catechol in which the dissociated H adsorbed on the surface as hydroxylate facilitating the diffusion of the molecule. Since DNT does not leave H on the surface this kind of diffusion pathway is unavailable for DNT molecules.
According to the high resolution STM image shown in Figure 3.2f, the bright protrusions are centered over the bright rows, i.e. 5-fold Ti atoms in the substrate. This agrees with the expected adsorption configuration in which the nitro-oxygen coordinate to the substrate Ti-atoms (see Figure 3.2a,3.2b). Also, in Figure 3.2e, we observe that for low coverage of DNT, the adsorption of molecules is not just random but rather form linear clusters extending across the Ti rows up to about five molecules long. These linear clusters are either perpendicular to the rows or make an angle corresponds to molecules that are one unit cell offset in the neighboring rows. This may have resulted in due to some kinetic trapping or an attractive force present between the adsorbed molecules across the neighboring 5-fold Ti rows. In contrast to this, no such chain-like clusters were observed along the Ti rows due to the low mobility and/or weak attractive interaction between the molecules along the rows. However, there are just two molecules sometimes lying as close as...
~ 6 Å along the rows. This distance matches well with the separation of two surface unit cells of TiO$_2$(110) along [001] direction. Moreover, the height of the molecules are ~1.5 Å as measured by STM.

At high coverage, DNT molecules form an ordered overlayer with a 2×1 superstructure on TiO$_2$(110) and saturate with half a monolayer coverage (that is, if a monolayer is defined as one DNT molecule per unit cell of TiO$_2$(110)-1×1) (see Figure 3.3a). Anti-phase domain boundaries occur when the molecules are offset by one unit cell in neighboring Ti rows, as is expected for a 2×1 superstructure, and the overlayer unit cell appears as a c(2×2) superstructure. Figure 3.3a shows the unit cell for the 2×1 superstructure with dimensions ~ 6 Å × 6.5 Å (almost a square unit cell).

**Figure 3.3**: High coverage of DNT adsorbed on TiO$_2$(110). (a) STM image after saturation coverage of DNT. At saturation, (2×1) or c(2×2) superstructure is formed as shown in the insets. A minority adsorption feature is also visible in this image which covers ~5% of the surface. (b1-b6) Bias dependent STM. At low bias voltages (0.8-1.0 V) two domains can be observed. At 1.1-1.2 V a two lobe structure has been observed and at high voltages ~ 1.2 V, molecules were imaged as single protrusions. Reprinted with permission from reference [54].Copyright 2016-American Chemical Society.

Figure 3.3a also indicates presence of two different adsorption species. The one with strong contrast covers ~90% of the surface while the minority of ~5% has a lighter contrast. This contrast
difference may have resulted in due to two possible adsorption configurations. According to the molecular configuration of DNT, only one out of two nitro groups can absorb on the surface at a time. This can form bonds with the substrate with either methyl group pointing away from the surface or methyl group inclined at 30 degrees towards the surface as illustrated in Figure 3.3. However, the assumption that these species with lighter contrast could be some contaminant or another by-product of DNT cannot entirely be excluded.

Figure 3.3b shows the bias dependent STM which reveals the electrons tunneling into different molecular orbitals of DNT causing contrast changes in the image. At bias voltages as low as 0.8 V the periodicity of molecules can still be imaged. Interestingly, at 0.9 V, two different domains appeared both of which exhibited 2×1 superstructure. This kind of domains may have resulted in either as a consequence of two possible adsorption configurations or due to rotation of molecules around C-N bond. At higher bias voltages only one structure was observed and for 1.1-1.2 V a two-lobe feature appeared for each molecular site.

The DFT-based computational results on this system is discussed next for different coverages of DNT.

Single DNT molecule: Energetically most favorable adsorption configuration is bridge-bidentate adsorption where one nitro group coordinates with 5-fold Ti. As shown in Figure 3.4(a,d), for a single molecule adsorption, the methyl group-up and methyl group-to the side have similar energies of 1.36 eV and 1.44 eV. Energy for methyl group-to the side configuration has slightly higher energy due to a possible weak interaction between this group and the substrate. In order to make adsorption in neighboring 5-fold Ti sites possible, rotation of molecule seems essential.
Figure 3.4: DFT-based calculated structure for DNT adsorption on TiO\(_2\)(110). Calculated structures (top view) of (a,d) single DNT molecule, (b,c,e,f) two co-adsorbed DNT molecules, (g,h) four co-adsorbed DNT molecules on TiO\(_2\)(110) surface. Average adsorption energies are listed below each structure. (i) Simulated STM image of the more favorable adsorption structure a in a 3×3 expansion. Reprinted with permission from ref[54]. Copyright 2016-American Chemical Society.
Low coverage of DNT: To understand the inter-molecular interactions, co-adsorption of DNT molecules in one 4×2 surface cell have been considered. Figure 3.4(b, c, e, f) shows two such co-adsorbed molecules on 5-fold Ti atoms along the rows in planar configuration (planar configuration implies unrotated state of the molecule). Here, the distance between two DNT molecules facing each other is 6.489 Å which is equal to the lattice parameter and the adsorption energy is 1.16 eV. This energy is lower than that for a single DNT molecule. This implies that the co-adsorption across 5-fold Ti rows is unfavorable compared with single molecule adsorption when the distance between the molecules is large to give rise to vdW interactions. However, a drastic increase of the average adsorption energy was observed when the molecule has been rotated around the C-N bond of adsorbed nitro-group by about 30 degrees. This increase in energy may not just be associated with the rotation process but also due to an occurrence of the vdW interaction between molecules approaching each other by rotation. Nevertheless, this co-adsorption of molecules across 5-fold Ti rows is still less-favorable than single molecule adsorption. Turning into adsorption along the rows, we already mentioned that the planar DNT molecules bridge-bidentately adsorb on 5-fold Ti atoms. Due to its dimensions, this configuration prevents a molecule adsorbing to the next 5-fold Ti site along the row. Therefore, a rotation around the C-N bond is required in this case as well. 90° of such rotation removes the steric blocking completely. Similar to the previous case, the distance between molecules i.e. 5.9 Å which is equal to the lattice parameter in that direction, is too long to give rise to vdW interactions. However, the vdW interactions could be more favorable along the rows than across the rows due to the shorter distance between the sites along the rows than across the rows. This discussion of DFT results for low coverage DNT adsorption does not completely explain what has been observed in STM, where a few molecules long chain formation was observed across the rows while no such chains observed
along the rows. The reason for no lining up along the rows may be explained as a result of the immobility of DNT molecules at room temperature although the sites with lower energy exist along the rows. The reason for the occurrence of short chains across the rows, on the other hand, could be a result of kinetic trapping in these sites during the adsorption process. The two pathways that this could happen are: (i) immediately after adsorption, the molecule may diffuse a shorter distance until the adsorption energy is dissipated. Two such diffusing planar molecules may interact through vDW interactions on neighboring rows subsequently maximizing the interaction through rotation and attaining a local energy minimum. This may lead to strong kinetic trapping of molecules enabling them to occupy neighboring rows, (ii) an adsorbed molecule capturing a molecule that is close to the surface through vDW interactions guiding it to be adsorbed to a neighboring row. Both these pathways may lead to formation of short chains across the rows as observed in STM.

Monolayer coverage of DNT: Adsorption of four DNT molecules in a 4×2 surface cell (full coverage) can result in a 2×1 or a c(2×2) superstructure (Figure 3.4(g,h))The latter corresponds to anti-phase domain boundaries caused by one unit cell offset between the molecules adsorbed in neighboring rows. The interaction across the rows for c(2×2) superstructure is energetically less favorable than the other. Figure 3.4i is the simulated STM image for a monolayer coverage of DNT with 2×1 superstructure. Pairs of lobes can be observed from nitro-group and phenyl ring which is in agreement with experimental STM at low bias voltages.

**Thermal Stability, Reactions and UV-Light Induced Desorption of DNT:** In order to study the thermal stability and reactions, a sample with a close to-monolayer coverage of DNT was prepared and then annealed to different temperatures in UHV. As can be seen in Figure 3.5b, annealing to
250 °C results in larger prostrations while for temperature higher than ~300 °C, DNT completely disappears leaving only a few isolated large protrusions. This may suggest that ~300 °C is the temperature needed for DNT to desorb from the surface. When annealing to temperatures around ~350 °C the remaining larger protrusions disappeared exhibiting reduced TiOx islands on the surface, which usually form when subsurface Ti interstitials diffuse to the surface and react with adsorbed oxygen. This observation is similar to what has been observed for acetate in the literature. Therefore, for recovering the close-to-stoichiometric surface originally started with, annealing to higher than 350 °C is needed. It is clear that before thermal desorption DNT participates in other reactions, presumably with the excess Ti in the surface.

**Figure 3.5:** STM images showing the thermal reactions of DNT. (a) Incomplete monolayer of DNT after deposition at room temperature. (b, c, d) after annealing at 250 °C, 300 °C, and 350 °C. Image size is 50 nm× 50 nm. Reprinted with permission from ref[54].Copyright 2016-American Chemical Society.
In order to gain more insight about these reactions, XPS studies were carried out in the second UHV system maintaining the same adsorption and desorption conditions Figure 3.6.

**Figure 3.6**: XPS studies of DNT adsorption and thermal reactions on TiO$_2$(110). (a) RT adsorption with increasing DNT exposure. (b) Thermal desorption/reaction of DNT, (c) adsorption reaction of DNT with TiO$_2$(110) held at 350 ºC. Reprinted with permission from reference[54], Copyright 2016-American Chemical Society.
(Figure 3.6(a1-a3)) shows room temperature adsorption of DNT on TiO$_2$(110). As can be seen, the C 1s and N 1s peak intensities increase with the exposure time and reach a saturation. Upon adsorption of DNT, Ti 2p peak undergoes a rigid shift of $\sim$0.2 eV to lower binding energy regime and the Ti$^{3+}$ shoulder feature (which generally exists in Ti 2p XPS in vacuum cleaned or reduced samples) quenches. In other words, the reduced TiO$_2$ sample oxidizes upon DNT adsorption. These effects are consistent with transfer of electrons from the TiO$_2$ substrate to DNT molecules. The peak shift is consistent with the upward band bending of TiO$_2$ which in fact the main effect that enables gas-detection.

The surface with a saturated coverage of DNT was then annealed to different temperatures and the C 1s, N 1s, Ti 2p signals were monitored. As shown in Figure 3.6b a high(low) binding energy shoulder appeared in Ti 2p for annealing temperature $\sim$200 °C and 300 °C. Dosing DNT at elevated temperatures, on the other hand, causes the Ti$^{3+}$ to continuously increase as shown in Figure 3.6c. This implies that this Ti$^{3+}$ shoulder feature is not just a consequence of O-vacancies but due to some reaction of DNT with the substrate. This is also visible in N 1s peak evolution with temperature (see Figure 3.6b2 and c2). N 1s undergoes a broadening of the peak shape upon annealing to 300 °C and also upon dosing DNT at elevated temperature. However, the C 1s peak shape, in both cases, remains the same shape but decreases in intensity with temperatures. This suggests that the reaction of nitro-group of DNT with the TiO$_2$ substrate at elevated temperatures may have formed a titanium-oxynitride which give rise to the second component in N 1s peak and the shoulder feature in Ti 2p peak. Supporting this statement, the low binding energy component of Ti 2p peak shows a shift of $\sim$2 eV to lower binding energy (compared to that of TiO$_2$) which matches well with the peak position of Ti oxynitride. Therefore it can be concluded
that the larger protrusions observed in STM images were these titanium-oxynitride reaction products resulted from reactions of DNT with thermally activated Ti-interstitial diffusion.

Since the temperature induced reactions leave strong reaction products on the TiO₂ surface, thermal-desorption does not seem to be suited for DNT desorption and recovering the surface of TiO₂(110) as a gas sensor. Therefore, a non-thermal desorption method that is UV-light induced desorption was tested. Interestingly, as can be seen in Figure 3.7, DNT can be effectively desorbed from TiO₂ via photon-activated process upon UV irradiation. Although photocatalytic decomposition of DNT by TiO₂ is reported in the past, further investigation may be needed to explain the exact process involved in UV-light induced desorption. Nevertheless, in terms of gas sensing, this indeed seems to be a promising method in restoring TiO₂(110) surface.

![Figure 3.7: UV light induced desorption of DNT. STM images of saturation coverage of DNT on TiO₂(110) (a) before and (b) after shining with UV light. DNT seems to be effectively desorbed by photon activated process. Reprinted with permission from reference[54], Copyright 2016-American Chemical Society.](image)

### 3.1.1.3 Conclusions

2,4-DNT adsorbs on TiO₂(110) surface in a bridge-bidentate fashion with the two nitro-oxygen atoms coordinated to two neighboring 5-fold Ti atoms along the Ti rows. At saturation coverage, a c(2×2) or a 2×1 superstructure formation was observed. Molecular rotation around the adsorbed
C-N bond seems essential for enabling dense packing. A stronger molecular interaction is resulted with the cost of rotational energy. The rotation of the molecule also enables higher surface coverage and an overall lowering of the energy due to the strong adsorption energy of DNT. Due the electron transfer from TiO$_2$ to the DNT molecules upon adsorption, causes oxidation of Ti$^{3+}$ and upward band bending as observed in XPS, which gives the gas response in semiconductive oxide gas sensors. At elevated temperatures, DNT first reacts with Ti interstitials, present in the slightly reduced TiO$_2$ substrates and then desorbs at temperatures higher than ~350 °C. The strong adsorption of DNT on the TiO$_2$(110) makes it an effective sensor for detecting gas-phase DNT. DNT desorption from this surface does not seem to be as effective as it has been reported for TiO$_2$-B sensors, which may not support bidentate adsorption configuration for the DNT molecules. According to our observations however, DNT can be effectively removed from the surface by UV irradiation suggesting a fast recovery time and thus another approach of making it an effective gas sensor.

3.1.2 Crystallographic Properties of TiO$_2$ in Photocatalysis

In this study, we use anatase (001) and rutile (101) thin films grown by PLD to compare the photocatalytic activities of the two different phases of TiO$_2$. Also we measure the photocatalytic activity as a function of thickness in order to explain the differences in the activity for the two phases. In addition to that, we use different orientations ((101), (111), (100) and (001)) of commercially available single crystalline rutile-TiO$_2$ samples to study the surface orientation dependence of TiO$_2$. Finally, we propose a simple and an efficient way of enhancing the photoactivity by vacuum reduction of TiO$_2$. 
3.1.2.1 Experimental Methods

Thin film deposition was done in a UHV chamber with a base pressure of $6 \times 10^{-10}$ Torr consists of a PLD system that uses a Nd:YAD laser (Symphotic Tii $\lambda = 355$ nm, repetition frequency 5 Hz) (see Figure 3.8 for the schematic of the set-up).

In making TiO$_2$ ablation targets, TiO$_2$ powder (predominantly anatase and rutile phases) with 99.995% purity was pressed into 1 inch diameter and ~0.25 inch thick round pellets at $1.6 \times 10^8$ Pa pressure and sintered for 8 hours at 1300 °C.

The sample was brought as close as ~8 cm to the target the distance at which deposition of any particulates was avoided. The rate of deposition was monitored using a quartz-micro balance.

For growing anatase-TiO$_2$(001) and rutile-TiO$_2$(101) epitaxial thin films, LaAlO$_3$(100) and Al$_2$O$_3$(1102) substrates were cleaned with acetone and ethanol (10 minutes in each solution) in an ultrasonic bath and then mounted side by side on a tantalum plate. The substrates were then introduced to the UHV chamber through a load lock and annealed in $2 \times 10^{-6}$ Torr of high purity oxygen at 600 °C for 2 hours right before deposition.

AFM images of such prepared substrates exhibit well-defined step structures. While deposition, the same annealing temperature and the oxygen pressure were maintained. The rate of deposition was maintained at ~ 0.7-0.9 nm/min.

In-situ RHEED was performed on the clean substrates and for the films after growth. The film morphology and rms-roughness were characterized by ex-situ NC-AFM (Park Scientific XE 70).
Epi-polished rutile single crystals with (101), (110), (100), and (001) orientations were purchased from MTI-corp. Orientation for these samples was confirmed by X-ray diffraction measurements. In order to improve the surface morphology, the as received samples were etched with 10% HF for ~30 minutes, sonicated in ethanol in ultrasonic bath for ~10 minutes, rinsed with DI water and annealed in the tube furnace in 200 mTorr of oxygen at 800 °C for 1 hour. The AFM images of such prepared samples exhibited well-defined stepped surfaces (Figure 3.12c). Photocatalytic activity was measured for as received samples, HF etched and oxygen annealed samples as well as for the vacuum annealed (600 °C for 30 minutes) samples. In addition to that, the (101) orientation of single crystalline rutile sample was annealed to different temperatures in UHV and the dependence of photoactivity with vacuum reduction was investigated.

The photocatalytic activity of the films was evaluated by measuring the photocatalytic decomposition of methyl orange (MO from Fisher Scientific) under UV irradiation (see Figure 3.9). The light source is a 100 W Hg arc lamp (Oriel). IR radiation from the light source was
filtered off by a water cooling system in order to avoid temperature activated decomposition of the solution.

5 mm × 5 mm sample was then mounted on a closed glass cuvette with a cut-off wavelength at ~350 nm (3.54 eV). Therefore only the near UV portion of the light could transmit through the glass cuvette and reach the sample. The intensity of the orange absorption peak at ~489 nm is a measure of the remaining methyl orange in the solution and was measured every 30 minutes using a UV-Visible spectrophotometer (see Figure 3.10a). The decrease in intensity with time was then fitted with an exponential decay function as shown in Figure 3.10b. The rate constant (i.e. rate of decomposition of methyl orange) extracted from this curve can then be considered as the photocatalytic activity of the sample after subtracting the base line (i.e. the decomposition of methyl orange without a photocatalytically active sample). Since the surface area and roughness checked in AFM, remained constant for all the samples the activity variations can be considered as only phase dependent or orientation dependent.
Figure 3.10: Photocatalytic activity measurements for anatase and rutile thin film samples. (a) Absorption spectra for methyl orange for different irradiation times as measured by UV-Vis spectrophotometer. The peak area is a measure of the remaining MO concentration. (b) Absorption peak area plotted against irradiation time for different film thicknesses. Photocatalytic decomposition rate for the sample can be extracted by fitting this with an exponential decay function. (c) The rate constant measured plotted against film thicknesses of rutile (black curve) and anatase (red curve). Maximum activity for anatase is reached at a film thickness of ~2.5 nm for rutile and ~5 nm for anatase. Reprinted with permission from ref[14], Copyright 2016-Nature Publishing group.

3.1.2.2 Results and Discussion

The results have been presented under three sub sections: (i) Photocatalytic activity of anatase and rutile thin films as a function of film thickness, (ii) Orientation dependence of photocatalytic activity of rutile single crystals, (iii) Vacuum reduction and photocatalytic activity of rutile TiO$_2$ single crystal and TiO$_2$ thin film samples.

