Photocatalysis and Grazing-Ion Beam Surface Modifications of Planar TiO2 Model Systems

Timothy Luttrell

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Photocatalysis and Grazing-Ion Beam Surface Modifications of Planar TiO$_2$ Model Systems

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of
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Date of Approval:
April 4, 2014

Keywords: epitaxial films, charge carrier diffusion, grazing incidence ion sputter, methyl orange

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Dedication

I am immensely fortunate to have the unwavering support of my incredible wife Melissa who has always believed in my abilities, continually challenged me for greater success, and innumerable sacrifices to help me arrive to this point. In addition, to my mother and grandmother for their many years of support through much needed advice, wisdom, and helping hands along the way. Lastly, to my extended family and friends who have always tolerated my conversation, given me much needed laughter, and continually providing me with that question every PhD candidate cannot possibly reach his dissertation without “When are you going to graduate?”
Acknowledgments

I would like to thank my advisor Dr. Matthias Batzill for the many years of bottomless scientific wisdom, patience to persevere through my numerous challenges, dedication to make me a better investigator, generous funding to give me the opportunity to pursue my dreams, and deep friendship for which I will be eternally grateful. Also, so much help was also given from Junguang Tao by readily providing his vast knowledge of XPS and photocatalysis. Additionally, many thanks to Sandamali Halpegamage for her many hours of experimental work adding to my results. I also appreciate the collaborative support from Dr. Eli Sutter, W.K. Li, and X.Q. Gong.

I also wish to also thank Dr. Anthony Buonaquisti for opening my mind to physics and intriguing me with his superb fundamental explanations of so many physical principles. I am thankful for the immense help of Daisy Matos, Candice Pietri, Luisa Ojeda, and Mary Ann Prowant, Bobby Hyde and the entire Physics staff. Furthermore, through the tireless efforts of Pritish Mukherjee, the USF Department of Physics has become an excellent research facility with world renowned faculty providing class leading technology for use. In addition, so much of my experimental design and construction would not be possible without the help of machinists Bob Harrington and James Christopher. Much gratitude to Dr. Rafik Addou, and Dr. James Lallo for wisdom always a few years ahead. Many thanks are also deserved to Arjun Dahal, Alan Kramer, Horacio Coy Diaz, Yujing Ma (Maggie), and Dr. Jayeeta Lahiri for their help with many of my experiments and loyal friendship.
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Abstract

This dissertation is related to the understanding of catalytic reactions of metal oxides. For several decades, the surfaces and bulk of materials have been probed to determine additional properties that relate to photocatalytic applications. This investigation furthers these efforts by the (a) modification of a metal oxide surface to isolate known influences of chemical properties and (b) proposing and utilizing a novel methodology for attribution of photocatalytic activity to a discernable influence. For the first effort, by effectively utilizing a known technique for a new application on a metal oxide, such isolations can be made despite unfavorable states. For the second effort, a reduction in the influence of surface states for metal oxides is effectively performed, providing the isolation of influences originating from the bulk. The challenge with such a proposal is verifying such bulk states have been adequately isolated as external influences would obviously distort any conclusions. Thus, techniques to both create such bulk states and eliminate unwanted combinations thereof are additionally required and must be provided for. Lastly, a determination of the photocatalytic activity is made to these states and results are provided.
1. Introduction

Due to the demands the ever increasing global population has placed upon the world’s limited resources, new technologies have emerged as the only real solution capable of solving such complex and large scale issues related to our environment. Significant efforts have been placed into developing clean, inexpensive, and sustainable principles and materials to mitigate the effects of human consumption. Just as many other seemingly unrelated technologies have moved to nanoscale materials and devices, so too has environmental research, employing many of the same principles. Solutions to both of these problems have relied heavily on collaborations between many scientific disciplines including physics, chemistry, biology, engineering, and medicine. Many of these principles have been the result of careful research into surface and bulk properties of materials. Certainly, surface science has opened many opportunities into furthering our understanding of interfaces, clusters, nanostructures, and biotechnology. For example, unique properties of tin oxide permit its use as a solid state gas sensor because in the presence of certain gases, the electrical conductance changes yielding detection \[16\]. This obviously has wide uses for security and medical applications. Additionally, petroleum reforming can be improved by utilizing multiple functional catalysts with surface active sites to increase quality of output such as increasing octane ratings \[17\]. Just as the surfaces of materials aid in the production of fuel, novel surfaces can assist in the conversion of the resulting pollutants harmful to the world’s ecosystem. The most popular of which is a three-way catalytic converter usually consisting of Pt to catalyze gases including nitrogen oxides, hydrocarbons, and carbon monoxide into cleaner gases such as nitrogen, oxygen, carbon dioxide, and water among others, depending on input gases \[18\]. Titanium dioxide (TiO\(_2\)), the
most well-known photocatalyst and the focus of this dissertation, has been the focus of intense efforts to increase its capabilities, efficiency, and therefore use for environmental impact. Due to its popularity and success, it has also become a model for many other metal oxides and other applicable systems. However, fundamental questions remain in relation to the surface and bulk properties of TiO₂. Specifically, what significant differences exist between the popular phases of TiO₂ related to photocatalytic activity? Additionally, what challenges remain that can be overcome with modifications to the surfaces of TiO₂ for the greatest impact on this and other metal oxides?

1.1 TiO₂

Titanium dioxide exists in three main structures: anatase, rutile, and brookite. Although several other structures are known to exist, they are of little importance in the context here. However, only the two most common polymorphs, anatase and rutile, will be examined here. The anatase and rutile structures of TiO₂ both have a tetragonal unit cell shown in Figure 1.1. However, their lattice spacing do differ and are listed in Table 1.1. These different values between phases also contribute to different atomic densities. In particular, rutile TiO₂ has six atoms per unit cell (two Ti and four O), while anatase has 12 atoms per unit cell (four Ti and eight O). Therefore,

<table>
<thead>
<tr>
<th>Structure</th>
<th>a=b, Å</th>
<th>c, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>3.782</td>
<td>9.502</td>
</tr>
<tr>
<td>Rutile</td>
<td>4.584</td>
<td>2.953</td>
</tr>
</tbody>
</table>

*Table 1.1 Lattice constants of TiO₂. A listing of the a, b, and c lattice constants of anatase and rutile TiO₂ [3].*

*Figure 1.1 Polymorphs of TiO₂. Shown are ball and stick models of two TiO₂ polymorphs, (a) rutile and (b) anatase. The large red spheres represent O atoms while the small blue spheres represent Ti atoms.*
given the differences in atomic density and unit cell dimensions, different densities are expected and given as 4.2 g/cm$^3$ and 3.9 g/cm$^3$ for rutile and anatase TiO$_2$ respectively [19].

Titanium dioxide (TiO$_2$) is utilized in a variety of applications for a number of seemingly unrelated uses. One of the most common and popular commercial uses is as a white pigment in paints and cosmetics, even in toothpastes. Much of their effectiveness is owed to its high refractive index relative to many other inorganic pigments and was even utilized as a sunscreen as early as 1952 [20]. Certainly, a pigment used in ambient conditions such as paint or cosmetics must be stable, degrade minimally, and of course be non-toxic. It is non-toxic to humans and animals in normal quantities and thus approved for use as food additive not to exceed 1% by weight. Even uses as implants have been approved by the U.S. Food and Drug Administration (FDA) [21, 22]. Furthermore, engineering fields have made improvements to its durability as well. Reports have suggested that hardness, wear, and corrosion have been improved by co-deposition of Ni and TiO$_2$ nanoparticles onto the surface of an Al alloy [23]. In addition, TiO$_2$ has found uses as a high surface area component in Dye-sensitized Solar Cells (DSSC), originally known as a Grätzel cell [24]. As mentioned earlier, TiO$_2$ has is a wide-band gap semiconductor, making it unsuitable for efficient terrestrial power applications under visible light. However, a DSSC compensates for this challenge by using a dye to absorb visible light and injecting photogenerated electrons into the CB of TiO$_2$. The electrons are subsequently carried from the TiO$_2$ to a transparent electrode such as FTO. Conversely, the photogenerated hole is carried from the dye through the electrolyte to the cathode, preserving the subsequent generation of photogenerated electrons and holes. Thus, satisfying the purpose of DSSCs by providing a current between the anode and cathode for electrical power [25]. Lastly, titanium dioxide is perhaps the most widely used photocatalyst for novel research and industrial use [26-28]. However, some of its original challenges to wide-spread commercial use still remain because of inefficiencies. Despite these obstacles, opportunities still remain for new uses and as models for many other metal oxides.
1.1.1 Band gap