Photocatalytic Activity of Anatase and Rutile Thin Films as a Function of Film Thickness:

Rutile and anatase films of thicknesses varying from 0.5 nm to 20 nm were grown by PLD. Figure 3.11(a,b,e,f) shows the in-situ RHEED patterns taken immediately after deposition. As can be seen, the RHEED pattern for anatase (001) films exhibited 4×1 superstructure spots (three spots between primary spots on the 0$^{th}$ Lau circle) originated from well-known 4×1 surface reconstruction. The streakiness of the diffraction spots for thicker samples might be due to the roughening of the surface. The RHEED pattern for rutile (101) films also shows pronounced diffraction spots, however, in this case, it was challenging to see additional half-order spots that are expected see for
the well-known 2×1 surface reconstruction for this particular orientation of rutile. This might also be due to surface roughening. As shown in the ex-situ AFM images in Figure 3.11(c,d,g,h), surface roughness of rutile thin films are comparably higher than that of anatase thin films. Anatase films have ~100 nm wide flat terraces while rutile films exhibit ~40 nm wide twinned orientations that are 90 degrees oriented with respect to each other.

![Figure 3.11](image)

**Figure 3.11**: RHEED and AFM for anatase and rutile TiO$_2$ thin films. Left side (a, b) RHEED patterns along <101> and <110> azimuths for anatase films. Superstructure streaks indicating 4×1 reconstruction of anatase surface are visible. (c, d) AFM images of anatase films showing atomically flat terraces. Right side (e, f) RHEED patterns along <010> and <−101> azimuths for rutile films. (g, h) AFM images of rutile films showing two crystal orientations due to twining in the film. Reprinted with permission from ref.[14], Copyright 2016-Nature Publishing group.

The photocatalytic decay constant or the rate constant for decomposition of methyl orange at the presence of each sample was then plotted with the film thickness (see Figure 3.10c). It is clear that for the thicker films, the photocatalytic activity saturates for both films and the activity of anatase is almost as twice as that of rutile which is consistent with the fact that anatase phase is more active than rutile phase. The important observation in this particular study is that for anatase films, the activity increases up to film thicknesses larger than ~5 nm; but for the rutile films, the activity only increases up to ~2.5 nm. What can be implied by this is, for anatase phase, the exciton generated deeper than ~5 nm from the surface is possible and the charge carriers can reach the surface to
participate in the photo decomposition reactions while for rutile this length is limited to ~2.5 nm.

Since the area of the sample surface being irradiated with near UV light and the growth conditions for the films were identical, the only variable here is the film thickness for both phases [apart from the photocatalytically inactive (large band gap) substrates that have been used for film growth]. Light absorption depth is much larger than the film thickness and thus is not the cause for saturation of activity for thicker films. Also, since the thickness of the films is smaller than the typical depletion lengths of oxides, the effects of band bending on the charge separation process can be excluded. By fitting the variation or the increase of photocatalytic activity with the film thickness for each phase, the charge diffusion length normal to the sample surface could be quantified. The function that has been used for the fitting is;

\[ K = C \left[ 1 - \exp\left( -\frac{d}{\lambda_{\text{diffusion}}} \right) \right] \]

where \( K \) is the decomposition rate constant (or the photocatalytic activity of the film), \( d \) is the thickness of the film. The fitting parameter \( C \) correspond to photocatalytic activity for very thick films or the bulk samples. Then \( \lambda_{\text{diffusion}} \) can be interpreted as the charge diffusion length normal to the surface. For the best fit, \( C \) and \( \lambda_{\text{diffusion}} \) for anatase turned out to be ~0.0033 and 3.2 nm respectively; while for rutile, those values were 0.0018 and 1.6 nm. This implies that the charge carrier diffusion length for anatase is about twice as large as that for rutile. It is reported in the past that the charge carrier mobility and charge carrier life time are larger for anatase than for rutile. These two properties can also be correlated with the larger charge carrier diffusion length in anatase than in rutile.

It is important at this point to discuss how the interface present in these films can affect the measured photocatalytic activities, since in pure TiO\(_2\) phases there are no such interfaces. The three main contributions arise from the interfaces are; (i) the differences in charge carrier trapping
and recombination at the interface for LAO and Al₂O₃ substrates, (ii) the differences in lattice mismatch between the two substrates causing different strains at the two interfaces consequently affecting the exciton diffusion length, (iii) differences in lattice mismatch and point defect formation. However, considering the similar activity for rutile single crystal and the 5 nm (the thickness where strain effects from the substrate may still be present) rutile thin film, the effects on photoactivity due to substrate induced strain can be discarded. On the other hand, the charge trapping and recombination effects at the interface can only modify the activity for films thinner than charge diffusion length (d < λ) and diminishes as d ~ λ. To study the contribution from lattice mismatch induced effects, activity of anatase films grown on LAO was compared with those grown on SrTiO₃ (or STO). Despite the larger lattice mismatch between STO and anatase (3.1%), the activity measured for the films was very close to that of the films grown on LAO where there is a smaller lattice mismatch (0.1%). This suggests that the lattice mismatch induced defects do not significantly affect the main conclusion of this study.

**Orientation Dependence of Photocatalytic Activity of Rutile Single Crystals:** Commercially available single crystal rutile TiO₂ samples were used for this study. Large enough pure anatase single crystal samples were unavailable to perform a similar study. Figure 3.12a shows the photocatalytic activity for the selected surface orientations of rutile single crystal sample for three different surface preparation procedures. Photocatalytic activity of as-received samples follow (101)> (110)> (001)> (100). The activity of (101) orientation, in this case, is similar to what was measured for rutile (101) thin film suggesting that the films are high quality and the observed twin domains in the films have no significant effect on the activity.
Figure 3.12: Orientation dependence of the photocatalytic activity for rutile TiO$_2$ single crystal samples. (a) Rate constant measured for rutile single crystals with four different surface orientations and three different sample preparation conditions. (101) is the most active surface orientation of rutile regardless of the preparation conditions. (b) AFM images for as received rutile single crystal samples. (c) AFM images for samples etched with 10% HF and annealed in oxygen. Well-defined step structure can be seen after HF treatment. Reprinted with permission from ref[14]. Copyright 2016-Nature Publishing group.
HF etching and tube furnace annealing in oxygen has caused the activity of all the samples to decrease compared to the activity of as-received samples. Formation of surface defects during oxygen annealing and resulting charge trapping have been reported in the past and may explain the activity drop. Vacuum reduction, on the other hand, has caused the activity of all the samples to increase following the same order in orientation dependence as in as-received samples.

Previously we discussed how the bulk properties (charge diffusion length) can influence the phase dependence of the photocatalytic activity in TiO$_2$. This can also be applied to the surface orientation dependence of the photocatalytic activity. For instance, the charge mobility in (001) and (100) directions at room temperature are reported as 8 cm$^2$/V.s and 1.4 cm$^2$/V.s respectively and the photocatalytic activity for (001) is larger than that for (100) orientation regardless of the surface preparation procedures. The charge mobility information for other surface orientations is not available to date and therefore cannot be correlated with the current observations in activity.

**Vacuum Reduction and Photocatalytic Activity of Single Crystal TiO$_2$ and Thin Film TiO$_2$ Samples:** Strong dependence of photocatalytic activity on vacuum reduction was observed for rutile TiO$_2$ single crystal sample. Vacuum reduction, as already discussed, cause formation of O-vacancies and Ti-interstitials. This also causes formation of color centers which enables visible light absorption. As shown in the photographs in Figure 3.13, the as-received transparent yellowish TiO$_2$ single crystals turned into dark bluish and opaque upon vacuum reduction. The sample annealed to high temperatures ( ~ 900 °C) even shows a metallic shine.
Figure 3.13: Photocatalytic activity measured for rutile TiO$_2$(101) as a function of UHV annealing temperature. In between every reduction the sample was made stoichiometric by annealing at 900 °C in ambient pressure oxygen. Annealing duration at each temperature in UHV is 30 minutes except for the last data point at which the sample was annealed to 700 °C for 5 hours. Reprinted with permission from ref[15]. Copyright 2016-Elsevier.

Clearly, the photocatalytic activity increases with the reduction of the sample and at ~ 800 °C the activity is almost doubled compared to the as-received sample. This enhancement in activity can be explained by the increase in charge carrier generation by visible light absorption. This statement is somewhat arguable as the defects created during vacuum annealing are generally responsible for charge trapping and recombination causing the activity to decrease; however, the observations in this study show that these defects are after all not strong charge trapping sites. Although the vacuum reduction enhanced the photocatalytic activity of single crystal samples, the anatase and rutile thin film samples did not show such enhancement upon post growth vacuum annealing. This may be because the as-grown films were already reduced or due to interface induced defect formation causing diminishing of the enhancement of light absorption upon reduction of the thin films.
Another phenomena to pay attention in this photocatalytic process is the dye-sensitized decomposition in which the charges carriers created from direct excitation of dye molecules transfer to the photocatalyst and contribute to methyl orange decomposition. To address this question, a second cuvette filled with highly concentrated methyl orange was placed in front of the first cuvette in which the photocatalytic sample has been suspended. The absorption spectrum was taken for this second cuvette using the UV-Vis spectrophotometer and clearly it absorbed all the light in 380 nm- 520 nm regime. Therefore, in the new experimental set-up, the second cuvette acts as a filter to the light that causes direct excitation of the dye molecules. Interestingly, in this set-up, a similar enhancement in photoactivity was observed for the reduced samples. The decomposition of methyl orange was also tested by filtering the UV portion of the light by placing a UV filter in front of the reaction cell and only a negligible rate of decomposition was measured suggesting that the dye molecules do not get decomposed by visible light induced dye-sensitization. These tests support the fact that the enhancement in photoactivity in reduced samples is not affected by any dye-sensitized processes.

3.1.2.3 Conclusions

The growth of high quality TiO$_2$ anatase and rutile thin films was accomplished via PLD. Photocatalytic activity for anatase films was observed to be twice as high as that for rutile thin films which is consistent with the past studies. The difference in the activity for the two polymorphs seems to have originated from the larger charge diffusion length in anatase phase than for rutile phase. The surface orientation of TiO$_2$ affects the photocatalytic activity. For as received rutile single crystals, for instance, the photoactivity varies according to (101)>(110)>(001)>(100). The activity can be modified by various surface treatment methods. In general, oxygen annealing
causes the activity to decrease while vacuum annealing causes the activity to increase. The increased activity for vacuum reduced samples may be associated with an increase in charge carrier generation with visible light absorption. This was, however, not the case for thin film samples, since the as-grown films may already have reduced and the instability may have increased due to interface induced defect formation.

3.2 Monolayer Mixed Oxide Growth on TiO₂
Monolayer mixed oxide growth on TiO₂ was attempted with the desire to explore novel oxide surfaces and/or interface structures carrying interesting chemical functional properties that could contribute to enhance the performance of sensing and catalytic applications. The results have been discussed under the following subtopics: (i) Fe/TiO₂ (011) system-Growth behavior, electronic, chemical and structural properties, (ii) Structural verification of Fe-Ti-O mixed oxide monolayer, (iii) V/TiO₂(011), Cr/TiO₂(011), Ni/TiO₂(011) systems- Growth behavior, electronic, chemical and structural properties. In the first section, synthesis of a well-defined ordered mixed monolayer oxide of iron on TiO₂(011) and characterization of its fundamental electronic, chemical and structural properties using STM, XPS, ISS, UPS and DFT-based computational methods have been discussed. Secondly, the verification of the proposed structure for the Fe-Ti-O mixed oxide monolayer using XPD measurements was discussed. Lastly, the growth behavior, electronic, chemical and structural properties of a few other systems namely, V/TiO₂(011), Cr/TiO₂(011) and Ni/TiO₂(011), were studied with STM, XPS, UPS and DFT-based computational methods.

The results for this study are published in ACS Nano-with the title “Ordered Fe(II)Ti(IV)O₃ mixed monolayer oxide on rutile TiO₂(011)”[55] ,in Journal of Physical Chemistry C-with the title “Monolayer intermixed oxide surfaces: Fe, Ni, V, Cr oxides on Rutile-TiO₂(011)”[13], and in
Surface science—with the title “Fe(II)Ti(IV)O$_3$ Mixed Monolayer Oxide at Rutile TiO$_2$(011): Structures and Reactivities”[56]. Another was published recently to and submitted to the Journal Physical Chemistry C—with the title “An ordered Mixed Oxide Monolayer Formed by Iron Segregation on Rutile-TiO$_2$(011): Structural determination by X-ray photoelectron diffraction”[60].

3.2.1 Fe/TiO$_2$(011) System: Growth Behavior, Electronic, Chemical and Structural Properties

The preparation of an ordered mixed Fe-Ti oxide surface on TiO$_2$(011) is sensitive to the preparation conditions in a UHV chamber. Therefore the experimental part focuses on the morphology, Fe-oxidation state, and structural characterization as a function of preparation conditions and the thermal stability of the iron deposits. The computational part uses first principles density functional theory (DFT) simulations combined with generic algorithm based optimization methods to determine the stable structures of the ordered mixed oxide phase.

Figure 3.14: Schematic diagrams of the two UHV systems in which the experiments have been performed. One system is equipped with STM and the other one has XPS, UPS, ISS and STM. The main components used in each chamber are as labeled.
3.2.1.1 Experimental and Computational Methods

Experimental Methods: STM studies were performed in a UHV chamber with a base pressure of \( \sim 2 \times 10^{-10} \) Torr equipped with an Omicron VT-STM operated at room temperature (Figure 3.14 shows the schematics of the two UHV systems). Empty-state STM images were recorded at room temperature with electrochemically etched tungsten tips cleaned in-situ by voltage pulsing. XPS, UPS and ISS measurements were performed in a separate UHV chamber with a base pressure of \( \sim 5 \times 10^{-10} \) Torr. This second UHV chamber was also equipped with a RT-STM, which was used to make sure that the same surface structures were obtained. For electron and ion spectroscopy studies, a non-monochromatized dual-anode x-ray source (Omicron, DAR 400) for XPS, a He II VUV photon source (Omicron, HIS 13) for UPS, and a fine focused ion (He+ ions with primary energy \( \sim 1000 \) eV) gun for ISS measurements were used. The kinetic energy of the scattered electrons/ions were detected with a seven-channel hemispherical energy analyzer (Omicron, Sphera II). To increase the surface sensitivity in XPS measurements, data were collected with the analyzer at a grazing angle of 70° (measured from surface normal). For UPS and ISS the analyzer was normal to the surface. The scattering angle for ISS was 37° in our experimental set-up. The XPS data were acquired with Mg-K\( \alpha \) x-rays. The XPS peaks were fitted with Gaussian-Lorentzian peak shape after subtracting a Shirley background. Substrate preparation and the methodology for iron deposition as well as the subsequent annealing procedures were identical in the two UHV systems. Briefly, the commercially available TiO\(_2\)(011) single crystal substrate (from MTI corporation) was prepared by multiple cycles of Ar\(^+\) sputtering at room temperature (1 kV, 5 \( \mu \)A, 30 min) followed by UHV annealing at 700 \( ^\circ \)C for 30 minutes. The cleanliness of the surface was checked by STM. Fe was evaporated from an Fe-rod, heated in a water-cooled mini e-beam
evaporator with the substrate held at room temperature. The 2 minutes, 4 minutes and 7 minutes exposure periods were estimated from STM images to correspond to 0.25 ML, 0.5 ML and 0.75 ML surface coverage, respectively.

**Computational Methods:** In this work, generic algorithm optimization method embedded in the USPEX (Universal Structure Predictor Evolutionary Xtallography) code was used in order to predict the stable structures. This has been successfully used in the past for predicting stable structures for bulk crystals, nanoclusters, surface reconstructions etc. As a global optimization method, the USPEX code uses four ways (heredity, mutation, and transmutation, random) to produce surface structures and the whole prediction usually requires hundreds or thousands of individual structure relaxations. DFT calculations were performed using Vienna ab initio simulation package (VASP) with generalized gradient approximation (GGA) using all-electron projector augmented wave method. 3s, 3p, 3d and 4s of Ti and Fe were treated as valance electrons. The kinetic energy cut-off was 400 eV for the plane-wave basis set which was used to expand valance electronic states. The calculated lattice parameters of bulk rutile TiO₂ are a=b=4.660 Å, c=2.973 Å, and in good agreement with experimental values. The reconstructed rutile-TiO₂(011) was modeled by a surface slab extended in a (2×1) super cell and a Monkhorst-Pack grid of (1×2×1) k-point mesh was used for determining structures for the mixed oxide layer. The vacuum height was ~15 Å. In structural optimization, the atom positions in the surface region and the buffer region (i.e. the top two layers) were relaxed and each candidate surface structure was relaxed until the residual forces were below 0.05 eV/Å. STM image simulation was performed within Tersoff-Hamann’s approach in constant height mode. An empty state window was employed ~ 1.2 eV
above the edge of the conduction band while the STM images were plotted at 2 Å above the topmost atoms of the surface.

### 3.2.1.2 Experimental and Computational Results and Discussion

The surface structure and thermal evolution for three differently prepared iron deposits on TiO$_2$(011) are presented: (i) deposition of iron in UHV, (ii) iron deposition in an oxygen atmosphere of $5 \times 10^{-8}$ Torr and its thermal evolution by annealing in UHV, and (iii) an optimized procedure for obtaining only the mixed oxide phase, consisting of a combination of Fe-deposition in $5 \times 10^{-8}$ Torr and annealing in oxygen and UHV.

**Fe Deposition at Room Temperature and Annealing in UHV:** Fe was deposited in UHV at room temperature. STM images, shown in Figure 3.15, reveal the formation of clusters. The cluster size and density increased with deposition time. For low amounts of deposited Fe, the clusters appear flat, i.e. no more than a single atomic-layer in height and lateral dimensions of only 1-2 surface unit cells (see Figure 3.15c).

With increased Fe-deposition, a few thicker and bigger clusters occurred. These clusters are 2-3 atoms in height, but still only a couple of surface unit cells wide (see Figure 3.15e). Annealing of this Fe-deposit in UHV lead to a sintering of the iron clusters. Figure 3.15f and 3.15g show samples annealed at 400 °C and 525 °C, respectively.
To investigate the oxidation state of the deposited iron we conducted XPS studies. After deposition of Fe at room temperature, as shown in Figure 3.15d, the Fe-2p peak exhibits an oxidized Fe$^{2+}$ state with a binding energy of 710.1 eV and a metallic state with a binding energy at 706.8 eV. In addition, a satellite peak at an apparent binding energy of 715.2 eV is observed, a characteristic feature of FeO which corroborates the assignment of iron in a 2+ charge state. Oxidation of iron without the presence of oxygen in the atmosphere suggests a simultaneous reduction of the Ti at the interface. Indeed a small Ti$^{3+}$ is observed in the Ti-2p spectra in XPS. Annealing in UHV to sequentially higher temperatures causes a decrease of the Fe$^{2+}$ component, as shown in Figure 3.15d. This indicates that the larger clusters observed in STM are predominantly metallic Fe. The
observed decrease in the Fe\(^{2+}\) component during annealing may be a consequence of reduction of the iron at elevated temperature or diffusion of oxidized iron into the bulk. Further annealing to 650 °C results in a complete loss of iron signal in XPS and thus suggests that iron diffuses into the bulk is occurring at these temperatures. Overall, the picture described here for Fe-deposition without oxygen is very similar to the studies performed on TiO\(_2\)(110).