As was described, the anatase and rutile TiO$_2$ have different atomic configurations of the Ti and O lattice. One of the most obvious differences to explore in such a semiconductor exists in the electronic states of the two structures. In the physics of semiconductors, a band gap is defined as an energy regime where electron states are prohibited from existing. The band gap is bound by the conduction band (CB) at the top and the valence band (VB) at the bottom. A large agreement of research has demonstrated that the band gaps of anatase and rutile are at 3.20 eV and 3.03 eV respectively [29, 30]. In addition, the band gaps of TiO$_2$ are different types. A band gap in a semiconductor is either direct or indirect. Both the energy for the top of the valence band (VB) and the bottom conduction band (CB) are a function of wave vector $k$ and both vary accordingly. When the maximum value for the valence band and the minimum of the conduction band occur at the same wave vector $k$ in the Brillouin zone, the band gap is direct. When these two values occur at different wave vectors, the band gap is indirect. An example of a direct and indirect band gap is shown in Figure 1.2. There has been an intensive debate on whether anatase and rutile TiO$_2$ have direct or indirect band gaps. Several reports have suggested that anatase actually has an indirect band gap [31-35]. In contrast, the band gap for rutile is mostly considered to be direct because the difference in energy between the direct and indirect band gap is negligible (0.04 eV) [36]. Nonetheless, the direct/indirect nature and value have been suggested to be contributing factors in observed differences in photocatalytic activity. Such ambiguities are difficult to resolve as several other properties related to the influence of bulk and surface states are challenging to minimize.
1.1.2 TiO$_2$ surfaces

The anatase phase has essentially two widely studied surfaces as a result of their low energy states, (001) and (101) [37-39]. Both surfaces have alternating Ti and O rows with two-fold O atoms and five-fold coordinated Ti atoms. However, the (101) surface has an additional alternating row of six-fold Ti and three-fold O atoms that appear in the “trench.” As we see in Figure 1.3, the (001) surface is fairly flat relative to the slight corrugation on the (101) surface. Additionally, the anatase (001) surface can reconstruct in a (1x4) structure [33]. Because of the different constructions, each of these anatase TiO$_2$ surfaces have different surface energies. The energy of a surface can be defined for a temperature and pressure known as the Gibbs surface free energy and will be different values for different surfaces [40]. Larger surface energies are also usually associated with more corrugated surfaces. However, actual quantitative surface energy measurements are challenging to obtain but have been calculated for different TiO$_2$ surfaces as will be discussed later. Further complicating the determination of surface energies are steps, adatoms, vacancies, and other deviations from a perfect surface. Nonetheless, calculations have been made and given as {110} (1.09 J m$^{-2}$) > {001} (0.90 J m$^{-2}$) > {100} (0.53 J m$^{-2}$) > {101} (0.44 J m$^{-2}$) [41]. Certainly, the {110} surfaces have a much higher surface energy and would be the least common to occur within the group. In general, surfaces with higher average surface energies have higher reactivity [42]. Several theoretical calculations have suggested that the anatase
(001) surface is more reactive than the anatase (101) [36, 3]. Therefore, efforts have been made to stabilize such high reactivity surface. To do this, Yang et al utilized TiF₄ aq. solution as the precursor and HF acid as a controlling agent to generate anatase bipyramids of mostly {001} and {101} facets [43]. HF acid, the determinant factor in the production of these crystals, is thought to have two functions. The first function is to retard the hydrolysis of TiF₄ and the second function is to reduce the surface energy, effectively promoting isotropic growth along the [100] and [010] directions. Subsequent studies using HF as the controlling agent to produce such unstable (001) facets, demonstrated increased photocatalytic activity [39]. However, the activity was found to decrease after residual HF was washed from the crystal with NaOH [33]. It has been suggested that Ti-F-H complexes increases O₂ adsorption, improving charge separation yielding increased photocatalytic activity. Thus, could such attributed charge separation be accomplished by other means with more stability?

Rutile also has four common surfaces, (110), (100), (001), and (011). The (110) surface is the most investigated because of its high relative stability over the other three. The rutile (110) surface also has rows of alternating Ti and O atoms, but different from anatase (101), the Ti atoms are five-fold and six-fold coordinated to bridging two-fold coordinated and 3-fold coordinated O atoms respectively. Rutile (100) is

Figure 1.4 Ball and stick models of several rutile TiO₂ surfaces. The (110) surface (a) has five-fold Ti₅c and six-fold coordinated Ti atoms with bridging two-fold O₂c and three-fold O₃c atoms. The (100) surface (b) has Ti₅c and O₂c while (001) has Ti₄c and O₂c at the surface. The (011) surface (d) also has five-fold Ti and two-fold O.
similar to (110), with alternating two-fold coordinated bridging O atoms and five-fold coordinated Ti atoms, but without six-fold coordinated Ti atoms at the surface. Their geometries are given in Figure 1.4. Different from (110) and (100), the (001) surface is relatively flat with four-fold coordinated Ti atoms connected to bridging O atoms on either side of each row. This surface has much less thermal stability and is known to reconstruct at temperatures above 475°C [27]. Lastly, similar to the (100) surface, the (011) surface also has five-fold coordinated Ti and two-fold O atoms at the surface. Thus, the coordination number of the Ti and O atoms at the surface depends on not only the phase, but also the specific surface orientation. Because of these distinctions in surface architecture, the relationship of each surface to vacancies and adsorbates, can be different.

1.1.3 TiO$_2$ step edges

The surfaces of crystalline materials consist of atomic terraces with different structures and terminations. However, these surfaces may also exhibit defects as step edges of various constructions. The formation of step edges on metal oxides such as TiO$_2$ are dependent upon the surface and formation energy in thermodynamic equilibrium [44]. Step edges, and to a certain extent surfaces, that are auto-compensated are generally defined as non-polar and are usually more stable than their polar counterparts and thus more likely. Thus, by carefully calculating the formation energies of the steps based upon the corresponding structure, the relative stability of step edges can be determined. The anatase (101) surface is characterized by trapezoidal islands outlined by a series of step edges along four sides. Gong et al made calculations of the formation energies suggested that the step edges parallel to the [010] have a lower formation energy when constructed with five-fold Ti and two-fold O atoms compared to four-fold Ti and two-fold O atoms [45]. In addition, constructed step edges parallel to the [-111] only were suggested to be four-fold Ti and two-fold O atoms. The step edge with the lowest
formation energy of all steps evaluated was parallel to the [11-1] consisting of five-fold Ti and two-fold O atoms. Interestingly, the formation energies of these steps are in the same relative order as the extended surfaces to which these local steps represent. The [010] step edge, with a corresponding extended surface of {110} and a high surface energy, was shown to have the highest step formation energy while the [-111] step edge has the lowest step formation energy, corresponding to the extended surface of {112} [45]. Therefore, the relative energy of steps is comparable to the surfaces in which they are most resemble. Yet, other studies present the idea that reconstructions may enable auto-compensation. For example, rutile (110) has common atomic-height step edges parallel to the <001> and <111> directions [46]. STM measurements have observed that about half the <001> step edges possess a (4x1)-reconstruction [47]. A quick modeling of the surface reveals that if the Ti-O bonds, shown as the Ti$_{5c}$-O$_{3c}$ in Figure 1.4(a), are severed along the Ti rows, a row of in-plane Ti atoms remain. The study suggests a reconstruction results from the removal of three of the four in-plane Ti atoms accompanied by a neighboring O atom. This configuration is auto-compensated and is likely the (4x1)-reconstruction observed in STM measurements.

1.2 Photocatalysis

The distribution of energy is vastly unbalanced in the electromagnetic spectrum. We see in Figure 1.5 that the majority of energy is centered in the visible and infrared regime. As we saw earlier, most of this energy is therefore below the band gap of TiO$_2$ and therefore cannot generate charge carriers required for photocatalysis. Therefore, new

Figure 1.5 Solar energy as a function of wavelength. The intensity versus wavelength demonstrates a majority of energy available in the visible light regime. Fig. from ref. [11].
methods and techniques have been explored to improve the response of TiO$_2$ to become more efficient with the available spectrum. In a semiconductor such as TiO$_2$, incident photons with energies larger than the band gap may excite electrons from the valence band (VB) into the conduction band (CB) thus creating an exciton, also known as an electron-hole pair. If these electron-hole pairs can migrate to the surface or near-surface, they may separate and perform redox, or reduction-oxidation reaction at the surface of the semiconductor. At the surface of a photocatalyst, the electrons generated can reduce an electron acceptor while the holes generated can oxidize an electron donor. Since most photocatalytic reactions occur within some environmental condition, the chemical stability of the semiconductor is a major concern. Therefore, most photocatalysts are (wide band gap) metal oxides. In addition, a significant concern for an efficient photocatalyst is the availability of electrons and holes at the surface where the chemical reactions occur. Therefore, this requires the suppression of charge carrier recombination and trapping within the bulk while maintaining efficient transport of charge carriers from the bulk to the surface where the electron-hole separation and chemical reactions occur. Figure 1.6 illustrates such a possible de-excitation and surface reaction mechanism for photo-excited electron-hole pairs.