**Fe Deposition in an O\(_2\) (5×10\(^{-8}\) Torr) Atmosphere at Room Temperature and Annealing in UHV**: When Fe is deposited in a low O\(_2\) background pressure of 5 × 10\(^{-8}\) Torr at room temperature, formation of metallic clusters is avoided. Figure 3.16a-c show STM images for increasing deposition times in the sub-monolayer regime. The surface exhibits disordered structures but no large clusters. Subsequent annealing of these deposits to 400 °C in UHV also did not cause formation of larger clusters, in contrast to the above discussed UHV deposited iron. Instead, an ordered structure was observed after annealing to 400 °C. This is shown in Figure 3.16e and f. This structure is less corrugated than the 2×1-reconstruction of the pure TiO\(_2\)(011) surface, but may still be described as a 2×1 superstructure with respect to the (011) substrate. The structural details are discussed below. However, in addition to the two ordered surface structures, i.e. the clean TiO\(_2\)(011)-2×1 and the new ordered mixed Fe-Ti-oxide, there still remain many small clusters at the surface. In XPS, only Fe\(^{2+}\) is observed for the as-deposited Fe (in oxygen atmosphere) as well as for samples annealed to temperatures as high as up to 300 °C in UHV. At higher annealing temperatures metallic iron was eventually formed as indicated in the XPS spectra shown in Figure 3.16d. Higher annealing temperatures are discussed below for samples that start-off with a more uniform mixed oxide surface, the preparation of which is discussed next.
Figure 3.16: Fe deposition in an O\textsubscript{2} (5 \times 10^{-8} Torr) atmosphere at room temperature and annealing in UHV. STM images of Fe deposited on TiO\textsubscript{2}(011) in 5\times10^{-8} Torr O\textsubscript{2} background pressure at room temperature for (a) 2 min, (b) 4 min, (c) 7 min exposure periods, € after annealing 4 min Fe deposit in UHV at \sim 400 °C for 12 min, (f) after annealing 7 min Fe deposit in UHV at \sim 400 °C for 10 min. (d) XPS spectra for 2 min Fe deposit in 5\times10^{-8} Torr O\textsubscript{2} background pressure at room temperature and subsequent annealing for 10 min at 450 °C and 650 °C in UHV. All STM images were taken with \sim 1.2 V and 400 pA tunneling conditions. Reprinted with permission from ref\[55], Copyright 2016-American Chemical Society.

**Optimized Preparation for Ordered Mixed Fe-Ti Surface Phase:** In an attempt to prepare surfaces that are predominantly covered with the mixed Fe-Ti oxide surface, we combined Fe-deposition and annealing in oxygen atmosphere with vacuum annealing at 300 °C, i.e. a temperature for which we have demonstrated that the new phase is stable in UHV without reduction of the iron. We found that the best preparation conditions consists of room temperature deposition of Fe in 5 \times10^{-8} Torr of O\textsubscript{2}, immediately followed by annealing of the sample at 300 °C in the same oxygen background for 10 min. Then the O\textsubscript{2} was turned off and the sample was annealed for another 5-10 min at the same temperature in UHV. Such prepared samples exhibit up
to 90% of the surface covered with the new mixed Fe-Ti oxide phase as the STM image in Figure 3.17a shows.

![Figure 3.17: Optimized preparation for ordered mixed Fe-Ti surface phase. STM images (a) Fe deposited on TiO$_2$(011) in 5×10$^{-8}$ Torr O$_2$ background pressure at room temperature for 4 min exposure period and annealed immediately in 5×10$^{-8}$ Torr O$_2$ for 10 min followed by UHV annealing for about 10 min. (b) High-resolution STM of Fe-Ti mixed oxide phase. (c) After annealing, the new structure in UHV ~400 °C for 10 min and (d) after annealing in UHV at 550 °C for 10 min. All STM images were taken with ~1.2 V and 400 pA tunneling conditions. Reprinted with permission from ref[55], Copyright 2016-American Chemical Society.](image)

To obtain information about the composition of this surface layer, we conducted ISS experiments using He$^+$ ions. Due to the high probability of He-neutralization, this technique is very surface sensitive and primarily probes the surface composition of the topmost layer. Figure 3.18 shows the ISS data for the pristine TiO$_2$ surface and the surface ~90% covered with the new surface phase. For the latter, the Fe-peak is only slightly more intense than the Ti peak. Although the similar intensities for Ti and Fe suggest a close to 1:1 composition in the surface layer, the unknown
neutralization cross-sections for He\(^+\) ions scattered from Ti and Fe makes it impossible to accurate
determination of the composition. Vacuum annealing of the mixed surface oxide sample at 400 °C
for 10 min in UHV results in the formation of small clusters, as shown in the STM image in Figure
3.17c. With higher annealing temperatures, the size of these clusters increases, which can be seen
from Figure 3.17d for an annealing temperature of 550 °C.

![Image](image_url)

**Figure 3.18:** ISS for the TiO\(_2\)(011) surface before and after formation of Fe-Ti-O mixed oxide monolayer. The fluorine
peak is contamination. Reprinted with permission from ref[55], Copyright 2016-American Chemical Society.

A systematic XPS study of the oxidation state of Fe as a function of annealing temperature is
shown in Figure 3.19a. At 300 °C no metallic iron is detected and with increasing annealing
temperature the ratio of metallic-Fe to Fe\(^{2+}\) keeps increasing. The change of the Fe\(^{2+}\) and metallic
Fe peak intensity as a function of annealing temperature and normalized to the Ti-2p intensity,
shows the rapid decrease in intensity of the Fe\(^{2+}\) signal while the metallic-component increases
only weakly, in other words the total Fe-signal decreases with annealing temperatures. This
difference in the apparent rate of change of the two components is likely a consequence of the
different morphologies. The metallic-iron is assumed to be mainly present in the clusters that are
seen in STM occurring on the surface after annealing, while the Fe\(^{2+}\) signal, comes, at least
initially, from the 2D surface oxide phase. The higher sensitivity of XPS to dispersed species at the surface compared to iron in clusters can explain the overall (metallic plus Fe\(^{2+}\)) decrease in the Fe-2p signal with annealing temperature. Furthermore, some loss of Fe\(^{2+}\) species through diffusion into the bulk is likely.

We also monitored the Ti-2p and O-1s signals in XPS. For the Ti signal, we did not observe any additional formation of Ti\(^{3+}\) or lower oxidation states. Thus the formation of the mixed oxide surface appears to only consist of Ti\(^{4+}\) and Fe\(^{2+}\). A rigid shift of ~0.2 eV of the entire Ti-2p peak and the O-1s peak was observed upon formation of the Fe-Ti-mixed surface oxide compared to

![Figure 3.19: A systematic XPS study of the oxidation state of Fe as a function of annealing temperature. XPS for Fe deposition on TiO\(_2\)(011) for (a) room temperature Fe deposition and annealing to 550 °C from 300 °C in steps of 50 °C in O\(_2\) background pressure of 5×10\(^{-8}\) Torr. (b) Peak fitting for 350 °C annealed Fe deposit (the same fitting parameters were maintained for all other Fe 2p spectra in (a)). (c) Ti 2p peak for clean TiO\(_2\)(011) surface and for the Fe deposited and annealed samples at 350 and 550 °C. (d) Fe\(^{2+}\)/Ti\(^{4+}\) ratios with the annealing temperature. Reprinted with permission from ref[55], Copyright 2016-American Chemical Society.](image)
the pristine TiO$_2$(011)-2×1 surface. Such a shift is caused by an upward band bending of the TiO$_2$ at the surface, implying the formation of a positive space charge region in TiO$_2$ induced by the mixed-oxide surface layer.

In addition to core level photoemission spectroscopy we utilized UPS to monitor the formation of new valence band states. Figure 3.20 shows the valence bands of the pristine TiO$_2$(011)-2×1 surface and the valence band after formation of the mixed Fe-Ti-O surface oxide. The valence band maximum for the pristine TiO$_2$(011) surface is determined to be ~2.8 eV below the Fermi-level, consistent with a strongly n-type doped rutile TiO$_2$ sample. Some photoemission intensity was observed within the band gap. This is a combination from photoemission excited by the non-monochromatic He-lamp as well as defect induced true band gap states in TiO$_2$.

![Figure 3.20: UPS for TiO$_2$(011) before and after formation of Fe-Ti-O mixed oxide monolayer. (a) UPS for TiO2(011) sample before and after Fe deposition at room temperature in 5×10$^{-8}$ Torr of O$_2$ and annealing at ~300 °C in the same oxygen background. (b) zoomed in view of the low BE region. Reprinted with permission from ref[55], Copyright 2016-American Chemical Society.](image)

Upon formation of the mixed Fe-Ti-O surface oxide, a significant band gap narrowing was observed. The new valence band maximum is measured around 1.0 eV below the Fermi-edge and
we attribute this new valence band maximum within the bulk band gap of TiO$_2$ to the valence band of the mixed surface oxide. This valence band maximum may be compared to known bulk band gaps for ilmenite-Fe$^{2+}$Ti$^{4+}$O$_3$ of 2.5-2.9 eV. This means that the surface mixed oxide either has a much reduced band gap or the Fermi-level lies closer to mid-gap than it does for the TiO$_2$ substrate.

**Scanning Tunneling Microscopy of Ordered Structure:** The experimental studies suggest the formation of a mixed surface oxide with Fe:Ti ratio of about 1:1 and Fe in 2+ oxidation state. STM shows a well ordered structure with the same periodicity as the reconstructed pristine TiO$_2$ (011)-2×1 surface, i.e. a rectangular unit cell. Two protrusions per unit cell are imaged, i.e. a protrusion in every corner of the rectangular unit cell and another protrusion close to the center of the unit cell as schematically illustrated in Figure 3.21a. From STM this gives a surface structure that may be described as a c(2×1) unit cell. Previously we reported a similar structure after oxygen annealing of the pristine TiO$_2$(011) surface. Because of the similarities in the STM images as well as the valence band it is possible that the previously reported structure in fact was formed by iron impurity segregation and not a separate TiO$_2$ surface phase. The STM image shown in Figure 3.21b, shows both the structure of the TiO$_2$ (011)-2×1 substrate as well as the new mixed oxide surface. Gridlines indicate the lattice as measured from the TiO$_2$ (011)-2×1 substrate structure. This allows determination of the protrusions in the mixed oxide relative to the TiO$_2$ lattice. Furthermore, linear defects or domain boundaries are frequently observed in STM images of the mixed oxide surface phase. This is shown in Figure 3.21b and c. These straight domain boundaries are aligned with the <01-1> substrate direction. The unit cells marked in the Figure show that these domain boundaries correspond to a ~1/2 unit cell offset between neighboring domains.
DFT simulations performed in order to determine a possible atomic-scale structural model for this surface structure are discussed next.

**USPEX Optimization Results:** Complicated structures for the Fe-Ti-O monolayer were systematically calculated with the genetic algorithm aided total energy DFT calculations. GA method, in particular, helped generating large set of possible metastable and global minimum structures along with information on surface evolution.
The six lowest total energy structures are illustrated in Figure 3.22. The total energy for these structures are given in table 3.1. For the most stable mixed oxide surface layer shown in Figure 3.22a the Ti and Fe cations are uniformly distributed. The simulated STM image for this surface structure in Figure 3.22g very well agrees with the experimental STM images. It is apparent that the brightest features in the simulated STM have originated from the exposed Fe$^{2+}$ in the surface layer while the exposed O$_{2c}$ give less bright features.

The structure illustrated in Figure 3.22d shows that the FeO units form a dimer anchoring at the pristine TiO$_2$(011)-1×1 support and exhibit similarities with the ilmenite (012) surface. This structure, however does not reproduce STM that is consistent with the experimental STM results. The other structures in Figure 3.22 have similar characteristics for those in Figure 3.22a and Figure 3.22b except for some exchanged Fe and Ti positions.

According to the top view of the surface layer of the most stable structure, the Fe:Ti ratio is 2:1, that is the chemical formula for the surface can be given as FeTi$_2$O$_5$. Thus the composition proposed by experimental ISS was not supported by DFT.

Finally we want to point out that although the whole top layer TiO$_2$ as well as the added FeO were included in the mixed oxide structure search, no reconstruction as that of TiO$_2$(011)-2×1 was determined to favorably occur for the substrate. This suggests that the FeO deposition can remove the reconstruction of the clean TiO$_2$(011) surface, similar to the case reported for adsorptions of various organic molecules.

Table 3.1: Calculated relative energies of different surface structures with 1/3 ML FeO on rutile TiO$_2$(011)

<table>
<thead>
<tr>
<th>Structures</th>
<th>Fig 3.22a</th>
<th>Fig 3.22b</th>
<th>Fig 3.22c</th>
<th>Fig 3.22d</th>
<th>Fig 3.22e</th>
<th>Fig 3.22f</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ (eV)</td>
<td>-0.54</td>
<td>-0.02</td>
<td>-0.02</td>
<td>0</td>
<td>0.04</td>
<td>0.15</td>
</tr>
</tbody>
</table>

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Figure 3.22: DFT-based computational structures predicted for Fe-Ti-O mixed oxide monolayer. Side view of various calculated structural models for 1/3 ML FeO on rutile TiO$_2$(011) surface and the simulated STM images are shown. Ti atoms are in gray, O in red and Fe in violet. Reprinted with permission from ref[55], Copyright 2016-American Chemical Society.
3.2.1.3 Conclusions

This work demonstrates that well-ordered surface structures of monolayer mixed oxides may be obtained on single crystal surfaces under the right preparation conditions and thus novel mixed oxide monolayer materials can be synthesized and characterized by surface science investigations. While there are many more investigations of monolayer oxides on the rutile-$\text{TiO}_2(110)$ surface very few similarly well ordered oxide monolayers have been reported for that surface orientation. We consider that the less stable (011) surface that exhibits a $2\times1$ surface reconstruction may facilitate the formation of ordered mixed oxide surfaces. Thus it will be exciting to investigate how the other transition metals behave in the formation of the surface mixed oxide on $\text{TiO}_2(011)$. Identification, synthesis and compositional control of well-ordered mixed-oxide monolayers are prerequisites for atomic-scale understanding of these kinds of nanocatalysts. The studies reported here suggest that the $\text{TiO}_2(011)$ surface is a better model system for these kind of investigations than the more frequently used rutile $\text{TiO}_2(110)$ surface.

3.2.2 Structural Verification of the Fe-Ti-O Mixed Monolayer

As we discussed in section 3.2.1, stabilizing a surface-confined single atomic layer oxide is sensitive to preparation conditions in UHV. Previously we synthesized the FeTi$_2$O$_5$ monolayer in a system equipped with STM. Although STM can characterize surface morphology and identify the presence of new surface phases it is not well suited as a detailed structural probe. This makes confirmation of DFT-based theoretical structures uncertain despite the good agreement we obtained between simulated STM images and atomic-resolution images. XPD, on the other hand, is a structural probe, that if combined with soft-x rays can be extremely surface sensitive and thus a powerful probe of surface structures. Multiple electron scattering of photo-emitted electrons
probes the local environment of the emitting atom. Monitoring the photoemission intensity as a function of emission angle thus gives information on the structure surrounding emitters of a specific element. To interpret the photoelectron intensity variation in XPD, the measurements need to be compared to multiple electron scattering simulations of a model structure. The measured intensity variation as a function of angle is a super-positioning of all emitters of a specific element with different local environments and thus the simulations need to take into account all possible local configurations in a specific structural model. The agreement between measurement and simulated XPD for a model structure is judged by using Pendry R-factor analysis. Below we discuss the experimental and simulation methods in detail.

3.2.2.1 Experimental and Computational Methods

**Experimental**: All the photo emission and LEED experiments were performed in a UHV end station of the SuperESCA beamline at the Elettra synchrotron radiation facility, Trieste, Italy. The base pressure of the UHV system is \(~1\times10^{-10}\) mbar. The beamline provides photons with energy 85-1500 eV with a resolving power, \(E/\Delta E\), \(1\times10^4\) at 400 eV and \(5\times10^3\) at 900 eV. The kinetic energy of the emitted electrons was detected with a Phoibos (SPECS GmBH) electron energy analyzer equipped with a home-made delay-line detector. The chamber is also equipped with LEED and a mass spectrometer. The commercially available TiO\(_2\)(011) single crystal substrate (MTI corporation) was mounted on a Ta plate to which a thermocouple was spot welded very close to the sample. The Ta-plate and the sample were heated with a filament placed behind them. The sample was mounted on a 5 degrees-of-freedom manipulator. The sample was cleaned by multiple cycles of Ar\(^+\) sputtering at room temperature (1 kV, 6 μA, 20 min) followed by UHV annealing at
620 °C for 10 minutes. To ensure uniform cleaning, the sample was rotated to different combinations of polar/azimuthal angles during sputter and anneal cycles. Physical vapor deposition of Fe was done by heating a 2 mm diameter Fe rod in a water-cooled mini e-beam evaporator. To attain a uniform coverage, the sample was azimuthally rotated during deposition. For high-resolution XPS the sample surface was normal to the analyzer. In the course of XPD, the sample was rotated over polar θ and azimuthal Φ angles so that the polar angle runs from 0° (normal emission) to 70° out of normal (normal incidence conditions in the present set-up) and the azimuthal angle spans 90° for each θ. Figure 3.23 shows a schematic diagram of the beamline geometry and the sample orientation. XPS and XPD measurements were taken for the Ti-3s and Fe-3p peaks with a photon energy of 175 eV and energy resolution below 50 meV. In the high resolution spectra the binding energy has been calibrated with the Fermi level of a Ta-clip used for mounting the sample. For determining the XPD patterns, the core level photoemission peaks were fitted with a Doniach-Sunjic function convoluted with a Gaussian broadening.

**Computational:** XPD patterns were simulated by multiple electron scattering simulations implemented in the EDAC package[53]. The clusters for the structural models were constructed using atom coordinates determined in DFT simulations of various surface models. The size and the scattering volume of the cluster are defined by $R_{\text{max}}$ which is constrained by the computation time. Parabolic shape for the cluster was favored since it increases the contribution of scattering of atoms that lie between the emitters and the surface. The input parameters for the EDAC code for Ti 3s in clean TiO$_2$(011)-2×1 model structure and for Ti 3s and Fe 3p in FeTi$_2$O$_5$ model structure are summarized in table 3.2.
Figure 3.23: Schematic representation of the actual experimental XPD set up. The surface orientation of TiO$_2$(011)-2×1 sample w.r.t the analyzer and the photon beam is shown. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society

Table 3.2: Input parameters used in the EDAC code for different elements in the two structures.

<table>
<thead>
<tr>
<th>Initial state of element</th>
<th>$R_{\text{max}}$ (Å)</th>
<th>Emission Energy KE (eV)</th>
<th>Inner Potential $V_0$ (eV)</th>
<th>Inelastic Mean Free Path (Å)</th>
<th>Number of Emitters</th>
<th>Max.orbital quan.num. $l_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 3s for TiO$_2$(011)-2×1</td>
<td>15</td>
<td>112</td>
<td>10</td>
<td>5.8</td>
<td>20</td>
<td>8.1</td>
</tr>
<tr>
<td>FeTi$_2$O$_5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 3p for FeTi$_2$O$_5$</td>
<td>11</td>
<td>120</td>
<td>10</td>
<td>5.7</td>
<td>2</td>
<td>8.3</td>
</tr>
</tbody>
</table>

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For Fe-EDAC simulations of the FeTi$_2$O$_5$ structure only two Fe atoms per surface unit cell were considered as the emitters. In contrast, for Ti XPD simulations, Ti-emitters distributed down to ten or twelve layers (~10-12 Å) below the surface were considered in order to ensure that all the diffraction features were detected. A reasonable value for the Debye Temperature $\Theta_D$ (1000 K) was used in order to take into account for the thermal vibrations of the atoms. Polarization $p$-LP (which refers to linearly polarized light with the polarization vector contained in the plane of incident beam and the surface normal) and an emission angle window of 5° were chosen in accordance with the actual experimental conditions. $R_{\text{max}}$, $l_{\text{max}}$, IMFP, $\Theta_D$ and $V_0$ are not a-priory exactly known and thus were optimized to get better theory-experiment agreement; however, it should also be pointed out that small changes (+/- ~20%) of these values do not significantly change the simulated XPD patterns. The quantitative comparison of experimental and theoretical photoelectron diffraction data is carried out by calculating the reliability-factor

$$R = \frac{\sum_i (\chi_{\text{exp},i} - \chi_{\text{th},i})^2}{\sum_i (\chi_{\text{exp},i}^2 + \chi_{\text{th},i}^2)}$$

where, $\chi$ represents the modulation function defined as

$$\chi = \frac{I(\Theta, \Phi) - I_0(\Theta)}{I_0(\Theta)}$$

($I_0$ is the average intensity for each azimuthal scan at fixed polar angle $\Theta$), and the sum runs over all the available data points for the different angles. The lower the R factor the better is the agreement.

3.2.2.2 Experimental and Computational Results and Discussion

In this study, the formation of FeTi$_2$O$_5$ mixed oxide monolayer was carried out via two experimental path ways. Firstly, by annealing the clean TiO$_2$ sample in $1 \times 10^{-7}$ mbar O$_2$ at ~450 °C
and secondly, by depositing Fe in $1 \times 10^{-7}$ mbar O$_2$ at elevated temperature. In the following subsections we briefly review previously published STM and DFT results for clean TiO$_2$(011)-2×1 structure and the results for the FeTi$_2$O$_5$ mixed oxide structure discussed in section 3.2.1 in this chapter followed by the experimental and computational results of the current work.

**STM and DFT Structural Models of Clean TiO$_2$(011)-2×1 and FeTi$_2$O$_5$ Mixed Oxide Monolayer:** In section 3.2.1 we discussed the formation of FeTi$_2$O$_5$ monolayer on TiO$_2$(011)-2×1 substrate by depositing Fe in 5×10$^{-8}$ Torr of O$_2$ at room temperature and then annealing the sample to ~350 °C in the same oxygen background. Figure 3.24a and b show atomically resolved STM images for the clean TiO$_2$(011)-2×1 surface and for the FeTi$_2$O$_5$ mixed oxide surface. The insets show the rectangular unit cells for the two structures. It is apparent that both surfaces have the same unit cell symmetry and dimensions, i.e. the FeTi$_2$O$_5$ mixed monolayer forms also a (2×1) superstructure with respect to the rutile TiO$_2$(011) substrate. The corresponding DFT structural models for these two surfaces are shown in Figure 3.25a and c. The energetically most stable model of the clean TiO$_2$(011)-2×1 surface, that is the ‘Brookite(001)-like’ model, contains five-fold coordinated Ti atoms uniformly surrounded by neighboring O atoms. On the other hand, the FeTi$_2$O$_5$ surface consists of uniformly distributed Fe and Ti atoms in 1:2 ratio.

It should also be noted that the formation of intermixed monolayer has resulted in complete re-ordering of the originally reconstructed surface of clean TiO$_2$(011) surface. On the pure TiO$_2$(011)-2×1 surface, the features imaged in STM as bright oval shaped protrusions, arranged in zig-zag rows come from the topmost O$_{2c}$ atoms in the proposed structure. In contrast, simulated STM images of the FeTi$_2$O$_5$ surface structure suggest that the Fe atoms on the surface layer give rise to the brightest features in empty state STM images.
Figure 3.24: STM images of clean TiO$_2$(011)-2×1 structure and FeTi$_2$O$_5$ mixed oxide monolayer. (a) clean rutile-TiO$_2$(011)-2×1 surface. The inset shows the high resolution image of zig-zag rows run along [01-1] direction and the rectangular unit cell dimensions. Bright features are oxygen atoms located in the top most layer. (b) FeTi$_2$O$_5$ monolayer on rutile-TiO$_2$(011)-2×1 obtained by depositing Fe at room temperature in $5 \times 10^{-8}$Torr of oxygen and annealing at ~350°C in the same O$_2$ pressure. The inset shows the high resolution image of c(2×1) superstructure with rectangular unit cell. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society.

Figure 3.25: DFT-based structural models for TiO$_2$(011)-2×1 and FeTi$_2$O$_5$ mixed oxide monolayer. (a) DFT-based ‘Brookite(001)-like’ model proposed for TiO$_2$(011)-2×1 structure and (b) shows the top view of the (011) plane. (c) Lowest energy DFT-based structural model proposed for FeTi$_2$O$_5$ mixed oxide monolayer formed on TiO$_2$(011)-2×1 surface and (d) is the top view. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society.
While the model shown in Figure 3.25c for the FeTi₂O₅ surface is the most stable and has the best match to the STM studies, other stable surface models have been obtained from DFT as discussed before. These models and their corresponding simulated XPD patterns are shown in Appendix I, but neither of these structures exhibit any close resemblance to the measured XPD patterns and are therefore not further discussed.

**XPD and XPS of Clean TiO₂(011)-2×1 and FeTi₂O₅ Mixed Oxide Monolayer:** The XPS for a freshly sputtered clean TiO₂(011)-2×1 sample is shown in Figure 3.26a. The Ti 3s peak is broad due to sputter-induced reduction and the presence of Ti species (for e.g. Ti³⁺, Ti²⁺) overlapped with Ti⁴⁺. After annealing to temperatures higher than ~600 °C, the peak became narrower and shifted to higher binding energy, consistent with the recovery of the stoichiometric TiO₂ surface. The sample was annealed for ~10 minutes at this temperature in UHV. Then the temperature was lowered to 450 °C and 1×10⁻⁷ mbar O₂ was introduced in the chamber. In the presence of oxygen the Fe 3p signal started to grow (see Figure 3.26b) until saturation, then the oxygen was turned off. The Fe 3p/Ti 3s peak ratios for this process are plotted in Figure 3.27a. It is apparent that the rate of Fe-diffusion to the surface slows down with time, which may be a consequence of limited iron impurities in the bulk. Iron only segregates to the surface in the presence of an oxygen background, while annealing in UHV (or strongly reducing environment) allows iron to diffuse into the bulk.

The high resolution Ti 3s, Fe 3p and Fe 2p core level spectra for the sample with iron segregated from the bulk are shown in Figure 3.26c, Figure 3.26d respectively. The peak shapes and binding energies indicate that Fe is in a 2+ and Ti remains in a 4+ charge state for the iron-segregated surface.
**Figure 3.26:** Real time XPS for clean TiO$_2$(011) and for the formation of FeTi$_2$O$_5$ mixed monolayer. (a) XPS for clean TiO$_2$(011)-2x1 sample after sputtering at room temperature (bottom) and after annealing in UHV at 600 °C (top). (b) Growth of Fe 3p peak while annealing in 1x1 0.7 mbar of oxygen at ~450 °C. (c) High resolution spectra and peak fitting of Ti 3s, Fe 3p measured at photon energy of 175 eV, after annealing in oxygen and formation of FeTi$_2$O$_5$ mixed oxide monolayer. (d) High resolution spectra for Fe 2p measured at photon energy of 850 eV. The peak shape and position suggest that Fe is in 2+ charge state. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society

**Figure 3.27:** Fe 3p/ Ti 3s peak ratios plotted vs time. (a) the sample annealed in 1x1 0.7 mbar of oxygen at 450 °C and for (b) Fe deposition in 1x1 0.7 mbar of oxygen at 450 °C. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society
The measured Fe-3p/Ti-3s ratio of 0.23 can be used to estimate the amount of iron in the surface layer. If we assume that Fe atoms only reside in the topmost surface layer while the Ti-signal originates from surface as well as subsurface atoms we can find an expression for the ratio of the core-level intensity as follows:

\[
\frac{I_{\text{Ti}}}{I_{\text{Fe}}} = \frac{(1 - \alpha)A_{\text{Ti}}}{\alpha A_{\text{Fe}}} + \sum_{n=1}^{\infty} \frac{A_{\text{Ti}} e^{-n\Delta x/\lambda_{\text{IMFP-Ti}}}}{\alpha A_{\text{Fe}}}
\]

where \(\alpha\) denotes the fraction of iron atoms in the surface layer, \(\Delta x\) is the separation of atomic layers for a stratified crystal model, \(A_{\text{Ti}}\) and \(A_{\text{Fe}}\) are the atomic sensitivity factors for iron and titanium, respectively, and \(\lambda_{\text{Ti}}\) is the inelastic mean free path length for the Ti-3s photoelectrons. The atomic sensitivity factors at the photoelectron energies of 120 eV and 112 eV are estimated to \(A_{\text{Ti}} = 0.3\) and \(A_{\text{Fe}} = 0.9\) for Fe and Ti, respectively and the inelastic mean free path (\(\lambda_{\text{IMFP-Ti}}\)) for the Ti 3s photoelectrons at 112 eV kinetic energy is estimated to be 0.58 nm. The sample after annealing in oxygen shows an XPS ratio \(I_{\text{Ti}}/I_{\text{Fe}} = 4.0\), hence \(\alpha = 0.2\). Based on the observation of our previously reported STM, the surface segregates into a pure TiO\(_2\) phase and a FeTi\(_2\)O\(_5\) phase (see Figure 3.28). Thus all the iron signal originates from a phase with a Fe:Ti ratio of 1:2 and thus it is easily shown that \(\alpha = 0.2\) correspond to 2/3 of the surface covered with the mixed oxide. However, there are large uncertainties in the values for atomic sensitivity factors and the inelastic mean free path of the photoelectrons and thus an independent verification of the surface coverage is desirable. Thus next we deposited Fe on this sample in 1×10\(^{-7}\) mbar of O\(_2\) with the substrate held at \(\sim 450 \, ^\circ\)C in an attempt to form a complete monolayer of the mixed oxide surface.
Figure 3.28: STM image for TiO$_2$(011) sample annealed in $5 \times 10^{-8}$ Torr of O$_2$ at ~350 °C. The surface exhibits two phases. Clean TiO$_2$(011)-2×1 and FeTi$_2$O$_5$ phase.

The Ti-3s and Fe-3p signals were monitored while deposition and the change in Fe 3p: Ti 3s ratio is shown in Figure 3.27b. Although the Fe-flux was approximately constant, it is apparent that the ratio saturates at a value of 0.49. Such a saturation is explained if Fe only accumulates in the surface layer until the surface is completely covered with the FeTi$_2$O$_5$ phase and excess Fe diffuses into the bulk. This would further support the notion that the FeTi$_2$O$_5$ phase is a thermodynamically stable surface phase. In this scenario, the measured Fe 3p: Ti 3s peak intensity ratio is that for a complete FeTi$_2$O$_5$ monolayer on a TiO$_2$ substrate. Using the above expression we obtain $\alpha=0.4$, which is close but slightly higher than the value of $\alpha=1/3$ we would expect from the 1:2 ratio of Fe:Ti in the mixed oxide. Thus it appears that our chosen values for $\lambda_{\text{IMFP-Ti}}$, $A_{\text{Ti}}$, and $A_{\text{Fe}}$ slightly overestimate the iron concentration in the surface layer. This also suggests that the fraction of the mixed oxide just after oxygen annealing is closer to 50% rather than 66% and this is the assumption we will use in the following to calculate the XPD pattern.
XPD data were collected for the three samples discussed above, i.e. (i) a clean TiO$_2$(011)-2×1; (ii) low coverage (~1/2ML) of Fe-Ti-oxide prepared by segregating Fe from the bulk; and (iii) high coverage (~1 ML) of Fe-Ti-oxide prepared by depositing Fe in 1×10$^{-7}$ mbar at ~400-450 °C. XPD patterns were recorded for Ti 3s of the clean TiO$_2$(011)-2×1 and for Ti 3s and Fe 3p of the low coverage and the high coverage Fe-Ti-oxide sample. Figure 3.29a shows the experimental XPD for Ti 3s of the clean TiO$_2$(011)-2×1 sample. In Figure 3.29b the simulated XPD of Ti 3s for the TiO$_2$(011)-2×1 model is shown and in Figure 3.29c the experimental XPD is overlapped with the simulated XPD. As can be seen visually there is an excellent agreement between the theory and the experiment. The R factor calculated for the entire set of data is 0.22. Since the structural model for the TiO$_2$(011)-2×1 reconstruction was previously confirmed by surface x-ray diffraction, our XPD study is an additional confirmation of this structure. The R-factor we obtain for this known structure is an indication of the kind of agreement we can expect to obtain between the experimental and simulated XPD patterns for the correct structural model. For clarity, Figure 3.29d shows azimuthal plots for few of the selected polar angles marked in Figure 3.29a and Figure 3.29b by dashed circles. We see that the photoelectron intensity variations of respective profiles of theory and experiment follow very well and the R-factors for the individual profiles are indicated in the Figure.

Turning to the structure of the iron-titanium surface oxide, Figure 3.30a shows the experimental XPD for Ti 3s for the sample prepared by Fe-deposition and is assumed to cover almost the entire surface with the mixed ternary monolayer oxide. Figure 3.30b shows the simulated XPD of Ti 3s for the DFT-model of FeTi$_2$O$_5$. Figure 3.30c is experimental XPD overlapped with the simulated XPD. Once again, there is a very good agreement between the theory and the experiment. The R
factor for this plot was calculated as 0.23, which is almost identical to the agreement we obtained for the clean TiO$_2$(011)-2×1 surface.

Figure 3.29: Experimental and theoretical XPD patterns for Ti 3s in TiO$_2$(011)-2×1. (a) Experimental XPD pattern for Ti 3s of clean TiO$_2$(011)-2×1 surface. (b) Simulated XPD pattern of Ti 3s for ‘Brookite(001)-like’ model of TiO$_2$(011)-2×1 proposed by DFT-based calculations. (c) The experimental XPD overlapped with simulated XPD. The two patterns are in good agreement qualitatively and quantitatively (R=0.22). (d) Line profiles and R factors along azimuthal scans for selected polar angles. The polar angles selected are marked by dashed circles in XPD plots given in (a) and (b). Reprinted with permission from ref[60], Copyright 2016-American Chemical Society

No other structural model suggested by DFT simulations, resulted in XPD patterns that were close to the experimental data. The simulated XPD patterns for these structures and the corresponding R-factors are given in the appendix. Figure 3.30d shows line profiles over azimuthal angles for selected polar angles indicated by dashed circles in Figure 3.30a and Figure 3.30b. The intensity
variations of the theoretical and experimental line profiles follow in very good agreement, which is also shown by the low R-factors for the line profiles.

Figure 3.30: Experimental and theoretical XPD patterns for Ti 3s in FeTi$_2$O$_5$. (a) Experimental XPD pattern of Ti 3s for high coverage Fe-Ti-O sample prepared by Fe deposition in 1×1 0^7 mbar of O$_2$ and at ~450 °C. (b) Simulated XPD pattern of Ti 3s for DFT–based structural model of FeTi$_2$O$_5$ mixed oxide monolayer. (c) The experimental XPD overlapped with simulated XPD. The two patterns are in good agreement qualitatively and quantitatively (R=0.23). (d) Line profiles and R factors for azimuthal scans at some selected polar angles. The polar angles selected are marked by dashed circles in XPD plots given in (a) and (b). Reprinted with permission from ref[60]. Copyright 2016-American Chemical Society

The Ti-3s XPD for the sample prepared by Fe-segregation from the bulk is shown in Figure 3.31d. The XPD pattern obtained for a not completely covered surface should be the sum of the XPD patterns of the FeTi$_2$O$_5$ and the TiO$_2$(011)-2×1 surface phases.
Figure 3.31: Experimental and theoretical XPD patterns for Ti 3s in FeTi$_2$O$_5$ 50% coverage. (a) Simulated XPD pattern of Ti 3s for DFT structural model proposed for TiO$_2$(011)-2x1. (b) The simulated XPD pattern of Ti 3s for DFT structural model proposed for FeTi$_2$O$_5$ mixed oxide monolayer. (c) The 1:1 mixture of two simulated XPD patterns. (d) The experimental XPD of Ti 3s for low coverage Fe-Ti-O sample prepared by annealing the clean TiO$_2$(011) substrate in 1x1 0.7 mbar of O$_2$ at ~450 °C. It is clear that the experimental XPD best matches with the weighted mixture of the two simulated patterns. (e) R factor for low coverage FeTi$_2$O$_5$ sample. Red data represents R factor calculated using different mixing ratios of simulated XPD of TiO$_2$(011)-2x1: FeTi$_2$O$_5$ models. Blue data represents R factor calculated using different mixing ratios of experimental XPD of clean TiO$_2$(011)-2x1 and high coverage (~1 ML) FeTi$_2$O$_5$ sample. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society

A mixing of the simulated intensity of these two surface structures in a ratio of 1:1 reproduces the experimental XPD pattern very well as Figure 3.31c shows, in agreement with our estimation for the surface coverage from XPS intensity ratios discussed above.

For further verification of the coverage, the R factor was calculated for different mixing ratios of the clean TiO$_2$(011)-2x1 and FeTi$_2$O$_5$ XPD intensities using simulated structures and also using the experimental XPD intensities for the clean sample and for the sample covered fully with FeTi$_2$O$_5$ (see Figure 3.31e). In fact the minimum R factor was obtained for the 1:1 mixture of clean
TiO$_2$(011)- 2×1 : FeTi$_2$O$_5$. This not only verifies that the sample prepared by oxygen annealing consists of 50% of Fe-Ti-O structure and 50% of clean TiO$_2$(011)-2×1 structure, but also verifies the composition of the new phase is indeed FeTi$_2$O$_5$, in which Fe:Ti ratio is 1:2.