Figure 1.6 De-excitation and surface reaction mechanism excitons. Incident photon energy strikes the photocatalyst creating electron-hole pair. The electron is free to migrate to the surface where it can recombine with hole (1), recombine in the bulk with a hole (2), or be accepted by an electron acceptor (3). The created hole can also migrate to the surface where it can combine with an electron from a donor (4). The excitation of the electron from the VB to the CB and the hole from the CB to the VB is shown in the upper right corner.
1.3 Surface/Interface contribution of TiO$_2$ to photocatalysis

The relevance of surfaces and interfaces can be easily discussed by dividing into three main categories. Generally, the lower the coordination of Ti or O results in a higher reactivity with the adsorbate thus different surfaces may have different reactivities [48, 3]. For example, the rutile (110) and (100) surfaces have five-fold coordinated Ti atoms while the rutile (001) has four-fold coordinated Ti atoms. Second, the electronic states of a clean, defective, or adsorbate surface may have different influences on the separation or trapping of excitons and charge carriers at the surface. Third, the alterations defects make to the surface of TiO$_2$ create may significantly affect the binding of molecules on the surface. Third, the potential differences at the surface including work function and flat band potentials can also have an effect on the photocatalytic activity of TiO$_2$. These two factors may have an influence on the transfer of charge between TiO$_2$ and adsorbates.

1.3.1 Coordination

To begin, we review the reactivity of the differently coordinated facets of TiO$_2$. Lowekamp et al created rutile TiO$_2$ polycrystalline ceramics including individual crystallites, followed by subsequent polishing and annealing to produce multiple surface orientations summarized in Figure 1.7 [8]. The samples were deposited with a 2.5 nm
layer of 0.1 M AgNO$_3$ and exposed to UV light, followed by imaging with contact atomic force microscopy to determine the amount of Ag on the surface. To quantitatively determine the amount of crystallographic planes, electron backscattered diffraction patterns were taken and correlated with the earlier AFM images to correlate the photocatalysis of AgNO$_3$ to Ag on the surface of TiO$_2$. In brief, the four-fold Ti atoms were found to be in high density on steps within the \{101\} and \{111\} surfaces that demonstrated high Ag deposition while the \{110\} surfaces, having small densities of four-fold Ti atoms on steps, demonstrated little Ag deposition from photocatalysis. Other reports have suggested that these four-fold coordinated Ti sites have strong tendencies to participate in certain partial oxidation reactions [49, 50]. In particular, while octahedral Ti is known to photocatalytically decompose NO into NO$_2$, tetrahedral Ti$^{4+}$ has been shown to decompose NO into O$_2$, N$_2$, and N$_2$O [51]. This suggests the existence of selective chemical reactions for different Ti sites. Certainly, differently coordinated Ti sites on clean surfaces may not only demonstrate differences in reactivity under UV irradiation, there also appears to be differences in surfaces with defects as well. Although it appears that differently coordinated active sites have shown differences in photocatalytic activity, there is significant evidence to support the concept that coordination is not the only factor and charge carrier behavior may play a significant role.

Active sites along step edges may act as binding sites for chemical reactions on TiO$_2$. Hebenstreit et al observed four-fold Ti$^{4+}$ atoms on anatase (101) along the [-1-11] and [-1-1-1]-oriented step edges and suggested that they may be binding sites for adsorbed atoms [52]. Similarly, Martinez et al demonstrated that creating reduced rutile (110) surfaces by high temperature vacuum annealing, the step edges hold O vacancies along the <1-11> step edge that may be active sites for ethanol dissociation [53]. Other efforts have been made to compare the relative contributions of such step edges to photocatalysis. Specifically, vicinal surfaces of rutile TiO$_2$(110) with high densities of step edges parallel to the [011] and [1-11] directions demonstrated higher rates of photodegradation of methylene blue than rutile (110) with lower
step density. More importantly, step edges parallel to the [011] were shown to yield higher rates of the same dye degradation than the step edges parallel to the [1-11] direction [54]. It has been suggested that the step edges of these surfaces have a much higher density of shallow electron and deep hole traps relative to the terraces and attributable to their coordination. Furthermore, the [011] step edges are believed to have a higher quantity of shallow electron traps while the deep hole traps are only present on the [1-11] step edges, explaining the differences in photodegradation rates.

1.3.2 Charge trapping at the surface

Defects at oxide surfaces are considered a core component of chemical functionalities of oxides. Oxygen vacancies have been shown to be points at which water easily dissociates to form two bridging OH groups [55]. Figure 1.8 depicts an oxygen vacancy and a single hydroxyl on the surface at the bridging oxygen locations. Not only are the hydroxyls themselves important in the role of catalysis, the Ti-O-H complexes are thought to be trap locations for charge carriers. Studies have utilized electron paramagnetic resonance to show that Ti$^{3+}$(OH) complexes can act as electron traps [56]. In addition, Ti-O-H groups may act as hole traps, becoming Ti$^{4+}$(OH) radicals [57]. As we described earlier, the behavior of these electrons and holes are key principles in photocatalysis. Oxygen vacancies and hydroxyls also donate electrons to the surrounding Ti-atoms, filling Ti-3d states and thus introducing localized states. Each individual oxygen vacancy yields two additional extra electrons with additional Ti 3d electronic states approximately 2 eV above the VB maximum in the band gap [58]. Tao et al have suggested that, although the coordination...
between the two differently coordinated Ti on the \{101\} and \{110\} is different, the difference in photocatalytic activity is the result of differences in charge carrier behavior at the surface [59]. The binding energy of excess charges (induced by electron donation from an adsorbed hydrogen) was found to be higher on the (011)-2x1 reconstructed surface than the (110) surface. Therefore, the electron-hole separation and electron trapping is more beneficial for oxidation reaction and thus photocatalysis. This illustrates a pathway how surface structure can affect surface charge trapping and interface charge transfer due to variations in energy-level of impurity induced excess electrons and/or excited charge carriers. These surface structural effects may be utilized to benefit photocatalysis.

1.3.3 Potential differences at the surface

1.3.3.1 Work function

The work function of a solid face is the minimum amount of energy to displace an electron from a point within a solid to another point infinitely far from the surface. This can also be defined as the minimum amount of energy required to take an electron from the Fermi level to vacuum and can be a property of the face of the solid. This is given as

$$\varphi = -(E_F - E_0)$$

(1.1)

where $E_F$ is the Fermi energy and $E_0$ is the vacuum level energy [60]. In metals, the work function is strongly correlated to the surface dipole formations. These dipoles are the result of electron density from wave functions extending from the surface and the net positive charge close to the surface of a electron depleted region [12]. Given that the work function represents an electron’s ability to traverse the surface, alterations to a pristine surface such as adsorbates can easily alter the work function. Similarly for semiconductors, these defects, including vacancies, and adsorbates on the surface may also present a higher density of band gap states
which affect the dipoles at the surface. These band gap states may also offer additional pathways for the electrons to traverse into the vacuum, thus also affecting the work function.

Differences in the work function between crystal planes have been reported. For anatase surfaces, the order of work function has been calculated to be (110) < (001) < (100) < (101) [4]. Their values are given in Table 1.2. This suggests the possibility of differences in dipole moment which may reflect changes in the electron distribution and density at the surface. Such differences in dipole moment may affect the path of electrons and holes. Thus, contributing to observed differences in photocatalytic activity.

In addition, defects and adsorbates at the surface can change the work function according to different particular defects. Borodin et al explored how the work function changed for the different unreconstructed surfaces of rutile (110) according to preparation conditions [12] These include reduction, a hydroxylation and oxidation, only hydroxylation, and reduction then oxidation. The samples were prepared and subjected to metastable impact electron spectroscopy and (MIES) [61]. Figure 1.9 displays the resulting MIES spectra for all four individual samples. We can immediately see from the figures that all four surfaces have different values for work function. The reduced TiO$_2$(110) surface has a work function of 5.2 eV. The work function decreases to 4.9 eV when the surface is hydroxylated. When the hydroxylated surface is

<table>
<thead>
<tr>
<th>Surface</th>
<th>Work Function, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(101)</td>
<td>6.578</td>
</tr>
<tr>
<td>(100)</td>
<td>5.010</td>
</tr>
<tr>
<td>(001)</td>
<td>4.924</td>
</tr>
<tr>
<td>(110)</td>
<td>4.599</td>
</tr>
</tbody>
</table>

Table 1.2 Work function values for different surface of anatase TiO$_2$. For theoretical calculations, almost 2 eV difference is calculated between different surfaces of anatase TiO$_2$ [4].
further annealed with molecular oxygen, the work function increases to 5.35 eV. Lastly, by oxidizing the reduced surface with molecular oxygen at high temperature, the work function increases to 5.5 eV.

1.3.3.2 Flat band potential

Different from the work function of TiO$_2$ in vacuum, the flat band potential expresses the relationship between a semiconductor such as TiO$_2$ and the energy levels of the electrolyte. When contact occurs between TiO$_2$ and an electrolyte, the Fermi level $E_F$ of TiO$_2$ and the electrochemical level of the electrolyte $E_{\text{redox}}$ will attempt to reach equilibrium. If the Fermi level of TiO$_2$ is initially above the redox level of the electrolyte, an electron will be transferred from TiO$_2$ to the electrolyte in order to establish equilibrium, leaving excess positive charges and also generating a Helmholtz double layer at the electrolyte interface. This results in an upward bending of the bands. If the Fermi level is initially below the Redox level, excess electrons will be transferred into TiO$_2$ resulting in an accumulation layer leaving excess positive charges in the electrolyte with downward bending of the bands [62, 63]. For each system of TiO$_2$ and an electrolyte, there is a potential, known as flat band potential, to make the energy bands of TiO$_2$ flat, eliminating space charge from TiO$_2$.