While the Ti-3s XPD shows good agreement with the FeTi$_2$O$_5$ DFT model, the agreement with the Fe-3p XPD is less satisfying. Figure 3.32a shows the simulated XPD of Fe 3p for the FeTi$_2$O$_5$ model and Figure 3.32b and Figure 3.32c show the experimental XPD data for Fe 3p for low coverage and for high coverage Fe-Ti-oxide sample respectively.

![Experimental and theoretical XPD patterns for Fe 3p in FeTi$_2$O$_5$. (a) Simulated XPD of Fe 3p for DFT-based structural model proposed for FeTi$_2$O$_5$ mixed oxide monolayer. (b) Experimental XPD of Fe 3p for Fe-Ti-O sample prepared by annealing the clean TiO$_2$(011) substrate in 1×1 0.7 mbar of O$_2$ at ~450 °C. (c) Experimental XPD pattern of Fe 3p for high coverage Fe-Ti-O sample prepared by Fe deposition in 1×1 0.7 mbar of O$_2$ and at ~450 °C. (d) Line profiles and R factors of azimuthal scans for selected polar angles. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society](image-url)
The same general XPD pattern for low and high Fe coverage is in agreement with the observed phase segregation and iron only being present in FeTi$_2$O$_5$ domains at the surface. Although visual inspection of the simulated XPD pattern with that of experimental results shows close similarities, the calculated R-factor is only 0.59.

The disagreements between the simulations and the XPD data can also be seen from the line scans, although better R-factors are obtained from the line scans. The reasons for the relative worse agreement between the simulated and measured XPD data can have various origins. The much noisier signal for Fe-3p and the resulting weaker intensity modulations in XPD compared to Ti 3s affects the calculated R-factors. The weaker Fe-signal is a consequence of the lower Fe-concentration in the sample but also occurrence of disordered clusters and/or defects (e.g. antiphase domain boundaries) in the monolayer phase cannot be excluded which will adversely affect the XPD measurements.

**LEED Patterns of Clean TiO$_2$(011)-2×1 and FeTi$_2$O$_5$ Mixed Oxide Monolayer:** LEED patterns were recorded for several different primary electron energies and the patterns for 71 eV are shown in Figure 3.33a and b. The unit cell for clean TiO$_2$(011)-2×1 and for the new Fe-Ti oxide monolayer have the same symmetry and size. This is in consistent with the proposed structural model. In STM images of the FeTi$_2$O$_5$ mixed oxide monolayer we observed a high density of antiphase domain boundaries with ½ a unit cell offset along [01-1] direction. These domain boundaries may give rise to the streakiness of the LEED patterns after forming the Fe-Ti-oxide layer. The LEED patterns for both the TiO$_2$(011)-2×1 surface as well as the FeTi$_2$O$_5$ surface exhibit ‘missing’ (2n-1,0) spots. This indicates a glide plane symmetry of the unit cell of both structures in agreement with the proposed structural models as explained in Figure 3.33c and d.
Figure 3.33: LEED and glide plane symmetry patterns for TiO$_2$(011)-2×1 and for FeTi$_2$O$_5$. (a) LEED for clean TiO$_2$(011)-2×1 sample. (b) LEED for the high coverage Fe-Ti-O sample prepared by Fe deposition in 1×1 0.7 mbar of O$_2$ and at ~450 °C, at electron energy of 71 eV. The size and the symmetry of the surface unit cell seem to be the same for both samples. Both patterns have missing spots suggesting the glide plane symmetry in the two structures. (c) The glide plane symmetry explained for TiO$_2$(011)-2×1 surface. For this surface there is one glide plane axis runs along (01-1) direction. (d) The glide plane symmetry explained for FeTi$_2$O$_5$ mixed oxide surface that runs along (01-1) direction. Reprinted with permission from ref[60], Copyright 2016-American Chemical Society.
3.2.2.3 Conclusions

The structural model of the FeTi$_2$O$_5$ surface oxide proposed by DFT was confirmed in the study presented here by synchrotron XPD measurements. In addition to that, we show that on the rutile TiO$_2$(011) surface iron impurities segregate to the surface in the presence of an oxygen background pressure. Furthermore, by vapor deposition of iron we observe that the iron content in the surface layer at elevated temperature is limited to the formation of a stable mixed oxide phase with a FeTi$_2$O$_5$ structure, while excess iron diffuses into the bulk. This suggests that this iron-titanium oxide phase is a particularly stable surface phase. The preferred formation of this ordered phase is also apparent from the observed phase separation into a pure TiO$_2$(011)-2×1 and this iron-containing phase, in cases where there is not sufficient iron to complete a monolayer.

3.2.3 V/TiO$_2$(011), Cr/TiO$_2$(011), Ni/TiO$_2$(011): Growth Behavior, Electronic, Chemical and Structural Properties

In section 3.2.1 we discussed formation of ordered monolayer (or sub-monolayer) mixed oxide of FeTi$_2$O$_5$ on TiO$_2$(011)-2×1 and the structural model proposed for this monolayer was verified by XPD measurements in section 3.2.2. Here we extend these studies to the systems V/TiO$_2$(011), Cr/TiO$_2$(011) and Ni/TiO$_2$(011) in an attempt to investigate generality for the formation of intermixed oxides.

As mentioned earlier, the formation and characterization of single atomic layer materials at surfaces require controlled conditions and highly surface sensitive methods. Single crystal surface science studies with controlled vapor deposition of transition metals in UHV or in very low pressure oxygen background can provide this information. Especially, STM is well-suited for identification of structural surface phases. Similarly challenging to experimental characterization
of multicomponent oxide surfaces is their prediction by computational methods. In this study we combined experimental synthesis and characterization of multi-element oxide monolayers with advanced algorithm for surface structure prediction. The detailed experimental and computational approaches are described below.

3.2.3.1 Experimental and Computational Methods

**Experimental:** The commercially available TiO$_2$(011) single crystal substrates (MTI corporation) were prepared by multiple cycles of Ar$^+$ sputtering at room temperature (1 kV, 5 μA, 30 min) followed by UHV annealing at 700 °C for 30 minutes. The cleanliness of the surface was checked by STM. Physical vapor deposition of V, Cr, and Ni was done by heating a 2mm diameter V-, Cr-, or a Ni-rod in a mini e-beam evaporator. The STM studies were performed in an UHV chamber with a base pressure of ~2×10$^{-10}$ Torr equipped with an Omicron VT-STM operated at room temperature. Empty-state STM images were recorded at room temperature with electrochemically etched tungsten tips cleaned in-situ by voltage pulsing. All the STM images presented here were taken around 1.2 V bias voltage and ~400 pA tunnel current. XPS and UPS measurements were performed in a separate UHV chamber with a base pressure of ~ 5×10$^{-10}$ Torr. For the photoemission, a non-monochromatized dual-anode x-ray source (Omicron, DAR 400) for XPS and a He II VUV photon source (Omicron, HIS 13) for UPS were used. The kinetic energy of the emitted electrons was detected with a seven-channel hemispherical energy analyzer (Omicron, Sphera II). In XPS and UPS the analyzer was normal to the surface. The XPS data for vanadium and chromium were acquired with Mg-Kα x-rays; while for nickel Al-Kα x-rays was used. Substrate preparation and the methodology for vanadium/vanadia deposition as well as the
subsequent annealing procedures were identical in the two UHV systems. Nickel-oxide/TiO$_2$(011) and chromia/TiO$_2$(011) samples were prepared in the STM chamber and transferred into the photoemission chamber via a vacuum suitcase with a base pressure of $\sim 10^{-8}$ Torr.

XPS peak fitting: The peak fitting parameters (-binding energy (BE) and full-width at half-maximum (FWHM)) used for each element and oxidation state are summarized in Table 3.3 along with the references.

Briefly; the V 2p$_{3/2}$ peak was fitted with a Gaussian (70%)-Lorentzian (30%) peak shape after subtracting a Shirley background applied across V 2p$_{3/2}$ portion (V 2p$_{1/2}$ portion has been avoided as it overlaps with a substrate feature that lies between 518-524 eV, which makes it difficult to reliably deconvolute the V-2p$_{1/2}$ signal from the substrate photoemission signal). The peak positions for different charge states of vanadia are referenced to the O 1s peak set to 530.4 eV. The broadening of V$^{2+}$, V$^{3+}$ and V$^{4+}$ compared to the sharp metallic V peak is related to the number of available final state configurations that occurs as a result of multiplet splitting. In other words, the coupling of unpaired electrons in a core hole created by photoemission with an outer shell electron can give rise to several different final states resulting in broadening of peaks. Despite the multi-component nature of the V-2p peak, we fit the entire envelop of 2p$_{3/2}$ by assigning a single peak for each charge state of V.

The Cr 2p$_{3/2}$ peak was best fitted with two Gaussian (70%)-Lorentzian (30%) peaks modified by an asymmetric form A (0.32, 0.6, 10) where 0.32 and 0.6 define the spread of the ‘tail’ on either side of the peak while the parameter 10 specifies the width of the Gaussian used to convolute the Lorentzian curve. The two peaks were attributed to Cr$^{3+}$ and Cr$^{2+}$ with the peak positions shown in Table 3.3. Here, the Shirley background has been extended to include the 2p$_{1/2}$ portion as well, however only the 2p$_{3/2}$ portion has been fitted.
The Ni 2p$_{3/2}$ peak was fitted with four components maintaining Gaussian (70%)-Lorentzian (30%) peak shapes. A Shirley background has been applied across the entire 2p portion and only the 2p$_{3/2}$ portion was fitted. As reported in the literature, the two components located at 853.6 eV and 855.7 eV are due to the multiplet splitting of Ni$^{2+}$ 2p$_{3/2}$ peak. In addition to that, there is one strong satellite feature at 860.7 eV and a weaker satellite feature at 863.5 eV.

Table 3.3: XPS fitting parameters for 2p$_{3/2}$ components of V, Cr, Ni and Ti 2p peaks

<table>
<thead>
<tr>
<th>Element</th>
<th>Species</th>
<th>Peak Position (eV)</th>
<th>FWHM (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>V 2p$_{3/2}$</td>
<td>V$^{2+}$</td>
<td>513.1</td>
<td>1.8</td>
<td>[57, 58]</td>
</tr>
<tr>
<td></td>
<td>V$^{3+}$</td>
<td>515.2</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V$^{4+}$</td>
<td>516.3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cr 2p$_{3/2}$</td>
<td>Cr$^{2+}$</td>
<td>576.1</td>
<td>2</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>Cr$^{3+}$</td>
<td>577.0</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Ni 2p$_{3/2}$</td>
<td>Ni$^{2+}$ peak 1</td>
<td>853.6</td>
<td>1.5</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>Ni$^{2+}$ peak 2</td>
<td>855.7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Satellite 1</td>
<td>860.7</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Satellite 2</td>
<td>863.5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ti 2p$_{3/2}$</td>
<td>Ti$^0$</td>
<td>454.6</td>
<td>1.2</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>Ti$^{2+}$</td>
<td>456.5</td>
<td>1.5</td>
<td></td>
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<tr>
<td></td>
<td>Ti$^{3+}$</td>
<td>457.6</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti$^{4+}$</td>
<td>459.1</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

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The Ti 2p$_{3/2}$ peak has been fitted with 1 to 4 components depending on the reduction level of the substrate (while depositing vanadium/vanadia). Non-reduced Ti 2p$_{3/2}$ can be fitted with a single peak which is assigned to Ti$^{4+}$. Upon reduction, two or three more components appear due to Ti$^{3+}$,
Ti$^{2+}$ or Ti$^0$. 3+ and 2+ components are fairly similar in width and slightly broader than 4+ component as reported in the literature. The Ti-components were all fitted with a Gaussian (70%)-Lorentzian (30%) peak shape after applying a Shirley background across 2p3/2 portion.

**Computational:** We used the genetic algorithm optimization method embedded in the Universal Structure Predictor Evolutionary Xtallography (USPEX) code to search for the possible stable surface structures, which has been successfully applied for predicting stable structures of bulk crystals, nanoclusters, surface reconstruction, and polymers. As a global optimization method, the USPEX code uses four ways, namely random, hereditary, mutation, and transmutation, to produce surface structures, and the whole prediction usually requires hundreds or thousands of individual structure relaxations. In our calculations, mixed-metal oxide surfaces were modeled by periodic slabs; each candidate surface structure was divided into vacuum region, surface region, and substrate region that contains buffer and fixed layers. Only the surface region was involved in the process of generating new structures. The DFT calculations were carried out using the Vienna ab initio simulation package (VASP) with the generalized gradient approximation (GGA) using the all-electron projector-augmented wave method. The valence electronic states were expanded in plane wave basis sets with an energy cutoff of 400 eV. The Monkhorst-Pack grid of (1×2×1) k-point mesh was used, and each candidate structure was relaxed until the residual forces were below 0.05 eV/Å. The calculated lattice parameters of bulk rutile TiO$_2$ are $a = b = 4.660$ Å, $c = 2.973$ Å, in consistence with experimented values. As the TiO$_2$(011) shows a complex surface reconstruction with 2×1 periodicity, it was modeled with a slab containing four TiO$_2$ units each layer in a 2×1 supercell. The vacuum region height was about 15 Å. The substrate region consisted of four TiO$_2$ layers, of which the top two layers (the buffer region) were allowed to relax and the
bottom two were fixed. The surface region contained the reconstructed layer and 2MO (M = Fe, Ni, Cr, V) units in each surface cell. Details of the STM simulations can be found in our early studies discussed in section 3.2.1.

3.2.3.2 Experimental and Computational Results

We present our experimental studies for the various transition metal oxide intermixed monolayers, deposited on TiO$_2$(011), followed by the computational analysis of stable surface structures and comparison of their simulated STM images with the experimental ones. We discuss the experimental results for every transition metal separately and draw-up some similarities and differences in the discussion section. For completeness, we start with a brief review of the Fe-TiO$_2$(011) system, which is already discussed in section 3.2.1.

The Fe-TiO$_2$(011) System: We have shown that vapor depositing Fe onto TiO$_2$(011)-2×1 surface in 5 ×10$^{-8}$ Torr O$_2$ and subsequent annealing in the same oxygen atmosphere to ~ 350 °C results in the formation of a monolayer mixed FeTi$_2$O$_5$ oxide. XPS showed that the iron is in a 2+ charge state. The most stable structure predicted by DFT-based computational methods for this monolayer surface structure produced simulated STM that was very well matched to the experimental STM measurements as shown in Figure 3.34a and b and is consistent with the DFT simulations discussed below for the other transition metal systems. Figure 3.34c shows a larger scale STM image for low Fe-coverage. In this image it can be seen that the surface segregates into two compositional phases, a clean 2×1 reconstructed TiO$_2$ surface and the mixed oxide FeTi$_2$O$_5$ surface.

Depending on the oxidation potential of the gas phase, different outcomes are obtained upon annealing. Annealing in ultra-high vacuum (UHV) results in the reduction of Fe from the surface
layer at around 400 °C, which causes the formation of metallic Fe clusters. Annealing in as little as $10^{-8}$ Torr oxygen keeps the iron oxidized but the iron eventually diffuses into the bulk at ~ 600 °C. By controlling the Fe-deposition and annealing procedure we obtain an almost completely covered surface with a FeTi$_2$O$_5$ composition (see Figure 3.34e).

![Diagram of FeTi$_2$O$_5$ surface structure](image)

**Figure 3.34:** FeTi$_2$O$_5$ mixed oxide surface on TiO$_2$(011). (a) Top-view of DFT based simulated structure and simulated STM image of FeTi$_2$O$_5$ surface (b). STM images for (c) sub-monolayer of Fe deposited on rutile-TiO$_2$(011) and annealed to ~350 °C in 5 ×10$^{-8}$ Torr O$_2$. The surface is seen to be segregated into two structures, corresponding to FeTi$_2$O$_5$ and pure TiO$_2$(011)-2x1. High resolution images of the bare TiO$_2$(011)-2x1 substrate and the ordered FeTi$_2$O$_5$ monolayer are shown in (d) with the unit cell dimensions indicated. An STM image of a sample with an almost complete monolayer of FeTi$_2$O$_5$ is shown in (e), prepared under the same conditions as in (c) but with a higher initial Fe coverage. Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.

This indicates that this is an energetically stable monolayer structure with no competing phases under mildly oxidizing conditions. In addition, Fe remains at the surface for fairly high annealing
temperatures indicating significant barriers for Fe-diffusion into the bulk of TiO₂. For the other transition metals studied here easier diffusion into the bulk and or competition with other oxides complicate the sample preparation of a single phase surface oxide. However, as we discuss in the following, for all the transition metals investigated in this work, some regions were identified for specific preparation conditions that exhibited a very similar mixed surface oxide like the FeTi₂O₅ structure.

**The V-TiO₂(011) System:** As has already been shown for Fe on TiO₂(011), the surface structure and oxidation state of the transition metal depends sensitively on the preparation conditions. Therefore, we discuss the surface properties as a function of preparation conditions for all the different transition metals under investigation. Different elements require different oxidation potential for formation of oxidized species and thus the range of oxygen pressures employed to obtain a transition metal oxide interface varies. For vanadium we distinguish deposition and annealing in UHV or 5 × 10⁻⁸ Torr of O₂. For vanadium, which exhibits multiple oxidation states, we also first investigate multilayers to obtain good reference spectra in XPS.

**Multilayer Vanadium:** First we discuss XPS studies of a multilayer V film. This mainly serves as a reference for the studies of the (sub)monolayer amounts of V, which is the focus of this manuscript. Figure 3.35a shows V 2p spectra for multilayer V deposited in UHV at room temperature. For this ‘thick’ film, metallic V was observed with a binding energy for the V 2p peak at 512.3 eV. At the same time the Ti-substrate is being reduced. This is apparent by the formation of Ti³⁺, Ti²⁺ and even Ti⁰ components in the Ti 2p spectrum with binding energies at 457.6 eV, 456.5 eV and 454.6 eV respectively (see Figure 3.35c). Conservation of oxygen in the sample suggests that some vanadium needs to be oxidized and this is observed by the low binding
energy ‘tail’ of the V-peak. Annealing to different temperatures in UHV results in various changes to the V-2p peak. Annealing to temperatures below 250 °C does not change the photoemission features of V-2p significantly. Annealing to temperatures higher than 400 °C results in a decrease of the intensity likely indicating V-diffusion into the bulk, but some clustering of V may also contribute to the decreased intensity. Importantly, the vanadium becomes exceedingly oxidized by reacting with substrate oxygen. No metallic V can be detected anymore at 400 °C and the V peak can be satisfactorily fit by two components associated with V^{2+} peak at 513.1 eV and a V^{3+} peak at 515.2 eV, as shown in Figure 3.35b. The intensity of both of these components decreases further upon annealing to higher temperatures, but the V^{2+} component remains even after annealing to ~575 °C for 10 minutes in UHV. The Ti peak maintains a fairly large 3+ component but lower oxidation states disappear with annealing.