The flat band potential has been shown to be different between the anatase and rutile phases and surfaces of TiO$_2$. In particular, the flat band potential of the rutile phase is slightly more positive than the anatase phase [30]. Furthermore, the anatase (101) surface has shown a greater (more positive) flat band potential than the anatase (001) surface [64]. Yet other reports have shown that the rutile (100) surface has a flat band potential -0.1 eV more than rutile (110) [65, 66]. Adsorption of certain species onto TiO$_2$ will also change the flat band potential. In particular, adsorption of H$^+$ ions can raise the flat band potential by 0.2 eV [67]. This shift has been suggested to increase electron transfer from the electrolyte into the CB of TiO$_2$, reducing
recombination. Another important influence to the flat band potential of semiconductors is the pH. For example, experiments performed at room temperature on TiO$_2$ have suggested that the band edges shift -59 meV for every unit increase in pH [68]. Thus, a shift in the electrolyte pH could easily shift the flat band potential and alter the photocatalytic activity.

1.4 Bulk contribution of TiO$_2$ to photocatalysis

The exciton diffusion length is very simply the average displacement an exciton through a material without recombining or otherwise being absorbed by another reaction. It is given by the equation

$$L = \sqrt{D\tau}$$

(1.2)

where $D$ is the diffusion coefficient and $\tau$ is the exciton lifetime [69]. $D$ is given by Einstein’s relation

$$D = \frac{kT\mu}{q}$$

(1.3)

with $k_B$ is Boltzmann’s constant, $T$ is temperature, $\mu$ is the mobility, and $q$ is carrier charge [70]. Several studies have already been performed that have relevance to TiO$_2$. Early reports were supported by optically pumping a sample of interest with laser of sufficient power while simultaneously measuring the absorbance. Rothenberger et al employed a similar such technique to determine the average carrier lifetime in TiO$_2$ colloidal particles to be approximately 30 ns for a particle diameter of 12 nm [71]. More importantly, the CB electrons were found to be trapped very quickly within the time the 30 ps wide pump pulse rises while the trapping of valence band holes took considerably longer, around 250 ns. Obviously, the average time it takes an electron and hole to recombine is approximately 10x less than it takes for a hole to be trapped. This extended hole trap time may not be beneficial for photocatalysis. If trapping
occurs within the bulk, an extended hole trap time would thus delay, or possibly prohibit, reduction of the electron donor at the surface where reactions occur.

Furthermore, TiO₂ colloidal particles with a 2.1 nm diameter have been demonstrated to recombine faster, suggesting recombination times depend at least in part on particle size [72]. Much of the literature also suggests a relationship between recombination times and particle size. Time resolved microwave conductivity (TRMC) has also proven useful to determine these lifetimes in anatase and rutile TiO₂. To do this, powder samples were subjected to a simultaneous illumination by a laser and microwave pulse. The change in the power reflected from the microwave signal is proportional to the number of excess electrons. This idea assumes that the electron’s mobility is much greater than the hole’s mobility and therefore the hole does not add significantly to the reflectivity of the microwave signal [73]. From the measurements, the rutile structure demonstrated a very short electron lifetime, likely due to its higher recombination rate, compared to the anatase structure which can trap holes quickly, possibly at the surface [7]. We see these results in Figure 1.10. It is challenging to equate long decay times to an increase in photocatalytic activity. Principally, this is because these TRMC measurements are a measure of electron lifetimes only and not a direct indication of whether the electrons are trapped at the surface where they participate in reduction, or within the bulk where they cannot participate. Nonetheless, differences in charge carrier lifetime appear to exist between the phases of TiO₂.
1.4.1 Excitonic behavior

Building on the ideas of charge carrier transport in photocatalysts, we now explore excitonic behavior. As we described earlier, incident light on a semiconductor like TiO$_2$ creates electron-hole pairs known as excitons. These electrons-hole pairs are bound together via the Coulomb interaction with an overall zero sum charge and a dipole moment. Each exciton has a binding energy that specifies the energy required to separate the electron and hole from each other. However, the amount of this binding energy is dependent upon the type of exciton. Frenkel excitons, having typical values of single eV binding energies, are usually found in organic materials while Wannier-Mott excitons have much lower binding energies of 5-20 meV found in typical semiconductors [74]. In addition to the energy differences, the Frenkel excitons have small radii of $\sim$10 Å while the radii of Wannier-Mott is much larger $\sim$100 Å. To determine these energies and radii for the Mott-Wannier, we explore the applicable Bohr radius model of Hydrogen. The well-known equation for the ground state energy of Hydrogen, also known as the Rydberg energy, is given as

$$R_y \approx \frac{-e^2}{8\pi\varepsilon_0 a_0} = 13.6 \text{ eV}$$

(1.4)

with $a_0$ as the Bohr radius [74]. This simply represents the energy required to remove an electron from H. However, to effectively calculate the binding energy of the excitons, modifications must be made to the Rydberg equation to include the dielectric constant $\varepsilon_r$ and the reduced mass $m^*_r$ to obtain

$$R_y = 13.6 \cdot \frac{m^*_r}{n^2m_e} \left(\frac{1}{\varepsilon_r}\right)^2$$

(1.5)

. The reduced mass $m^*_r$ is calculated as

$$m^*_r = \frac{m_e^*m_h^*}{m_e^* + m_h^*}$$

(1.6)
where \( m^* \) and \( m^* \) is the effective mass of the electron and hole respectively. Thus, we get the exciton binding energy as a function of \( n=1, 2, 3... \) as

\[
E_{\text{exciton}}(n) = -\frac{R_y}{n^2} + \frac{\hbar^2 k_{\text{exciton}}^2}{2m^*} + E_g
\]  

(1.7)

where \( k_{\text{exciton}} \) is the exciton wave vector and \( E_g \) is the energy of gap [74]. Given these additional relationships, the exciton radii can also be calculated, originating from the Bohr model. Using the Bohr model to represent the radius of the electron at level \( n \), one obtains

\[
r_n = n^2 a_0 = \frac{4\pi \hbar^2 n^2 \varepsilon_0}{m_e e^2}
\]  

(1.8)

with \( a_0 = 0.53 \, \text{Å} \) as the Bohr radius. Therefore the exciton radii at a given energy for \( n \) is

\[
r_n = 0.53 \frac{n^2 m_e e^2}{m^*}
\]  

(1.9)

in units of Angstroms [74]. The exciton energy and the exciton radii are dependent on the value of the reduced mass and the dielectric constant. A few reports have suggested values of reduced mass for TiO\(_2\), giving a lower reduced mass for anatase than rutile. Anatase has a reduced mass \( \sim 1 \, m_e \) [75] and rutile has a reduced mass \( \sim 8 - 20 \, m_e \) [76, 77]. Values for the dielectric constants are given as 44 for anatase and 120 for rutile [78]. Although several other values have been reported, rutile generally has a larger dielectric constant [79]. Thus, assuming the larger value for the effective mass of rutile, the exciton radius is \( r_n \sim 3 \, \text{Å} \) for rutile compared to \( r_n \sim 23 \, \text{Å} \) for anatase. In general, a smaller reduced mass suggests a higher mobility.

Certainly, these observed differences in exciton radii are helpful but not conclusive in demonstrating why some studies have suggested anatase has a higher photocatalytic activity than rutile.
1.4.2 Bulk charge carrier transport

As photogenerated charge carriers are generated within the bulk, they must migrate to the surface for redox reactions to occur. One report has suggested a link between photocatalytic activity of a metal-oxide and distinct differences in the band structure along different crystallographic directions. Giocondi et al suggested that differences in photocatalytic activity between the \{100\} and \{110\} surfaces of SrTiO$_3$ are from preferential excitation of charge carriers with momentum in the [100] direction, thus perpendicular to the \{100\} surface [5]. To understand this, one can look at the band structure of SrTiO$_3$ in Figure 1.11 [5]. Wave vectors with momentum in the [100] direction are excited with energies between the band gap and 4.1 eV. Excitations can occur along the [110] and [111] near Γ, however they are much lower in quantity than the states along [100]. Others suggest that since the <100> direction of preferential charge carrier diffusion is not completely perpendicular to the <110> direction, a large difference should not be found in the amount of charge carriers transported and therefore no disproportional difference in photocatalytic activity should be seen [80]. Certainly, given these discoveries for SrTiO$_3$, it is not difficult to argue that these anisotropic dependencies of charge carriers may also apply to TiO$_2$ as well.

![Figure 1.11 Band structure of SrTiO$_3$. The shaded regions highlight possible excitations of 4.1 eV along the [100], and to a lesser extent [110] and [111]. Fig. from ref. [5].](image)
1.4.3 Electron and hole trapping

Once charge carriers are generated, they have 3 distinct eventual outcomes as either recombining in the bulk, recombining at the surface, or participating in a reaction at the surface. Electron traps or hole traps may influence which outcome occurs. Traps are divided into two categories: deep traps and shallow traps. Shallow traps within the band gap, which are close to the VB minimum or the CB maximum, and deep traps, which are near the center of the band gap. Because of the shallow traps close proximity to the CB or VB, their energy is approximately the same value for thermal excitation in a solid (<1eV) [81]. Conversely, deep traps usually have energy much larger than shallow traps because of their deeper location within the band gap (>1.5eV). Traps typically decay as a result of either recombination or ionization by a photon [82]. Electron traps exist in different locations. As we have argued previously, the easy and most common answer to the location of electron traps is at the surface as several different references support [83-86]. In particular, unsaturated Ti atoms from reduction, can trap photogenerated electrons [87] However, several other locations have been shown to hold electron traps as well, particularly at locations within the bulk [88, 89]. Both individual and paired interstitial Ti sites trap electrons as well [90]. There seems to be a strong correlation between sample preparation and the location of electron trap locations as certain preparations favor different states of Ti\(^{3+}\) ions for example. However, a similar investigation of hole trapping is certainly more difficult. Principally, this is

---

**Figure 1.12** A diagram of the anatase TiO\(_2\) crystal structure with the electron and hole traps with their respective locations. The holes trapped on OH groups (A), electrons trapped on surface Ti (B), electrons trapped on O radicals (C), holes trapped on Ti-O (D), and inner trapped electrons (E). Fig. from ref [14].
due to significant challenges with injecting holes into the VB of TiO$_2$ [91]. Several reports have suggested that hole trapping occurs at an under-coordinated O$^-$ site on the surface on the surface of TiO$_2$ [92, 93]. These techniques have included electronic paramagnetic resonance (EPR), photoluminescence (PL), and transient absorption spectroscopy (TAS) [94, 95, 66]. Yet, other reports have indicated evidence for hole trapping just beneath the hydrated surface as Ti$^{4+}$O$^-$Ti$^{4+}$OH [96]. Figure 1.12 provides a summary of most of these electron and hole traps.
2. Surface Modifications of TiO$_2$

The purpose of this chapter is to provide an overview of surface modifications by low energy (~1 keV) ion irradiation. In the previous section, we provided a number of fundamental physical and chemical properties and principles related to TiO$_2$ photocatalysis. In addition, many of these principles related to titania have much broader implications and uses in other metal oxides as well, perhaps to serve many other different and distinct purposes. We have discussed that the coordination of surface atoms affects the surface chemical properties, especially undercoordinated atom-sites compared to a perfectly bulk terminated surface are more chemically active. Atoms at step-edges that terminate atomically flat terraces are less coordinated than atoms at the terrace. Thus, surfaces with a high density of step edges may be expected to exhibit different chemical functionalities compared to a surface having little or no step edges. The primary technique employed here to make a highly stepped surface is utilizing ion sputtering. In this introduction, we give a general overview of ion-surface interactions relevant to such studies. We first explore the (a) interaction of ions and solids including normal and grazing incidence sputtering followed by (b) the experimental equipment necessary to make such interactions possible. Subsequently, a description of our characterization and analysis methods are given. Finally we attach the published results in Appendix 4.

2.1 Introduction

Surface morphology, in particular undercoordinated sites, are believed to be correlated to influences on photocatalysis. Earlier, several examples within the surfaces of TiO$_2$ were indeed given to show such relations. However, little evidence was provided for the relationships
of undercoordinated sites, occupied on step edges, and adsorbate binding, a necessary requirement for photocatalysis. Perhaps by exploring such expressions, starting with simple adsorbates, such a relationship can be said. First, the termination of the atomic lattice as a step edge, provides very special chemical properties that can provide for different chemical functions. Second, these same step edges may exhibit localized electronic states that can affect charge trapping of photoexcited charge carriers and subsequently affect charge transfer from the substrate to adsorbates.

Very few studies of the chemical properties of step edges on metal oxide surfaces have been reported. However, one such report does assess the chemical properties of step edges on anatase TiO$_2$ (101) where Gong et al performed DFT studies to evaluate such reactivity [97]. In these studies, the reaction of water, methanol, and formic acid with step edges were probed. The reactivity of these three different molecules were evaluated for adsorption on steps edges of the (112) and (100) facets. The (101) terraces were shown to molecularly adsorb all three molecules without any dissociation requiring very little adsorption energy. All three molecules are bonded with the oxygen from each molecule to the five-fold coordinated Ti atom and hydrogen H-bonded (two for water) to the two-fold coordinated oxygen atom. However, water and methanol are more energetically favored to non-dissociatively adsorb on steps edges of (112) facets while dissociatively adsorption is more energetically favored for the step edges of (100) facets. The oxygen of water and methanol are bonded to the five-fold coordinated Ti atom at the step edge of (112) facet while the nearest hydrogen is H-bonded to a two-fold coordinated oxygen atom on the lower terrace. For bonding on the step edge on the (100) facet, the oxygen of the dissociated water and methanol molecule is bonded to the five-fold coordinated Ti. Different from water and methanol, formic acid was calculated to energetically favor dissociative bidentate adsorption on both the step edges, encouraged by the two five-fold coordinated Ti atoms to bond with the two oxygen atoms in formic acid (HCOOH). In comparing the energies of
adsorption between step edge and terrace adsorption, results demonstrate that adsorption depends on the molecule being adsorbed. Water is less likely to dissociatively adsorb at a step edge on the (100) facet than on the (101) terrace. However, methanol is more likely to dissociatively adsorb on the same step edge than molecularly on the (101) terrace. Therefore, DFT calculations have provided, at least theoretically, that step edges offer distinctive and favorable reaction sites for surface chemical reactions on oxides. To investigate the role of such step edges on TiO$_2$ experimentally, a method for preparing stepped surfaces is required. Here, we propose such a method by grazing incidence ion sputtering for the preparation of such stepped surfaces.

### 2.2 Ion solid interactions

In this section, the techniques and principles related to ion bombardment of solid surfaces is explored. The bombardment of ions onto surfaces into two categories: sputtering and ion implantation. Although ion implantation has a several uses, further expansion of the subject is beyond the scope here. However, the surfaces of solids can be eroded with such sputtering from the resulting collisions of externally excited particles including atoms, ions, electrons, and photons [98]. Many uses for chemical sputtering exists in preparing materials, especially metal oxides, for utilization in photocatalysis. However, given the previous discussions related to step edges and their relevance to photocatalysis, we focus here on the kinetic energy transfers that physical sputtering may provide for its investigation.

When sputtering occurs, a particle is excited along a given path onto the sample. After an incident particle strikes the surface of a material, a number of possibilities exist. Possible outcomes include backscattering, equilibrium at the surface or in the bulk, generation of electronic transitions resulting in secondary electrons, and alterations or breaking of chemical bonds from the surface or within the bulk. These collisions can be define as either inelastic or
elastic collisions. According to Behrisch et al, elastic collisions resulting from ion sputtering are divided into three categories: the single knockon, linear cascade, and the thermal spike [99].

1. **Knockon sputtering**

   For the knockon sputtering, the energy from the incident ion, possibly already having experienced previous collisions, is transferred to the atoms in the target. After energy transfer, if the target atoms have enough energy to overcome the binding energy to the matrix, they may exit the surface. The now moving target atoms will travel from a certain thickness, Δx. Based upon this principle of transport, the sputtering yield will be based upon these ejected atoms from this defined layer and related to the cross section. Single knockon sputtering is usually known for grazing incidence ions, as well as with light ions [99].

2. **Linear cascade**

   Different from single knockon collisions, linear cascade collisions are based upon higher incident ion energy. Because of the energy increase, their collisions will also create secondary recoils. If these recoil atoms have enough energy, they can migrate to the surface and possibly escape. The linear cascade reaction is the most frequent and relevant to a multitude of angles and energies [99].

3. **Spike**

   A lesser important regime for the context here is the spike regime. Energies required to make such excitations are normally in the millions of electron volts and/or for the heaviest ions. Because of such high energies or masses, the recoil collisions are so densely populated that most atoms are in motion within what is known as the spike volume [99].
Figure 2.1 Three types of elastic sputtering. For (a) single knockon sputtering, this process transfer the energy from the incident ion into the target atom which can be ejected from the surface depending on its energy and location. Also, linear cascade sputtering (b) results in many cascade collisions. Lastly, spike sputtering (c), with extremely high ion energies and/or masses, allows transfer of energy to more densely packed target atoms. Fig. from ref. [10].

Figure 2.1 shows such sputtering regimes for elastic collisions. If we define transfer energy $T_m$ as

$$T_m = \frac{4m_1m_2}{(m_1+m_2)^2} E_i = \gamma E_i$$

(2.1)

with the mass of the incident ion $m_1$ and the mass of the target atom $m_2$, $E_i$ as the initial energy of the incident particle, and $E_f$ as the energy transferred to the target atom. Earlier, we mentioned the cross section and it is defined as the probability of one particle penetrating a path length $\Delta x$ in a medium of other target atoms. This probability is given by

$$P = N x \sigma$$

(2.2)

where $N$ is the atomic density per volume and $\sigma$ is the cross section [99]. The cross section then becomes

$$d\sigma(E,T) = \frac{d\sigma}{dT} dT$$

(2.3)

However, using the interaction by Rutherford scattering from the Coulomb repulsion of the nuclei from Bohr we get

27
\[ d\sigma(E, T) = \pi \frac{m_1}{m_2} Z_1^2 Z_2^2 e^4 \frac{dT}{E_T^2} \]  

(2.4)

where \( Z_1 e \) and \( Z_2 e \) are the charges. The energy transfer \( T \) must be positive but less than \( T_m \).