Sub-Monolayer Vanadium: Figure 3.35d shows XPS for low V coverage deposited in UHV at room temperature. Unlike for the thicker V-film, no metallic V was observed. The V-2p peak mainly consists of V^{2+} and possibly some minority components of higher oxidation states. Also, only a small Ti^{3+} shoulder is observed for the TiO_{2}(011) substrate, as can be seen in Figure 3.35f. Annealing this sample to ~ 250-400 °C in UHV causes the formation of V^{3+}, as the peak fitting in Figure 3.35e shows, but some small amount of V^{2+} also remains. Annealing to 575 °C results in vanadium diffusion into the bulk and disappearance of a vanadium signal in XPS. In contrast to annealing in UHV, annealing in 5×10^{-8} Torr of O\textsubscript{2} results in a conversion of V^{2+} species into higher oxidation states. The V-2p peak is best fit with a combination of V^{3+} (at 515.2 eV) and V^{4+} (at 516.3 eV), as shown in Figure 3.35h. Annealing to above 400 °C again results in disappearance of the vanadium signal due to V-diffusion into the bulk.
Figure 3.35: XPS of vanadium on TiO$_2$(011) for different deposition conditions. Left column shows XPS spectra of V-2p, middle column peak fitting to V-2p$^{3/2}$, and right column shows the Ti-2p peak. The sample investigated in (a),(b), and (c) is a multilayer vanadium deposited on TiO$_2$ at room temperature and subsequently annealed in UHV to temperatures indicated. (d), (e), and (f) show XP spectra for sub-monolayer amount of V deposited at RT and annealed in UHV. (g), (h), (i) show XP spectra with V deposited in UHV and subsequent annealing in 5 ×10$^{-8}$ Torr O$_2$. (j), (k), and (l) V was deposited in 5 ×10$^{-8}$ Torr O$_2$. Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.
Moreover, after annealing in oxygen, a shift of ~0.2 eV to lower binding energy occurs for the Ti 2p peak (see Figure 3.35i), which is commonly observed for oxygen exposure of TiO₂ and is associated with a surface band bending.

We also investigated the oxidation states of vanadium if we deposit V directly in a 5 \times 10^{-8} \text{Torr} \ O₂ background. As can be seen in Figure 3.35j we only obtain a mixture of V^{3+} and V^{4+} and no V^{2+} after room temperature deposition. Annealing this deposit in UHV, results in some reduction of vanadium which is apparent by the formation of V^{2+} as shown in Figure 3.35j and k. The formation of V^{2+} can be suppressed by annealing in 5 \times 10^{-8} \text{Torr} \ O₂, as is shown in Figure 3.35m and n. Furthermore, annealing in 5 \times 10^{-8} \text{Torr} \ O₂ also suppresses formation of Ti^{3+} which forms on vacuum annealed samples as can be seen from comparison of Figure 3.35l and o.

Thus XPS measurements suggest the formation of two distinct combinations of V-charge states on the TiO₂(011) surface in the sub monolayer regime. Under reducing conditions V^{2+} is observed, which may coexist with higher oxidation states. Either by direct deposition in oxygen or by annealing under mildly oxidizing environments (5 \times 10^{-8} \text{Torr} \ O₂) only higher oxidation states of V, i.e 3+ and 4+ are observed. In order to measure if these V charge states can be assigned to any specific ordered surface structure, STM studies have been performed in a separate chamber under the same preparation conditions.

STM of Sub-Monolayer Vanadium: Figure 3.36a shows STM images of V deposited at RT in vacuum, which exhibits disordered small clusters that, based on the XPS studies, are oxidized V^{2+} clusters. Annealing in UHV at ~ 400 °C causes formation of an ordered surface structure. Our best attempts to cover as much of the surface with this new structure resulted in a coverage of ~60 % of the surface (see Figure 3.36b).
Further annealing of this sample to 500 °C still shows the ordered structure but with a reduced coverage (Figure 3.36c). As shown in Figure 3.36d, the ordered surface layer appears to be forming a c(2×1) superstructure with very similar appearance in STM to the above discussed intermixed FeTi$_2$O$_5$ surface. The surface also segregates into two compositional surface phases. One phase is pure TiO$_2$(011) with its characteristic 2×1 reconstruction, the other phase is a surface alloy with V. From comparison of the surface domains that remains in a 2×1 reconstruction of the clean TiO$_2$(011) surface it is evident that the bright protrusions in STM images align with the ridges and the valleys of the pristine TiO$_2$(011)-(2×1) surface as depicted in Figure 3.36e. In XPS, after
annealing, we always also see a significant $\text{V}^{3+}$ contribution, which we suggest may come from disordered regions, as well as clusters that remain at the surface. From the similarity with the FeTi$_2$O$_5$ mixed surface alloy we conclude that the intermixed vanadia-titania surface is isostructural to the c(2×1)-FeTi$_2$O$_5$ surface.

![Figure 3.37: V deposition in oxygen and annealing in UHV. STM images of (a) Vanadium deposited on TiO$_2$(011) at room temperature in $5 \times 10^{-8}$ Torr of O$_2$ for 4 min exposure time, (b) after annealing the V deposit in UHV at 500 °C for 10 minutes. Areas marked by red rectangles show surface structures resembling the one shown in Figure 3. A higher resolution image of the surface structure is shown in (c). Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.](image)

Deposition of V in O$_2$ at RT also results in clusters at the surface. Subsequent annealing to 400-500 °C in oxygen background or UHV results in a row-structure with the same 2×1 periodicity of the TiO$_2$(011) reconstruction. The same structure can also be obtained by UHV deposition of vanadium and subsequent annealing in $5 \times 10^{-8}$ Torr O$_2$. From XPS we know that this structure is
a mixture of V-3+ and 4+. For samples annealed in UHV, small regions of the above mentioned c(2×1) structure can also be observed as highlighted in Figure 3.37b. This is consistent with the observation of some V\(^{2+}\) for such sample preparation procedures.

Valence band measurements by UPS are reported in Figure 3.38 for the various surface preparation conditions. V deposition in UHV and annealing in UHV results in a valence band maximum at ~0.5 eV which we mainly attribute to the formation of the ordered VTi_2O_5 intermixed surface layer.

**Figure 3.38:** Valence band spectra for vanadium oxide on TiO_2(011). Spectra shown in (a) and (b) were obtained for samples prepared by V deposited at room temperature in UHV and subsequently annealed in UHV. Spectra shown in (c) and (d) were obtained on samples prepared by V deposited at room temperature in 5 ×10^-8 Torr of O_2 and subsequent annealing in UHV. Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.

Deposition in oxygen at room temperature results in a VBM at around 1 eV, which is attributed to the mixed oxide surface containing V\(^{3+}\) and V\(^{4+}\). After annealing in UHV, which we know from XPS causes some formation of V\(^{2+}\), we observe a reformation of a VBM at ~0.5 eV. The latter VB
spectrum is described by a combination of the spectra of vacuum prepared sample and the oxygen prepared sample and thus is likely the result of a phase mixture of the two vanadium surface oxides. Thus from a combination of STM, XPS, and UPS we conclude that a \( \text{V}^{2+}\text{Ti}^{4+}_{2}\text{O}_{5} \) structure, isostructural to the previously reported \( \text{Fe}^{2+}\text{Ti}^{4+}_{2}\text{O}_{5} \) structure, can form under reducing conditions in UHV. However, under even slightly oxidizing conditions \( (5 \times 10^{-8} \text{ Torr O}_2) \) \( \text{V}^{3+} \) and \( \text{V}^{4+} \) is prevalent that forms a row structure that seems to be templated on the \( \text{TiO}_2(011)-2\times1 \) reconstruction. Currently we do not have atomic details of these higher vanadium oxide structures.

**The Cr-TiO\(_2\)(011) System:** Chromium is expected to be in between of V and Fe in terms of its reactivity with lattice oxygen. It has been previously reported that metallic Cr deposited on TiO\(_2\) will extract lattice oxygen and thus one may expect that Cr forms an intermixed oxide just by UHV deposition and annealing, similar to V. However, as shown in Figure 3.39a, chromium deposited in UHV and annealed to \( \sim350 \, ^\circ\text{C} \) for \( \sim30 \) minutes only shows small disordered clusters and no ordered intermixed surface oxide. To achieve ordering, Cr has been deposited in \( 5 \times 10^{-8} \) Torr of oxygen and annealed in UHV, under these conditions larger Cr-oxide clusters are observed (Figure 3.39b), which may be indicative of suppressed diffusion into the bulk. To obtain some ordered structures that resemble the intermixed oxides of V and Fe, chromium had to be deposited in \( 5 \times 10^{-8} \) Torr of oxygen with the substrate held at \( \sim350 \, ^\circ\text{C} \). After the deposition, oxygen was turned off and annealing was continued for another 10 minutes in UHV at \( \sim600 \, ^\circ\text{C} \). Thus, optimum preparation for intermixed chromia surface oxide is indeed somewhere in between the conditions for V and Fe in terms of oxygen exposure during annealing. The resulting surface structure is shown in Figure 3.39c. It is evident that in some areas of the sample the c(2\(\times\)1) structure has
formed, which we associate with an intermixed CrTi$_2$O$_5$ monolayer. A high resolution STM of this structure is shown in Figure 3.39d.

![Figure 3.39: STM images of Cr deposited on TiO$_2$(011). (a) Cr deposited in UHV at room temperature and annealed in UHV at 350 °C, (b) Cr deposited in 5 × 10$^{-8}$ Torr of O$_2$ at room temperature and annealed in UHV at 350 °C, (c) Cr deposited (4 min exposure) at ~350 °C in 5 × 10$^{-8}$ Torr of O$_2$ and annealed in UHV at 600 °C for 5 min. The surface is covered with monolayer Cr$_2$O$_3$ islands. In between these islands the clean TiO$_2$(011)-2×1 surface is mostly imaged, however, in small regions indicated by arrows an ordered structure of CrTi$_2$O$_5$ can be identified. In (d) higher resolution image of the ordered CrTi$_2$O$_5$ structure is shown. (e) Cr deposited and annealed at the same conditions as in ‘c’ but for slightly longer Cr deposition time (6 min), in this case mainly Cr$_2$O$_3$-islands and mixed CrTi$_2$O$_5$ regions (marked by arrows) are observed. Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.

In addition to the intermixed oxide the sample also exhibits a high density of monolayer height islands that are oriented with the TiO$_2$(011) substrate. These are likely Cr$_2$O$_3$ epitaxial islands on TiO$_2$(011), suggesting that rutile TiO$_2$(011) may be a good substrate for the growth of epitaxial Cr$_2$O$_3$ films. It is known that rutile TiO$_2$(011) or rutile SnO$_2$(011) grows epitaxially on corundum-Al$_2$O$_3$(012) substrates, so the corundum-chromia islands are likely to have the same epitaxial
relationship with corundum Cr$_2$O$_3$(012) on rutile TiO$_2$(011). (The epitaxial relationship between Cr$_2$O$_3$(012) and rutile TiO$_2$(011) has further been verified by XPD measurements performed on thick Cr$_2$O$_3$ films grown on rutile TiO$_2$(011) [these results are not discussed under this section since it does not belong in the topic of monolayer growth and thus given in Appendix III]). Figure 3.39e shows a sample prepared under the same conditions but for slightly higher exposure of chromium. In this case, the bare TiO$_2$(011)-2×1 substrate is no longer visible and the sample mainly consists of the above mentioned islands; yet the ordered c(2×1) monolayer structure is also clearly visible in some small areas in between the islands as pointed out by the arrows in the Figure. XPS performed on this sample is shown in Figure 3.40a and b.

**Figure 3.40:** Photoemission characterization of chromia on TiO$_2$(011). The sample was prepared by Cr deposition in 5 × 10$^{-8}$ Torr O$_2$ and subsequent annealing to 600 °C in UHV. X-ray photoemission spectra of (a) Cr 2p and (b) Ti 2p. UV photoemission spectra are shown in (c) of clean Rutile-TiO$_2$(011) and Cr-Ti-O sample. (d) shows a zoomed in view of low BE region of (c). Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.
The oxidation states of Cr is predominantly 3+, but there is a small shoulder at the low binding energy side, which can be attributed to Cr$^{2+}$. Ti is 4+ with a 0.2 eV shift due to band bending. UPS measurements in Figure 3.40c and d show two new states in the band gap. One may be attributed to the Cr$_2$O$_3$ islands and the other to formation of mixed CrTi$_2$O$_5$ intermixed monolayer oxide. Comparison to the band edge for thicker Cr$_2$O$_3$ films allows us to assign the band edge at $\sim$1.5 eV binding energy to Cr$_2$O$_3$ and the edge at $\sim$2.2 eV to the intermixed CrTi$_2$O$_5$ monolayer oxide.

**The Ni-TiO$_2$(011) System:** Compared to iron, nickel is expected to be more difficult to oxidize. On the other hand, NiTiO$_3$ is known to exist in the same FeTiO$_3$-ilmenite structure in the bulk and thus may also be a candidate for forming similar monolayer mixed oxides on titania substrates. UHV deposited Ni on titania substrates have shown *not* to react with the titania support but instead form metallic clusters. This is confirmed in Figure 3.41.

![Figure 3.41: STM images of Ni deposition in UHV. 1 min deposition time (a) and after annealing to 450 °C in UHV for 10 min (b). Ni-deposition for 4 min deposition time is shown in (c) and the same sample after annealing to 750 °C for 60 min is shown in (d). Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.](image-url)
This shows STM images after Ni deposition and annealing in UHV. For low coverage (Figure 3.41a), about 0.4 nm tall metallic Ni clusters were observed. For high coverage of Ni (Figure 3.41c), the substrate was covered by densely packed disordered Ni clusters. Annealing in UHV resulted in sintering of the clusters. Thus to achieve formation of Ni oxide and intermixing with the substrate Ni needs to be deposited under oxidizing conditions. Various procedures have been explored and the important ones are discussed in the following.

In order to compare with iron, for which $5 \times 10^{-8}$ Torr of oxygen was sufficient to form the intermixed oxide structure the same oxygen pressure was employed for Ni. However, this only leads to formation of Ni clusters as shown in Figure 3.42a and b.

![Figure 3.42: STM images of oxidized Ni on TiO$_2$(011). Sample prepared by Ni deposition at room temperature in $5 \times 10^{-8}$ Torr of oxygen is shown in (a), and the same sample after annealing to 350 °C for 10 min in $5 \times 10^{-8}$ Torr O$_2$ is shown in (b). STM images of samples prepared by Ni deposition for 20 seconds (c) and 90 seconds (e) at room temperature in $5 \times 10^{-8}$ Torr of O$_2$ and subsequently annealed at 350 °C in $5 \times 10^{-7}$ Torr O$_2$. (d) and (f) show higher resolution images of the ordered NiTi$_2$O$_5$ monolayer regions. Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.]
Annealing of Ni-deposits in $5 \times 10^{-5}$ Torr of oxygen, on the other hand, caused roughing of the surface, likely due to re-oxidation of titanium interstitials from the bulk, which made imaging of the surface with reasonable resolution impossible. Partially ordered intermixed oxide surface that resembled the structure observed for VTi$_2$O$_5$ and FeTi$_2$O$_5$ intermixed surfaces were obtained for preparation procedures in $5 \times 10^{-7}$ Torr of oxygen. First Ni was deposited at room temperature in oxygen and subsequently the sample was annealed to ~350 °C in oxygen. Figure 3.42c and d shows such prepared surface with very low amount of Ni; while Figure 3.42e and f shows a sample prepared with the same conditions but with ~ 4 times as much Ni.

In both cases small ordered domains that we attribute to the formation of NiTi$_2$O$_5$ intermixed surface oxide are observed. With increasing Ni amount more of the surface could be covered by the intermixed oxide, however, formation of undefined clusters also increased. Cluster formation was somewhat suppressed if Ni was deposited directly at ~350 °C in $5 \times 10^{-7}$ Torr oxygen.

XPS was performed in order to determine the oxidation state of Ni and Ti in this film. As shown in Figure 3.43a, Ni only exhibits a Ni$^{2+}$ (at binding energy 853.6 eV) charge state and no metallic Ni (~852 eV) was observed. Figure 3.43b shows Ti 2p peak for the clean TiO$_2$(011) and for the Ni-Ti oxide film. In both cases Ti remains 4+ and only a small ~0.1 eV shift of the Ti peak is observed, which we again attribute to band bending. The UPS valence band spectra, shown in Figure 3.34c and d, indicates new density of states within the bulk band gap of pristine rutile-TiO$_2$(011); which can be a result of the new intermixed NiTi$_2$O$_5$ surface structure. These gap states exhibit a VBM of ~ 0.8 eV below the Fermi-level.
Figure 3.43: Photoemission characterization of oxidized nickel on TiO$_2$(011). Ni was deposited at room temperature in $5 \times 10^{-8}$ Torr of O$_2$ and subsequently annealed at 350 °C in $5 \times 10^{-7}$ Torr O$_2$. X-ray photoemission spectra of Ni 2p and Ti 2p are shown in (a) and (b), respectively. UV photoemission spectra of clean TiO$_2$(011) surface and the Ni-Ti-O sample are shown in (c) and a zoomed in view of low BE region is shown in (d). Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.

Calculated Structures of Mixed Oxide Monolayer Surface: While the combination of two different metal species in mixed-metal oxide surfaces can produce complicated structures, prediction of their exact structures from first principle calculations remains a challenge. In particular, a robust optimization strategy other than those based on bulk-truncated substrates with arbitrary construction of add-on dopants is highly desired. In the current work, genetic algorithm optimization scheme was adopted in combination with total energy DFT calculations for generating and optimizing surface structures. The 2×1 rutile TiO$_2$(011) surface cells containing 1/3 monolayer of metal oxide units (with respect to the number of surface TiO$_2$ units) on top were considered in the search for possible mixed MTi$_2$O$_5$ (M=Fe, Ni, Cr, V) surface oxides. For each 2×1 surface cell of rutile TiO$_2$(011), four TiO$_2$ units are exposed, and they have the same height.
on an unreconstructed surface while two of them rise above the other two on a 2×1 reconstructed surface. In section 3.2.1, we have discussed an ordered Fe-Ti mixed oxide surface layer on the rutile TiO$_2$(011) surface. We performed calculations in a similar way in this work to search for the mixed oxide surface containing 1/3 ML of MO (2MO in one surface cell, M=Ni, Cr, V). Among all the obtained surfaces, the two models with the lowest total energies and simulated STM images are illustrated in Figure 3.44.

Generally, these structures still have the two characteristic conformations of the FeTi$_2$O$_5$ mixed-metal oxide monolayer surfaces. For one model, the two MO (M=Ni, Cr, V) units form a dimer anchoring at the pristine TiO$_2$(011)-1×1 support, and for the other model, the Ti and M (M=Ni, Cr, V) cations are uniformly distributed in the surface layer. We also simulated and compared the STM images of the two model surfaces.