We see with the \( 1/T^2 \) relationship, a smaller energy transfer \( T \) increases \( d\sigma \). Also, \( d\sigma \) decreases with larger \( E_i \). This expresses larger energy transfers not as efficient as smaller ones. For low energies relevant here, the cross section can be approximated as

\[ d\sigma \approx C_m E^{-m} T^{-1} dT \quad 0 \leq T \leq T_m \]  

(2.5)

using

\[ C_m = \frac{\pi}{2} \lambda m a^2 \left( \frac{m_1}{m_2} \right)^m \left( \frac{2 Z_1 Z_2 e^2}{a} \right)^{2m} \]  

(2.6)

[99]. \( C_m \) is therefore dependent on \( \lambda_m \) with \( m \) being between 1 and 0 according to high or low energies respectively. For low energies, \( m=0 \) and implies a constant cross section. Furthermore, modifications to surfaces are substantially influenced by relations between sputtering yield and incident angle of a colliding beam. Figure 2.2 represents the sputter yield versus incidence angle. According to Sigmund’s theory, the sputter yield \( Y \) is dependent upon ion energy \( E \) and incident angle \( \Theta \) as determined relative to the surface normal (axis \( x \)) to be

\[ Y(E, \Theta) = \Lambda F_D(E, \Theta, 0) \]  

(2.7)
where $F_D(E, \Theta, x) \, dx$ is the average energy deposited in a layer $(x, \, dx)$ from incident energetic particles. $\Lambda$ is a constant of the material based upon factors including surface binding energy and a cross section for target atoms striking the surface at low energies$[100-102]$. Simply, the sputter yield is the average number of atoms ejected from the surface per incident ion. $\Lambda$ is given by the equation

$$\Lambda = \frac{0.042}{NU_0} \tag{2.8}$$

where $U_0$ is the binding energy of the surface, and $N$ is the atomic density$[10]$. We express the average energy deposited in a layer as

$$F_D(E, \Theta, x) = \alpha NS_n(E) \tag{2.9}$$

where $\alpha$ is a dimensionless function depending on the incidence angle, the mass ratios, and the ion energy$[103]$. $S_n(E)$ is referred to as the nuclear stopping cross section given as

$$S_n(E) = \frac{1}{1-m} C_m \, \gamma^{1-m} E^{1-2m} \tag{2.10}$$

$[99]$. This expression represents energy loss from the nuclear interaction per unit length and atomic density. Essentially, at lower incident ion energies, $S_n(E)$ increases because the ions spend more time interacting with the nuclei of the target atoms. At higher energies, the ions are less affected by the nucleus because of the less exposure from higher velocities. We take the Thomas-Fermi cross section given earlier as

$$d\sigma \equiv CE^{-mT^{-1-m}}dT \tag{2.11}$$

with energy transfer $T$ and $m = 0$ and

$$C = .5\pi\lambda_0a^2 \tag{2.12}$$

where $\lambda_0 = 24$ and $a = 0.219$. Sigmund therefore calculated the sputtering yield as a function of angle of incidence as

$$Y = \frac{1}{\pi^2} \frac{F(E, \theta, x)}{U_0} \, dx \tag{2.13}$$
and effective depth of origin of the sputtered atoms as

$$\Delta x = \frac{3}{4} \frac{1}{NC_0}$$  \hspace{1cm} (2.14)

Sigmund furthermore surmised a Gaussian distribution for the energy impending on the sputtered surface to get the normalized sputter yield as

$$\frac{Y(E,\theta)}{Y(E,0)} = (\cos \Theta)^f$$  \hspace{1cm} (2.15)

with $f = 1-2$ varying with mass of surface atom and ion. The sputtering yield will increase as the angle of incidence (relative to surface normal) is increased. However, as the angle of incidence becomes parallel to the surface, the sputter yield is observed to decrease, certainly not in agreement with Sigmund’s theory. Nonetheless, by increasing the angle of incidence of ion sputtering to grazing, the sputter yield will be reduced for terraces yet possibly providing a markedly higher sputter yield for steps, encouraging surface modification.

### 2.3 Ion beams and surface morphology

As we have observed with single crystal samples, the surface morphology is rarely absolutely flat. Instead, it is characterized by many types of steps, vacancy islands, adatoms, and kinks. With the dawn of the nanoscale age, large investments have been made to manipulate the atomic scale for optimization of macroscopic properties. Earlier, we demonstrated such differences in properties relevant to photocatalysis of metal oxides, in particular TiO$_2$. We now explore the roles that ion-solid interactions and the manipulations that can be made to further this field.

Surfaces exposed to ion irradiation respond differently due to different factors, resulting in clear preferences of ion yield. Clear differences have been observed on the surface, not only between the bulk but also along different crystallographic orientations, often times resulting in different stoichiometry. We will see that ion beam sputtering yields will function directly from
these differences, giving way to new structures. We can divide the effects of ion sputtering as discussed here into two mechanisms: primary and secondary. The primary mechanism is based upon the individual interactions of each ion with the target surface. Relevant properties related to these mechanisms include incidence angle, beam energy, ion mass, surface orientation, and crystallographic direction. The secondary mechanism is based upon ultimate extensions of primary effects such as exposure times. Thus far, the sputter yield has only been discussed in general terms with little mentioned as to how the yield may originate from different sources such as in multi-element targets, non-stoichiometric surfaces, and different azimuthal directions. To account for such influences, we use the relationship

\[ Y = \sum_i Y_i = \sum_i Y_i^C c_i \]  \hspace{1cm} (2.16)

where \( c_i \) is component concentration of the \( i^{\text{th}} \) component and \( Y_i^C \) is the component sputter yield [104]. Simply, this provides the overall sputter yield to be divided into its characteristic components with individual contributions such as those yields originating from step edges and terraces. This will be very useful later when the effects of grazing incidence ion sputtering on \( \text{TiO}_2 \) is evaluated. These components may originate from different sources within the surface or even from within the bulk. Additionally, Sigmund and Lam suggested different contributions from different depths given as

\[ Y = \int_0^\infty \sigma_i(x) N_i dx \]  \hspace{1cm} (2.17)

with \( N_i(x) \) as the atomic density of \( i^{\text{th}} \) molecules at a position \( x \) from the surface and \( \sigma_i(x) \) quantifying the response of the sputtering of the same type of molecule \( x \) from the surface [105].
This enables one to model the sputter yield according to differences in sputter behavior that vary by depth. Sputter yields may differ according to many principles including surface binding energy at various positions of target atoms at the surface [106, 107], temperature[108, 109], and incident ion energy [110, 111]. If a targeted surface has differences in surface binding energy between different atoms, targets with lower binding energy will be preferentially sputtered. Conversely, targets with a higher binding surface energy will be preferentially sputtered less. Subsequently, a gradient between sputtering yields will be observed for target atoms with different surface binding energies. These differences in sputter yield, as a result of differences in surface binding energy, can alter the concentration of the surface leaving a higher concentration of higher binding energy atoms on the surface. We see results similar to this in Figure 2.3. The ratio of the surface binding ratios of different metals to silicon were compared to the corresponding sputter yield ratios. It can be noted that for WSi$_2$, the ratio of W sputter yield to Si sputter yield drops as the ratio of their surface binding energy increases [9]. A relationship between sputter yield, target masses, and surface binding energy has been established and is given by

\[
\frac{Y_2}{Y_1} = \left( \frac{M_2}{M_1} \right)^{2m} \left( \frac{U_2}{U_1} \right)^{1-2m} \tag{2.18}
\]

where $Y_1^c$ and $Y_2^c$ are the sputter yields of targets 1 and 2 respectively, $M_1$ and $M_2$ are the masses of the targets 1 and 2 respectively, and $U_1$ and $U_2$ are the surface binding energies of

![Figure 2.3 Preferential sputter according to surface binding energy. In the figure, W represents tungsten, Si represents silicon, Y represents yield, and U represents surface binding energy. By plotting the ratio of the sputter yield $Y_w/Y_s$ against the ratio of surface binding energy $U_w/U_s$, it is shown that preferential sputter will occur for targets with lower binding energy. Fig. from ref. [9].](image-url)
target atoms 1 and 2 respectively [99, 112]. The value \( m \), as we observed earlier, varies between 1 and 0 for high energy or low energy incident ions respectively. Therefore, for low energy incident ions, the surface binding energy dominates. Obviously, influences such as incident angle and incident energy (beyond \( m \)) are not included in determining such yield ratios for this equation. This is primarily due to the dominance of the linear cascade mechanism which, for the most part, is not largely affected by these influences but is mostly dominated by random transport [104]. Higher energy incident ions above 50 keV have a slightly different equation for sputter yield ratios but is beyond the scope of this brief. Similar to acid etching, ion sputtering can also selectively etch metallic atoms from the surface to polish and refine surface on the atomic level [113].

We previously showed that preferential sputter yield was influenced by the mass of target atoms and surface binding energies. However, it is also important to note how the incident ion energy affects sputter yield while maintaining the mass and binding energy dependencies. To investigate this, we search for an expression to explain how ion energy may affect preferential sputter yield. Earlier, we presented the equation for nuclear stopping cross section written as

\[
S_n(E) = \frac{1}{1-m} C_m y^{1-m} E^{1-2m} \quad (2.19)
\]

[99]. From the \( E^{1-2m} \) dependency, we see that as the energy (\( E \)) of the incident ions goes up, the nuclear stopping cross section also increases but does eventually drop as observed in Figure 2.4. Furthermore, increases in ion energy will less affect the rate of preferential
sputtering for systems with large differences in mass while affecting systems more that have strong relation of preferential sputtering to surface binding energy [104]. In addition to bi-metal surfaces, metal oxides also have sensitivities to changes in beam energy and ion mass as well. Ion sputtering has been well established as an excellent technique to clean the surfaces of metal oxides for experiments in vacuum. However, similar to the preferential sputtering described for bi-metal surfaces with different target masses and binding energies, metal oxides have susceptibilities to becomes reduced (less oxygen) at the surface as a result of ion sputtering. We take for example the system Ta$_2$O$_5$. Taglauer and Heiland evaluated the changes made to Ta$_2$O$_5$ surface as a result of heavy and light ion masses in addition to dependencies on incident ion energy [6]. Figure 2.5 reveals peak-to-peak auger electron spectroscopy (AES) measurements as a function of ion dose. The ratio of the Ta to O peaks from AES is proportional to the sputter yield ratio of Ta to O. The first result to notate is the increase in yield for Ta over O for use of a lighter mass ion, He$^+$, in place of Ar$^+$ at an angle of
30° off the surface normal. Additionally, by reducing the incident ion energy only with the same incident ion, the preferential sputter yield for Ta increases, resulting in a further reduction at the surface. By further increasing the ion beam energy, the surface becomes more oxidized. This is significant because it indicates that the Ta and O can be selectively sputtered based upon incident ion energy and ion. Further increasing the ion mass alone with Ar⁺ can further oxidize the surface back to a comparable level after the first sputter with Ar⁺. Thus, preferential sputtering mechanisms do indeed exist to provide modifications to surfaces.

2.4 Ion sputtering of surfaces

Within the last several decades, advancements have been made to microscopy technologies enabling detailed understandings of material surfaces and interfaces. Without these advancements, many of the effects of ion sputtering on surfaces would not be fully understood. The surfaces of materials, in particular single crystals, always have a miscut from the low-index plane which results in many of the step edges we have already discussed. There are many more defects besides step edges and terraces that have relevance to ion sputtering effects. These important defects are given and described in Figure 2.6. We can see kinks are discontinuities along the step edges, adatoms are additional atoms on the surface, and vacancies as discontinuities in the terrace surface. Naturally, a high number of these defects will reduce the migration of adsorbates on the surface but enable a higher number of adsorbate sites. On the contrary, a flat surface with little such defects will allow for improved mobility for adsorbates and other molecules on the surface. Although many of these defects...
are fairly well understood for a number of materials, much of their creation and disappearance are related strongly to statistical models. If an incident ion creates a vacancy on a terrace similar to ones shown above, it can migrate to a step edge given sufficient mobility arising from adequate surface temperature. Additionally, the vacancy can migrate the length of the step until a kink is encountered in which case the step edge become shortened [15]. Given repeated vacancy migration to and along steps, terraces can actually reduce in size by way of continual step edges recession. However, these mechanism are heavily based upon the mobility of the vacancies themselves with the step edges continually attempting to reduce their energy with migration. If the surface temperature is too low, vacancies can still be created but will diffuse at a much lower rate if at all. If the vacancies become stagnant, they can collect and produce monolayer vacancy islands which can collect additional vacancies from their increased size. Additionally, further vacancy creation within the vacancy islands will result in expansion of the larger vacancy island to additional layers beneath [15]. Figure 2.7 shows the progression of vacancy islands to steps at elevated temperatures, combination of vacancy islands at reduced temperatures, and deepening of vacancy island clusters at even lower temperatures. The interaction of vacancy islands and the step edges they will eventually encounter will result in oscillations between flat terraces and large openings on the surface. In both scenarios of step retraction and vacancy island expansion controlled by thermal energy, Figure 2.7 Vacancy island progression. Diagram representing the creation of vacancy islands with the (top) migration to step edges followed by eventual step-terrace retraction, (middle) the agglomeration of vacancy islands yielding two-dimensional expansion, and (bottom) the creation of vacancy islands within vacancy island clusters giving three-dimensional expansion of vacancies. Fig. from ref. [15].
the surface is sputtered away with any residual contaminants being removed along with them. Therefore, the temperature at which ion sputtering occurs can be very influential on the eventual morphology of the sputtered surface.

Thus, given the principles provided above, we build the basis for effectively utilizing ion sputtering for the preferential sputtering of metal oxide surfaces such as TiO$_2$. We have already observed how differences in ionic mass, temperature, incident angle, and target mass affect the various surfaces of materials. However, we propose a technique here to reduce the angle of incidence to grazing. This, therefore, reduces the penetration depth of the incident ion and transfers the ions momentum to a vector roughly parallel to the surface. How will such angles of incidence affect the sputter yield given such reductions typically reduce it to minimal amounts? Additionally, given the tendency of vacancy islands to migrate to step terraces at elevated temperatures, how will grazing incidence sputtering affect these vacancies and the steps they migrate to? Lastly, given the differences in atomic density for different low-index directions of rutile TiO$_2$, how will such sputter yields be affected by these low angles? We seek to clear and concise answers to these questions in the upcoming sections.

2.5 Experimental procedures for TiO$_2$ surface modifications

To produce surface modifications to TiO$_2$ with ion beam sputtering, we demonstrate the experimental equipment and techniques related to its use. All experiments were performed in an Omicron GmbH stainless steel UHV chamber equipped with a variable temperature scanning tunneling microscope (STM). The chamber consists of several available ports for manipulation, gas supplies, electrical feed-thru, and pumping. To establish UHV conditions, the system is evacuated from atmosphere with a mechanical roughing pump placed in series with a turbomolecular pump. The roughing pump provides a backing vacuum to the turbomolecular pump which provides and ultimate pressure of $<1\times10^{-8}$ Torr into the main chamber and attached
load-lock. After a minimum chamber pressure is achieved as measured by a hot-filament ionization gauge, the entire chamber, load-lock and attached accessories are baked to ~150°C to increase the mobility of water vapor remaining in the chamber and on all internal component walls. At elevated temperature, the water vapor can be successfully removed from the chamber yielding an ultimate pressure of <1x10⁻¹⁰ Torr with use of an ion pump attached at the base of the chamber. The ion pump removes residual gases from the main chamber by ionizing a small volume of the gases within the pump exposed to a magnetic field supplied from magnets located on the external walls of the ion pump. The ionized gases are thus accelerated into plates within the ion pump where they are indefinitely trapped, prohibiting further diffusion into the remaining volume of the chamber. A Ti filament may also be sublimated periodically with a current of ~30A which can also trap localized background gases from the high reactivity of the hot Ti filament. Valves may isolate the turbomolecular pump and ion pump individually depending the vacuum requirements of the system. To supply process gases to the main chamber, high precision leak valves are attached to the main chamber and connected to low pressure regulators and ultra-high purity gases such as Argon required for sputtering. These leak valves contain ruby crystal mating surfaces to allow substantial control over the flow rates of required gases, often controllable to within ±1x10⁻¹⁰ Torr l/sec. Manipulation and heating is performed within a commercially built sample holder containing a BN ceramic DC heater with capabilities >900°C. The single crystal rutile TiO₂ sample are mounted to Mo sample plates with Ta wire straps across the corners to ensure good thermal contact and transfer of heat. The sample plate is electrically isolated from the manipulator however conductivity is maintained through an electrical feed-thru outside the chamber. The current passing from the sample plate and sample created as a result of the ion impacts is measured with a Keithley 6400 series picoammeter. To generate a beam of charged particles for ion sputtering, a sputter gun
manufactured by LK-technologies is utilized with an accompanying power supply/control unit. A picture and diagram of the UHV ion sputter chamber is given in Appendix 1.