As one can see, the first model gives the brightest features corresponding to the exposed M$^{2+}$ (M=Ni, Cr, V). At the same time, except for that of the NiTi$_2$O$_5$, the second model with the uniformly distributed Ti and M cations also gives the brightest features corresponding to the exposed M$^{2+}$ (M=Cr, V). The relative total energies of these structures are listed in table 3.4. The calculations predict that the second structure is less stable for the MTi$_2$O$_5$ (M=Ni, Cr, V) monolayer mixed oxides, in contrast to FeTi$_2$O$_5$ for which this structure was determined to be energetically favorable.

<table>
<thead>
<tr>
<th>Structures</th>
<th>FeTi$_2$O$_5$/TiO$_2$(011)</th>
<th>NiTi$_2$O$_5$/TiO$_2$(011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[56]Figure 1d</td>
<td>Figure 3.44a</td>
</tr>
<tr>
<td>$\Delta E$, eV</td>
<td>0</td>
<td>0.07</td>
</tr>
<tr>
<td>Structures</td>
<td>CrTi$_2$O$_5$/TiO$_2$(011)</td>
<td>VTi$_2$O$_5$/TiO$_2$(011)</td>
</tr>
<tr>
<td></td>
<td>Figure 3.34e</td>
<td>Figure 3.34i</td>
</tr>
<tr>
<td>$\Delta E$, eV</td>
<td>0</td>
<td>0.20</td>
</tr>
</tbody>
</table>

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Figure 3.44: DFT structural models for VTi$_2$O$_5$, CrTi$_2$O$_5$ and NiTi$_2$O$_5$ mixed monolayers on TiO$_2$(011)-2×1. Side views of two calculated structural models (left and right) for mixed monolayer oxides with half a monolayer of MO (M=Ni (a, b), Cr (e, f), V (i, j)) on a rutile TiO$_2$(011) surface and their corresponding simulated STM images. Ni atoms are in pink, Cr in blue, V in yellow, Ti in gray, and O in red. Reprinted with permission from ref[13], Copyright 2016-American Chemical Society.
3.2.3.3 Discussion of the Results

Intermixed oxides that are limited to the surface atomic layer of TiO$_2$(011) substrate are observed for V, Fe, Cr, and Ni deposited on TiO$_2$(011)-2×1. Formation of a similar structure for the intermixed oxide layer for all the transition metals investigated here is surprising but may reflect that Fe, V, Ni and Cr sesquioxides all crystallize in the corundum structure and, furthermore, FeTiO$_3$ and NiTiO$_3$ can exhibit the ilmenite structure in the bulk with Fe and Ni in a 2+ charge state. However, it should be pointed out that the surface structure of the intermixed monolayer does not have any obvious relationship with any surface structure of these bulk oxides. Therefore, these surface intermixed oxides have different properties compared to the bulk truncations of bulk mixed oxides and are therefore a distinct class of materials. The observed intermixed oxide surfaces have a well-defined composition and thus may be defined as a line phase in a M (M=V, Fe, Cr, Ni)- TiO$_2$(011) surface phase diagram with a MTi$_2$O$_5$ composition. This composition and structure must exhibit a minimum in surface free energy, but is not necessarily lower than the surface free energy of the clean TiO$_2$(011)-2×1 surface. The existence of two minima in the free energy as a function of transition metal composition is deduced from the behavior of the surface to segregates into a MTi$_2$O$_5$ and a clean TiO$_2$(011)-2×1 phase for a given coverage of M. In the case of two minima in the free energy as a function of composition, the ratio of the amount of these two phases is given by the lever rule and intermediate compositions are not observed. A similar phase segregation has been observed for surface alloying in metals e.g. for Ag on Pt(100). From this argument we expect that we can prepare a full layer of the intermixed oxide as we increase the coverage of M. This is approximately observed for Fe and V, although M diffusion into the bulk does not allow a linear correlation between deposited M and surface coverage of the MTi$_2$O$_5$ surface phase. For the other cations, namely Ni and Cr, the MTi$_2$O$_5$ phase competes with other
phases, e.g. a Cr$_2$O$_3$ surface layer and this competition between various phases makes it difficult to prepare a uniform surface with only MTi$_2$O$_5$.

It is tempting to compare the surface structures to known bulk phases. Especially the Fe-Ti oxide system is known to form many complex minerals. Particularly important are the ilmenite phase (FeTiO$_3$), the pseudobrookite (Fe$_2$TiO$_5$) and ferropseudobrookite (FeTi$_2$O$_5$) phases. From a charge state argument, both ilmenite and ferropseudobrookite have the Fe in a 2+ state while Ti is always 4+. Compositionally, the ferropseudobrookite matches the composition of our monolayer structure. However, we have found no evidence that our structure can be grown to more than a monolayer, and thus it is a true monolayer confined 2D-oxide.

As mixed oxide surfaces exhibit complicated structures, computational simulation and screening of possible structural models is desirable for predicting intermixed oxide surfaces. While the large parameter space makes a purely computational based prediction of surface structures currently unrealistic, in combination with experiments the parameter space can be reduced and experimental results can be verified. Through a global evolutionary algorithm aided DFT calculation, we obtained two model structures for a M/TiO$_2$(011) intermixed oxide, that are both well-ordered and quite stable. For the mixed-metal oxide surfaces containing Fe cations, the model with uniformly distributed Fe at the TiO$_2$(011) surface is more stable compared to the model with dimeric FeO units anchoring at the pristine TiO$_2$(011)-1×1 surface. Interestingly, for the mixed-metal oxide monolayer containing the other metal elements (M=Ni, Cr, V), the ilmenite (012) type surfaces with the MO dimer anchoring at the pristine TiO$_2$(011)-1×1 substrate turn out to be computationally most stable. However, from the simulated STM images, the surfaces with uniformly distributed Fe, Ni, Cr and V all give features that are closest to the experimental results and thus we need to conclude that this is the structure we observe for all the transition metals.
A closer look at the structures (see Figure 3.45) indicates that the ilmenite (012) type surface occurs as the result of a complete de-reconstruction of the TiO$_2$(011)-2×1 surface, and appears to be the supported surface with isolated rows of MO dimers at the pristine TiO$_2$(011)-1×1 surface, which are separated by empty surface valleys. On the other hand, the mixed-metal oxide surface with the uniformly distributed MO units also appears to be the supported surface, but the substrate is still a disordered TiO$_2$(011). More importantly, the uniformly distributed MO units now bind with all the exposed surface TiO$_2$ species. Therefore, one explanation for the observation of the same structure for all the transition metals is that this structure of MTi$_2$O$_5$ surfaces (M= V, Fe, Cr, Ni) is more readily formed since the dislocation of ALL the surface atoms of the TiO$_2$(011) support can be initiated and facilitated by the MO units.

While it appears that the same MTi$_2$O$_5$ structure can be observed for all the transition metals investigated, their preparation conditions and the extent to which we succeeded in preparing surfaces with this structure varied largely. For V the intermixed oxide could be formed by vacuum deposition and annealing in UHV, i.e. under reducing conditions by reacting with the substrate oxygen. For the other transition metals (Fe, Cr, Ni), the MTi$_2$O$_5$ phase could only be formed if they were annealed in an oxygen background. The oxygen pressure necessary during annealing for formation of the intermixed oxides increased in the order of V, Cr, Fe, Ni from vacuum-only,
annealing in $5 \times 10^{-8}$ Torr oxygen and vacuum annealing, annealing in $5 \times 10^{-8}$ Torr oxygen, to annealing in $5 \times 10^{-7}$ Torr oxygen, respectively. This indicates that an increased oxygen pressure is required from the left to the right of the periodic table and correlates with the heat of formation for the different oxides as is summarized in Table 3.5. [60] The larger heat of formation for oxides for vanadium than that for TiO$_2$ also explains that vapor deposition of vanadium on TiO$_2$(011) results in abstraction of oxygen from the substrate, i.e. a reduction of TiO$_2$ and simultaneous oxidation of V. These trends for reaction of metal deposits on TiO$_2$ has been previously pointed out mainly for studies on TiO$_2$(110) where transition metals left of Co in the periodic table were able to react with lattice oxygen from TiO$_2$. This reaction is apparently not enough for Fe and Cr to form the intermixed oxide layer, but is sufficient for V.

Table 3.5: The Oxygen Pressure needed while deposition and annealing and the heat of formation of oxide for MO and M$_2$O$_3$ (M=V,Cr,Fe,Ni)

<table>
<thead>
<tr>
<th>M</th>
<th>M$^{2+}$O</th>
<th>O$_2$ Pressure (Torr)</th>
<th>M$_2$O$_3$</th>
<th>O$_2$ Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_f$ (kJ/mol)</td>
<td>While deposition</td>
<td>While annealing</td>
<td>$\Delta H_f$ (kJ/mol)</td>
</tr>
<tr>
<td>V</td>
<td>-431.79</td>
<td>None</td>
<td>None</td>
<td>-1228</td>
</tr>
<tr>
<td>Cr</td>
<td>Not available</td>
<td>$5 \times 10^{-8}$</td>
<td>None</td>
<td>-1134.7</td>
</tr>
<tr>
<td>Fe</td>
<td>-271.96</td>
<td>$5 \times 10^{-8}$</td>
<td>$5 \times 10^{-8}$</td>
<td>-824.25</td>
</tr>
<tr>
<td>Ni</td>
<td>-239.74</td>
<td>$5 \times 10^{-8}$</td>
<td>$5 \times 10^{-7}$</td>
<td>-489.5</td>
</tr>
</tbody>
</table>

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Competition with other surface oxides also complicates the preparation of the ordered MTi$_2$O$_5$ (M= V, Fe, Cr, Ni). In particular for V, higher oxides are preferred and this results in the formation of different surface structure with V in a 3+ and 4+ charge state in the presence of even low O$_2$
pressures of only $5 \times 10^{-8}$ Torr. Similarly for Cr, the formation of Cr$_2$O$_3$ monolayer on TiO$_2$(011) seems to form readily and this may compete with the formation of an intermixed surface. Finally, from UPS spectra we find the valence band maxima for the different intermixed oxides. These values are summarized in table 3.6. For all the intermixed oxide surface layers we find the valence band maximum within the band gap of the TiO$_2$ substrate. This can have three possible explanations: (i) the band gap of the intermixed oxide layer is smaller than that of TiO$_2$, (ii) the electron affinity (energy difference between conduction band minimum and vacuum level) of the intermixed oxide layer is smaller than that of the TiO$_2$ substrate, giving rise to a staggered band alignment and/or (iii) the monolayer material is intrinsically p-type doped. These three explanations are not exclusive but the observed band gap states are likely a consequence of a combination of them. Table 3.6, also gives values for the bulk band gaps of sesquioxides and this may be used as a rough indication of an expected band gap for a MTi$_2$O$_5$ mixed oxide by taking the average value of the TiO$_2$ band gap of 3 eV with that of the sesquioxides. This approach can, at best, explain the trend of the VBM of the surface MTi$_2$O$_5$ to shift to higher binding energies from V to Fe to Cr. No reliable band gap values exist for Ni$_2$O$_3$, but the larger band gap of bulk NiTiO$_3$ compared to FeTiO$_3$ appears to contradict with the measurements of the VBM of the intermixed oxide surfaces. However, differences in the electron affinity and doping can make up for this apparent contradiction in the trend. It is also worth pointing out that in most interfaces we observe a shift of the Ti-2p peak to lower binding energies which was explained by an upward band bending of the TiO$_2$ substrate upon formation of MTi$_2$O$_5$ layers. This would be consistent with a depletion region in a p-n junction, i.e. electrons from the n-type TiO$_2$ diffuse into a more p-type adlayer. Thus this suggests that most of the MTi$_2$O$_5$ monolayers, apart from the VTi$_2$O$_5$ layer that did not show any band bending, are more p-type than the strongly n-type TiO$_2$-substrate. This
in turn implies that the Fermi-level in the MTi$_2$O$_5$ layers lie relatively closer to the VBM compared to TiO$_2$ and this may also contribute to the position of the VBM for the MTi$_2$O$_5$ layers relative to the TiO$_2$ VBM.

Table 3.6: Measured valence band maxima in UPS in comparison to some bulk band gaps of related oxides.

<table>
<thead>
<tr>
<th></th>
<th>Experimental VBM</th>
<th>Bulk band gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTi$_2$O$_5$</td>
<td>0.5 eV</td>
<td>V$_2$O$_3$ = 0 eV</td>
</tr>
<tr>
<td>CrTi$_2$O$_5$</td>
<td>2.2 eV</td>
<td>Cr$_2$O$_3$ = 3.2-3.4 eV</td>
</tr>
<tr>
<td>FeTi$_2$O$_5$</td>
<td>1.0 eV</td>
<td>Bulk band gap ilmenite FeTiO$_3$ = 2.54</td>
</tr>
<tr>
<td>NiTi$_2$O$_5$</td>
<td>0.8 eV</td>
<td>Bulk band gap NiTiO$_3$ = 3.0 Ni$_2$O$_3$ = Not available</td>
</tr>
</tbody>
</table>

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While there remains uncertainty for the underlying reason for measured VBM positions there may be some practical importance in photocatalysis of these states. TiO$_2$ as the prototypical photocatalysts has been studied with many transition metal modifiers, including the elements discussed here. Both bulk dopants as well as surface modifiers have been investigated. Our study shows that the surface structure in the monolayer regime is very sensitive and this may explain some challenges to obtain reliable results on these complex materials. For the MTi$_2$O$_5$ monolayers, the VBM is above the VBM for TiO$_2$, thus this suggests that these monolayers may trap holes at the surface efficiently and thus may modify the photocatalytic activity of TiO$_2$.

3.2.3.4 Conclusions

A variety of transition metals on rutile TiO$_2$(011) form intermixed surface oxide phases with a M$^{2+}$Ti$^{4+}$_2O$_5$ composition. Since the (011) facet is the second most abundant surface orientation in
a rutile equilibrium crystal shape, these mixed surface oxides may be important for oxidation catalysis of supported transition metals as well as in photocatalysis. The surface science conditions limit our studies to low oxygen chemical potentials but it is also conceivable that late transition metals like Pd may also form intermixed oxide phases with the TiO$_2$(011) surface at sufficiently high oxidation potentials of the gas phase. We propose that the formation of an intermixed surface oxide on the TiO$_2$(011) surface is facilitated by the relative instability of the bulk truncation of the (011) surface which also results in the reconstruction of its pristine surface. This notion implies that other oxide surfaces with surface energy-lowering reconstructions may also be prone to formation of intermixed oxides in the surface layer and thus exhibit unique structural and chemical properties.

### 3.2.4. Applications of Mixed Monolayer Oxide Surfaces

A couple of M/TiO$_2$(011) (M=metal) systems that have been synthesized and characterized above were tested for their possible applications theoretically and/or experimentally. For instance, CO oxidation on Fe/TiO$_2$(011) system was investigated via DFT based calculations and photocatalytic measurements were performed experimentally on Cr/TiO$_2$(011) system. Unfortunately, the time restrictions and the limited availability of experimental techniques got in the way of testing the possible applications of all the systems that have been synthesized.

#### 3.2.4.1 Fe/TiO$_2$(011) in CO Oxidation

Accurate determination of the nature of active sites on a surface is the key to understanding the adsorption and reaction mechanisms thereby exploring ways to enhance the performance of applications such as heterogeneous catalysis. For the FeTi$_2$O$_5$ mixed monolayer, the exposed Fe
appear to be the active site for catalytic oxidation reactions since it is apparently the only adsorption site for CO (Details of the adsorption of CO and O$_2$ for this surface can be found in our published work in ref[56]). Catalytic oxidation of CO on this surface can be taken as the probe reaction in understanding catalytic activities of this surface. CO oxidation by an oxygen molecule may follow Langmuir-Hinshelwood mechanism or Eley-Rideal mechanism (where CO reacts with adsorbed O$_2$ following its own way or by combining directly with adsorbed gas phase oxygen) or Mars-van Krevelen (MvK) type catalytic cycle (where adsorbed CO reacts first with lattice oxygen and the missing lattice oxygen recovers by O$_2$ adsorption). MvK type reaction pathway is not favored on this surface since the energy for creating an oxygen vacancy was found to be quite high. The results of the current work shows that CO oxidation can occur through colliding with gas phase O$_2$ sitting on FeTi$_2$O$_5$ surface layer. The reaction pathway is shown in Figure 3.47. O$_2$ has two adsorption configurations on this surface namely, bidentate and monobidentate. Accordingly, the CO oxidation reaction pathways with surface oxygen can be shown as in Figure 3.47. For the pathway shown in Figure 3.47a, in the transition state, the OC-OO distance decreases to 1.642 Å and the barrier energy is 0.94 eV and thus formation of CO$_2$ occurs via CO reaction with O$_2$ with weak adsorption strength. Considering the pathway shown in Figure 3.47b, the OC-OO distance decreases to 1.705 Å in the transition state and the barrier is 0.61 eV and again the CO$_2$ formation occurs via reaction of two molecules with negligible adsorption energy. After desorption of CO$_2$, a single adsorbed O (O$_{ad}$) is left at exposed Fe which can react with another CO molecule. In the reaction pathway shown in Figure 3.47c, the gas phase CO directly collide with O$_{ad}$ and the OC- O$_{ad}$ becomes 1.834 Å in the transition state with barrier energy 0.36 eV. After desorption of CO$_2$ the surface recovers to its original state exhibiting a sustainable catalytic cycle for CO.
Figure 3.46: Detailed structures of FeTi$_2$O$_5$/TiO$_2$(011). (a) side view, (b) top view, (c) O vacancy-O$_v$ from top view. Reprinted with permission from ref[56]Copyright 2016-Elsevier.

Figure 3.47: CO adsorption on FeTi$_2$O$_5$ mixed oxide monolayer. Calculated energy profiles for CO oxidation by adsorbed (a,b) O$_2$ and (c) single O$_{ad}$ at the FeTi$_2$O$_5$/TiO$_2$(011) surface. IS,TS and FS stands for initial state, transition state and final state respectively. Reprinted with permission from ref[56]Copyright 2016-Elsevier.

3.2.4.2 Cr/TiO$_2$(011) in Photocatalysis

Two CrTi$_2$O$_5$ covered TiO$_2$(011) samples were prepared using the procedure discussed in section 3.2.3. One sample was covered with 1/2 ML CrTi$_2$O$_5$ while the other one had ~ 2 ML of chromia on the surface. The photocatalytic activity was measured for these samples using the same experimental set up discussed in section 3.1.2. As a control experiment, photocatalytic activity was measures for the clean TiO$_2$(011) sample that was subjected to the same cleaning/annealing conditions used for CrTi$_2$O$_5$ preparation. The results were also compared to the photocatalytic
activity of a vacuum annealed clean TiO$_2$(011) sample which, according to the discussion in section 3.1.2, is expected have a high activity. Figure 3.48a shows the photocatalytic activity for the four samples. Interestingly, the TiO$_2$(011) sample covered with 1/2 ML CrTi$_2$O$_5$ shows the highest activity while the sample covered with 2 ML of chromia did not show such enhancement compared to the clean TiO$_2$(011) sample. This may suggest that the mixed monolayer of CrTi$_2$O$_5$ is the contributing phase for the enhanced photocatalytic activity. A simple schematic of the interface band alignment for TiO$_2$(011) and CrTi$_2$O$_5$ is shown in Figure 3.48b which was constructed using the UPS and XPS measurements given in section 3.2.3. This may be used to explain the enhancement in photocatalytic activity of this system and can also be applied to explain the expected enhancement for the other systems that have been studied.

![Figure 3.48](image)

**Figure 3.48:** Photocatalysis on Cr/TiO$_2$(011). (a) Photocatalytic activity for control sample, vacuum annealed clean TiO$_2$(011) sample, TiO$_2$(011) covered with ½ ML CrTi$_2$O$_5$ and TiO$_2$(011) covered with 2ML chromia. (b) Band diagram for TiO$_2$(011) and CrTi$_2$O$_5$ interface.

According to the energy band diagram, the valance band maximum (VBM) for clean TiO$_2$(011) occurs at ~ 2.6 eV with respect to the Fermi level consistent with strong n-type doping (bulk band gap for rutile TiO$_2$ is ~3 eV). The valance band maximum for the new surface phase (CrTi$_2$O$_5$ in this case) is located ~2.2 eV. This may suggest reduction of bulk band gap by ~ 0.4 eV. In addition
to that, an upward band bending of ~0.2 eV has been observed in XPS indicating formation of a
depletion layer in the surface region. Therefore, the holes created during the photo-excitation
process may get trapped in the valance band states of the new surface phase which in turn facilitate
charge transfer to adsorbed molecules and reduce charge recombination contributing to the
increase in activity.
CHAPTER 04

SUMMARY AND OUTLOOK

Metal oxide surfaces and interfaces play a major role in technological devices and applications. Titanium dioxide, a semiconducting transition metal oxide, is one of the most popular among them due to its fascinating surface properties and its widely spanned applications. In this dissertation, we first study two of the most important applications of TiO$_2$ namely, gas sensing and photocatalysis, which are directly related to the surface properties of TiO$_2$. Understanding the surface properties and interactions at their fundamental level is crucial in tuning the device performances. Motivated by that, we have studied the gas sensing properties of TiO$_2$ in an atomistic level via experimenting the adsorption and desorption behavior of 2,4-DNT on TiO$_2$(110). The experimental findings were supported by DFT-based computer simulations. We have found that the strong adsorption of DNT on TiO$_2$(110) surface induces a good gas response signal making it a suitable candidate in detecting such trace impurities which, otherwise, are very difficult to detect due to their low vapor pressure. Due to reactions of DNT with TiO$_2$ surface at elevated temperatures, thermal desorption does not seem to be an easy way to recover the surface, which indeed a disadvantage for a gas sensing material. However, we showed that DNT can be efficiently desorbed by photon-induced desorption, i.e. by illuminating the TiO$_2$(110) surface with UV light, thereby providing an alternative and an efficient way of recovering the surface.

Photocatalysis, being the most promising characteristic of TiO$_2$, was our second property of TiO$_2$ to investigate. We have found that different polymorphs of TiO$_2$ show different photocatalytic
activities. Photocatalytic activity not only varies among different phases of TiO₂ but also depends on the surface orientation for the same polymorph. According to our observations, anatase phase of TiO₂ has longer charge diffusion length than in rutile phase of TiO₂ and thus makes anatase photocatalytically more active than rutile. Rutile TiO₂(101) surface orientation, on the other hand, shows the highest photocatalytic activity among the other rutile TiO₂ orientations. Furthermore, we observed that the vacuum annealed TiO₂ surfaces are twice as active as the as-received samples, suggesting that it is a simple and an efficient way of enhancing photoactivity.

Exploring new methodologies to enhance the TiO₂-based device performances is an ever growing area of research. Modifying the TiO₂ surfaces with different elements is one of the approaches. A major part of this dissertation was therefore devoted to synthesis and characterization of novel surface phases which could be better candidates for sensing and catalytic applications. We have concentrated our study on deposition of few of the selected transition metals/metal oxides on TiO₂(011) surface and we investigated the electronic, chemical and structural changes that the TiO₂ surface undergoes in the process.

In particular, we have studied Fe/TiO₂(011), V/TiO₂(011), Cr/TiO₂(011) and Ni/TiO₂(011) systems and our main goal was to explore novel monolayer (mixed oxide) ordered structures. All these systems were characterized in UHV in an atomistic level in an attempt to understand the fundamentals of growth behavior and properties. We succeeded in growing well-defined ordered mixed monolayer oxides on TiO₂(011) for all these transition metals that have a unique structure with the composition MTi₂O₅ (M=Fe, V, Cr, Ni). The growth conditioned maintained for formation of these structures on TiO₂(011) helps predicting the growth behavior of other elements in the periodic table and thus these systems can be used as model systems in attempting other
multi-component monolayer mixed oxides. Importantly, these structures exhibit new electronic properties that have the potential in participating in catalytic reactions in a beneficial way.

Since we are now able to synthesize well-defined novel mixed oxide monolayer structures on TiO$_2$, along with a solid understanding of their fundamental electronic properties, in the future, we aim for exploring the ways to use these systems in applications such as, in particular, heterogeneous catalysis. In fact, our theoretical collaborators have tested the applicability of FeTi$_2$O$_5$ mixed oxide monolayer in heterogeneous catalysis and have shown that it can be a good candidate for CO oxidation. Supporting this observation experimentally is challenging with our current resources and facilities; however, the newly established UHV systems comprised with more sophisticated surface science characterization techniques would enable these experiments in the near future.


APPENDIX I

STRUCTURES AND XPD PATTERNS OF OTHER Fe-Ti-O MODELS

Figure AI-1: Second most stable structural model of Fe-Ti-O. The side view-(a) and the top view-(b) (reference[55]). Simulated XPD patterns for Fe 3p- (c) and for Ti 3s- (d) of this structure and the R factors are as given in the table.
**Figure A1-2:** Third most stable structural model of Fe-Ti-O. The side view-(a) and the top view-(b) (reference[55]). Simulated XPD patterns for Fe 3p- (c) and for Ti 3s- (d) of this structure and the R factors are as given in the table.
Figure AI-3: Fourth most stable structural model of Fe-Ti-O. The side view-(a) and the top view-(b) (reference[55]). Simulated XPD patterns for Fe 3p- (c) and for Ti 3s- (d) of this structure and the R factors are as given in the table.
Figure AI-4: Fifth most stable structural model of Fe-Ti-O. The side view-(a) and the top view-(b) (reference[55]). Simulated XPD patterns for Fe 3p- (c) and for Ti 3s- (d) of this structure and the R factors are as given in the table.
Figure AI-5: Sixth most stable structural model of Fe-Ti-O. The side view-(a) and the top view-(b) (reference[55]). Simulated XPD patterns for Fe 3p- (c) and for Ti 3s- (d) of this structure and the R factors are as given in the table.
APPENDIX II

COMPLETE INPUT FILE FOR EDAC SIMULATION

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APPENDIX III

EPITAXIAL CHROMIA FILM GROWTH ON RUTILE TiO$_2$(011)

Chromium was deposited via Molecular Beam Evaporation (MBE) on Rutile-TiO$_2$(011) substrate held at ~300 °C in some oxygen background (6×10$^{-8}$Torr). Characterization was performed in Ultra High Vacuum cambers equipped with Scanning Tunneling Microscopy (STM), Photoemission Spectroscopy (XPS, UPS) and X-ray Photoelectron Diffraction (XPD). In sub-monolayer regime, Cr forms ordered mixed oxide species by intermixing with substrate Ti atoms which was discussed in Chapter 3. For higher coverages, Chromia (Cr$_2$O$_3$) films seem to have formed exhibiting Cr$_2$O$_3$(1-102)[20-2-1]||TiO$_2$(101)[-111] epitaxial relationship. These films are stable upto ~750 °C in UHV.

Experimental Methods

STM studies were performed in a UHV chamber with a base pressure of ~2×10$^{-10}$ Torr equipped with an Omicron VT-STM operated at room temperature. Empty-state STM images were recorded at room temperature with electrochemically etched tungsten tips cleaned in-situ by voltage pulsing. All the STM images presented here were taken around 1.2 V bias voltage and ~400 pA tunnel current. XPS and UPS measurements were performed in a separate UHV chamber with a base pressure of ~ 5×10$^{-8}$ Torr. Chromium oxide/TiO$_2$(011) samples were prepared in the STM chamber and transferred into the photoemission chamber via a vacuum suitcase with a base pressure of ~10$^{-8}$ Torr. The commercially available TiO$_2$ (011) single crystal substrate (from MTI corporation) was prepared by multiple cycles of Ar$^+$ sputtering at room temperature (1 kV, 5 μA, 30 min) followed by UHV annealing at 700 °C for
30 minutes. Cr deposition was done by physical vapor deposition by heating a Cr rod in a mini e-beam evaporator. For the photoemission, a non-monochromatized dual-anode x-ray source (Omicron, DAR 400) for XPS and a He II VUV photon source (Omicron, HIS 13) for UPS were used. The kinetic energy of the scattered electrons was detected with a seven-channel hemispherical energy analyzer (Omicron, Sphera II). The XPS data were acquired with Mg-Kα X-rays. Shirley background has been applied across the entire Cr 2p peak and the 2p₃/2 portion was best fitted with two Gaussian (70%)-Lorentzian (30%) peaks modified by an asymmetric form A (0.32, 0.6, 10) where 0.32 and 0.6 define the spread of the ‘tail’ on either side of the peak while the parameter 10 specifies the width of the Gaussian. The two peaks were attributed to Cr³⁺ (577.0 eV/ FWHM 2.5 eV) and Cr²⁺ (576.1 eV/ FWHM 2 eV) with the peak positions reported in the literature.

**Results and Discussion**

The morphology and properties of Chromia films were investigated as a function of thickness and annealing temperature. Below we discuss the results in (i) Morphology characterization with STM (ii) XPS studies for thick films and thin films and the thermal stability (iii) UPS for thick films and thin films (iv) XPD studies for thick films.

(i) Morphology characterization of thin and thick films of Chromia on Rutile-TiO₂(011) with STM

First, Cr was deposited in 6×10⁻⁸ Torr of oxygen background pressure with Rutile-TiO₂(011) substrate held at elevated temperature (~350 °C). After 4 minutes of exposure period, oxygen was turned off and the sample was continued to anneal in UHV at the same temperature for another 10 minutes. The STM for such prepared sample is shown in Figure AIII-1a and small clusters of ~1-2 atomic layers tall have been observed. This sample was then annealed in UHV at somewhat higher temperature (~450 °C) for 10 minutes. As shown in Figure AIII-1b, the coverage of small clusters seem to have reduced while some ordering occurs along the row structure of the substrate. This sample was further annealed at ~600 °C in UHV for 10 minutes and two distinct features appeared on the surface as shown in Figure AIII-1c. One
structure is well-ordered and forms c(2×1) structure with respect to the TiO$_2$(011)-2×1 reconstructed structure (This was discussed in detail in Chapter 3). The other structure seems to exhibit some ordering along the rows of the substrate but the exact structure is yet to be determined. In an attempt to get a monolayer coverage, the deposition time was extended to 7 minutes while maintaining the same conditions. Figure AIII-2a shows the STM image for this sample. After annealing this sample in UHV at ~600 °C for 10 minutes, a nicely ordered structure was observed as shown in Figure AIII-2b. This structure seems to be stable in UHV-annealing for longer periods (30-60 min) at ~600 °C. Figure AIII-4(a and b) show the STM for thicker Chromia films deposited under the same growth conditions.

![Figure AIII-1: STM of thin Chromia films. (a) Cr deposited in 6×10⁻⁸ Torr of oxygen at ~350 °C for 4 min exposure period and annealed in UHV at the same temperature for ~10min; (b) sample-a annealed further in UHV at 450 °C for 10 min; (c) sample-b annealed in UHV at 600 °C for 10 min; (d) zoomed in view of sample-c.](image-url)
Figure AIII-2: STM of thin Chromia films. (a) Cr deposited in $6 \times 10^{-8}$ Torr of oxygen at $\sim 350 \, ^\circ\text{C}$ for 7 min exposure period and annealed in UHV at the same temperature for $\sim$10 min; (b) sample-a annealed in UHV at 600 $^\circ\text{C}$ for 10 min.

Figure AIII-3: STM of thick Chromia films. (a) Cr deposited in $6 \times 10^{-8}$ Torr of O$_2$ at $\sim 350 \, ^\circ\text{C}$ for 30-60 min exposure period and annealed in UHV at the same temperature for $\sim$10 min; (b) sample-a annealed further in UHV at 600 $^\circ\text{C}$ for 10 min.
(ii) XPS studies for charge state and thermal stability characterization.

A thick (1 hr deposit~1nm) film has been prepared in the STM chamber and transferred to the XPS chamber using a vacuum suitcase. According to XPS spectra shown in Figure AIII-4, initially (i.e. right after transfer), Cr is in 3+ charge state and Ti is mainly 4+ but a small 3+ shoulder is present. Upon annealing, a small shoulder features appear in Cr 2p peak and also in Ti 2p peak in the low BE regime due to the slight vacuum reduction.

![Figure AIII-4: XPS of thick Chromia films.](image)

Figure AIII-4: XPS of thick Chromia films. (a) Cr deposited in $6 \times 10^8$ Torr of oxygen at ~350°C for ~10min exposure period and annealed in UHV at the same temperature for ~10min (transferred from STM chamber) overlapped with sample after annealing at 500°C 10 min in UHV; (b) Cr 2p3/2 peak fit for sample after transfer; (c) Cr 2p3/2 peak fit for sample after anneal at 500°C; (d, e, f) corresponding XPS for Ti 2p peaks.

(iii) UPS studies for thick and thin chromia films on rutile-TiO$_2$(011)

Figure AIII-5 shows the UPS spectra overlapped for clean TiO$_2$(011) sample, a thin( 7 min deposit) Cr-Ti-O film and for a thick (1 hr deposit). As can be seen, the oxygen 2p valance band edge lies ~0.5 eV higher than that of clean TiO$_2$(011) sample. Also, a density of state centered around 2.2 eV appears in the band
gap region of clean TiO$_2$(011). For the thin film, a shoulder feature appears around 2.1 eV which may have resulted due to formation of an interface structure that was discussed in Chapter 3.

Figure AIII-5: UPS for Chromia films. (a) clean TiO$_2$(011), for 7 min deposit, for 60 min deposit samples; (b) zoomed view of low BE region.

(iv) XPD studies for ~10nm thick Chromia film on rutile-TiO$_2$(011)

To study the epitaxial relationship between thick Chromia films and rutile-TiO$_2$(011) surface we performed XPD on a thick Chromia film. Cr$_2$O$_3$ crystallizes in Corundum structure as in r-cut Al$_2$O$_3$. We discussed earlier that r-cut Al$_2$O$_3$ is a well-suited substrate for growing high quality epitaxial rutile TiO$_2$(011) (which is identical to TiO$_2$(101)) thin films. Figure AIII-6 illustrates the expected lattice match between r-cut Cr$_2$O$_3$ and TiO$_2$(011) and r-cut Al$_2$O$_3$. Experimentally observed XPD pattern for Cr 2p is shown in Figure AIII-7. The pattern is clearly symmetric in one azimuth angle goes along the (1-10 2) plane. The experimental peak positions match with the simulated diffraction peak positions except for the minimum observed near zero. This may have due to the low resolution in XPS analyzer. XPD was also performed for Al$_2$O$_3$(1-102) single crystal sample which further confirms the epitaxy.
Figure AIII-6: Lattice match between rutile TiO$_2$(101), Corundum Cr$_2$O$_3$(1-102) and Corundum Al$_2$O$_3$(1-102). (a) top view and side view of (101) plane of rutile-TiO$_2$(101). (b) top view and side view of [-1 1 0 2] plane of corundum Cr$_2$O$_3$(1-102). (c) top view and side view of [1-10 2] plane of corundum Al$_2$O$_3$(1-102).

Figure AIII-7: XPD of thick Cr$_2$O$_3$ film on rutile TiO$_2$(011). On top is the experimental XPD for Cr 2p, middle one is the experimental XPD for single crystalline Alumina, Bottom one is simulated XPD for Cr 2p for single crystal Cr$_2$O$_3$ cluster.
APPENDIX IV
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APPENDIX V

LIST OF JOURNAL PUBLICATIONS OF THE AUTHOR


3. **Ordered Fe (II) Ti (IV) O₃ Mixed Monolayer Oxide on Rutile TiO₂ (011)**; Sandamali Halpegamage, Pan Ding, Xue-Qing Gong, Matthias Batzill; *ACS Nano*, 2015, 9 (8), pp 8627–8636; (Citations 7)

4. **Fe (II) Ti (IV) O₃ mixed oxide monolayer at rutile TiO₂ (011): Structures and reactivities**; Zhan-Hui Wen, Sandamali Halpegamage, Xue-Qing Gong, Matthias Batzill; *Surface Science*, 2016, 653, pp 34–40; (Citations 2)

5. **Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO₂ films**; Tim Luttrell, Sandamali Halpegamage, Junguang Tao, Alan Kramer, Eli Sutter, Matthias Batzill; *Scientific reports*, 2014, 4; (Citations 211)

7. Combined surface science and DFT study of the adsorption of dinitrotoluene (2, 4-DNT) on rutile TiO2 (110): molecular scale insight into sensing of explosives; Junguang Tao, Qian Cuan, Sandamali Halpegamage, Rafik Addou, Xue-Qing Gong, Matthias Batzill; *J. Phys. Chem. C, 2013, 117* (32), pp 16468–16476; (*Citations 3*)

8. Investigation of the dipole formation and growth behavior at In2O3| TiO2 heterojunctions using photoemission spectroscopy and atomic force microscopy; Michael Schaefer, Sandamali Halpegamage, Matthias Batzill, Rudy Schlaf; *J. Appl. Phys.*, 2016, 119, 065305

* Epitaxial Chromia Film Growth on rutile TiO2(011) by Pulsed Laser Deposition: Applications in Photocatalysis; Sandamali Halpegamage, Matthias Batzill; (In preparation)
ABOUT THE AUTHOR

Sandamali Halpegamage obtained her B.Sc. special degree in Physics from the University of Peradeniya, Sri Lanka. She joined the graduate program in the University of Mississippi, Oxford, MS, USA in 2010 and transferred to the University of South Florida, Tampa, FL, USA in 2011. During her time as a research assistant in Dr.Matthias Batzill’s group at USF, she published eight papers in peer-reviewed journals and was awarded the 2016-Summer Fellowship. Upon completion of her Ph.D. she starts working as a Post Doc. Research Associate in the same group. Her research interests are Surface Science of Titanium dioxide and its applications in gas sensing and photocatalysis, monolayer mixed oxides and 2D materials.