2.6 Characterization by scanning tunneling microscopy (STM)

To adequately investigate and determine the effects of grazing incidence ion sputtering on the surface of rutile TiO$_2$, an experimental technique is required to analyze the surface for defects caused by ion impact. Scanning tunneling microscopy (STM) has been well-proven to be capable of establishing atomic-level topography of metal oxide surface such as TiO$_2$. STM was originally developed by IBM researchers Gerd Binnig and Heinrich in 1981 and a Nobel Prize in Physics soon followed in 1986 to mark this significant discovery. As the name suggests, tunneling is the core principle for this technique. To quantum tunnel between atoms, a sharp tip usually made from W or Pt is brought in close contact to a surface, usually within 1 nm. A bias voltage is applied between the tip and the sample. Given a few volts bias voltage, common tunneling currents dependent on the material being studied range from picoamps to 10 nA. Therefore, this principle of tunneling combined with an effective feedback loop, is exploited for resolution at the atomic level. To obtain an accurate topography of the surface, the tip is moved via a piezo in the x and y direction across the surface. An additional piezo is controlled by the feedback loop which adjusts the vertical position to maintain the specified current set point thus ensuring proper tip-sample separation. Figure 2.8 represents a diagram of a simple STM setup.
For a more detailed approach, we offer principle of the wave function to express the behavior of the tunneling electron. To simplify this junction, we use the expression

$$\Psi(x) = \Psi(0)e^{-\kappa b}$$

(2.20)

for a rectangular barrier of width x where

$$\kappa = \sqrt{\frac{2m(\Phi - E)}{\hbar}}$$

(2.21)

for an electron with energy E and barrier potential \(\Phi\) [114]. Thus, the probability of the electron crossing to the barrier edge is proportional to

$$|\Psi(x)|^2 = |\Psi(0)|^2 e^{-2\kappa x}$$

(2.22)

. The potential bias of the tip and the sample V is approximated as

$$\Phi = \frac{1}{2}(\Phi_{tip} + \Phi_{sample})$$

(2.23)

. To determine the tunneling current, we similarly use the expression

$$I_T \propto \sum_{E_F} |\Psi(0)|^2 e^{-2\kappa x}$$

(2.24)

where \(E_F\) is the Fermi energy.
3. Photocatalysis of Thin Films of Anatase and Rutile TiO$_2$

One of the main questions in photocatalysis research has been why the two main polymorphs of TiO$_2$, i.e. rutile and anatase, exhibit largely different photocatalytic activity, with the anatase polymorph generally believed to be the better photocatalyst. By using epitaxial thin films with varying film thickness, it is demonstrated that the underlying reason for this difference in the photocatalytic activity of these two polymorphs lies in their bulk properties, i.e. exciton charge transport. Before we present the published results in Appendix 5, we provide some needed background on the experimental approach for the epitaxial growth of oxide thin films followed by the characterization of their structural and photocatalytic properties.

3.1 Introduction

Earlier, we observed many differences between anatase and rutile TiO$_2$, both related to the surface and bulk structure. Although these two phases share the same chemical components, they differ structurally and electronically. These distinctions translate into observed differences in their photocatalytic properties. However no significant conclusion has been made as to why these differences photocatalytic activity exist. As we reported, most argue that the reason for these differences lie at the surface of each phase but some believe that these differences lie solely within the bulk. Nonetheless, ambiguities still remain and we seek here, for the first time, to resolve such conflicts. Of course, to eliminate such ambiguities is very difficult. However, we propose a novel approach through the use of epitaxial thin films of anatase and rutile TiO$_2$. Ideally, by mitigating any net contribution to photocatalytic activity from the surface, an isolation of the contribution from the bulk can be determined. Certainly, obvious challenges
exist to eliminate the contribution from the surface of the two phases while still determining the photocatalytic activity. Therefore, by growing epitaxial anatase and rutile TiO$_2$ films that are otherwise identical except for their thickness, we can minimize the contribution to photocatalytic activity from the surface by determining changes in photocatalytic activity relative to film thickness. Thus, we will effectively model the rate of photocatalytic activity against the change in film thickness. These comparisons measure the relative charge carrier diffusion length attributed to differences existing in the bulk of TiO$_2$.

### 3.2 Epitaxial film growth

The word epitaxy originates from the Greek words *epi* meaning on or above and *taxis* meaning order. Therefore, we define epitaxial film growth as the well-ordered deposition of a material onto another well-ordered substrate which ultimately dictates, at least initially, a similar and well defined ordering from the substrate surface. The field of epitaxial film growth is a large area of study in and of itself with much of it beyond the scope of this brief. Here, however, we explore opportunities and principles related to the production of thin films of metal oxides. Essentially, there are two different and distinct epitaxial growth modes: homoepitaxy and heteroepitaxy. For homoepitaxial growth, an identical material to the substrate is grown directly onto the substrate resulting in a continuation of the film from the substrate. Although homoepitaxial growth has benefits for other film growths, it is of little value for the current discussion. In contrast, heteroepitaxial growth is the deposition of a material with a different composition relative to the substrate. Thus, this film growth can provide films of measurable thickness for comparisons needed for photocatalytic applications.

Several techniques that are capable of producing epitaxial thin films with good heteroepitaxial relationships. However, given certain requirements for the current study, many are not optimal for the current investigation. Here, we briefly investigate how such methods yield
such films, what can be principally learned from most of these techniques, and how the films for
the current study were developed and created. Additionally, there are a number of factors
besides growth technique that can affect the phase and even the quality of the epitaxial film.
These factors include growth rate, substrate temperature, background pressure and
environment, target composition, and many others. To begin a thin film deposition, one of the
first choices to be made is what type of substrate must be utilized to satisfy the given
requirements of the growth. Obviously, the choice of substrate can be influential in determining
the eventual quality, phase, and morphology of the film to serve the intended purpose. The
obvious choice is between an amorphous substrate, characterized by many different grains,
facets, and crystal structures that essentially does not represent a long range order compared to
a well-organized crystal structure observed in single crystal substrates. Amorphous substrates
such as quartz and glass is widely used in commercial and industrial designs and ultimately
devices because of it low cost of production. Additionally, chemical components of the substrate
can also become part of the eventual film often leading to undesirable effects. For example, Na+
and Si^{4+} from glass and Fe^{3+} and Cr^{3+} from stainless steel substrates have been shown to
penetrate into the TiO_{2} film from the substrate and lower the rates of photodegradation of malic
acid compared to a quartz substrate [115]. These impurities within the film may lead to electron-
hole recombination and drastically affect charge carrier recombination. Although TiO_{2} can be
successfully deposited onto amorphous quartz substrates, even without initial undesirable
impurities leading to recombination, sintering to approximately 700°C is required to obtain the
anatase phase. However, sintering to elevated temperatures also leads to the diffusion of Si
from the substrate’s surface, resulting in charge carrier recombination [116]. Sintering higher
than 700°C will lead to the conversion to rutile phases within the film. Although amorphous
substrates are practical for many TiO_{2} depositions, their application here would be impractical
given their inconsistency with depositing TiO_{2} thin films with uniform phases and will not likely
yield epitaxial films. To produce a more uniform and epitaxial film, the obvious move is to a
more uniform surface. Thus, single-crystalline substrates are an obvious choice. Although often impractical for wide scale production that amorphous substrates are recognized for, single crystal substrates offer long range order within the bulk of the film and at the surface. SrTiO$_3$ is one of the most widely utilized substrates to support epitaxial thin film TiO$_2$ growth, in particular the anatase phase [117-122]. The basis for which SrTiO$_3$ is a good substrate for epitaxial growth is due to the good lattice match compared to anatase TiO$_2$.

SrTiO$_3$, with its perovskite structure characterized by two cationic elements with one at the corners and one at the each corner and one at the center accompanies by an anion at the center, has a lattice constant $a = 3.905$ Å. This value is of course very close to the corresponding lattice in-plane lattice constant of 3.782 Å for anatase (100) and SrTiO$_3$(100) planes to be $\sim$3.04% [123]. Therefore, given this minimal difference between the substrate and the desired epitaxial film, minimal strain would be observed to establish an epitaxial relationship. However, despite the excellent lattice match between the substrate and the anatase TiO$_2$ film, unresolved issues related to the use of SrTiO$_3$ as a substrate for this study exist. One issue is that SrTiO$_3$ has been demonstrated to be a good photocatalyst, especially under UV illumination [124-127]. Additionally, Sr has been shown to migrate from the substrate into the film [128]. This occurs because the growth of TiO$_2$ onto SrTiO$_3$ is believed to occur in two different steps. Initially, when the first layers of deposition attempts to match the lattice of the substrate, a Sr$_x$TiO$_{2+x}$ structure results originating Sr from the substrate. Three-dimensional islands are formed to relax the new composition. The migration of Sr from the substrate creates a Sr-deficient region approximately 2-4nm thick at the interface between the film and substrate. Thus, other solutions were investigated. Most notably, LaAlO$_3$ has also been used successfully for growth of anatase TiO$_2$.

Figure 3.1 Ball and stick model for LaAlO$_3$ unit cell. The Al, La, and O atoms labeled blue, green, and red respectively.
epitaxial films. [129, 119, 130-132]. Similar to SrTiO$_3$, LaAlO$_3$ also has a perovskite structure as we observe in Figure 3.1. The cation elements are located at the corners and center of the unit cell, La and Al respectively, with the O anion located on the faces. However, the relevant advantage LaAlO$_3$ has over SrTiO$_3$ for substrates related to photocatalytic studies is that the former is not considered to generate any photocatalytic activity under the proposed conditions. This is directly related to the large band gap of ~5eV versus ~3.2eV for SrTiO$_3$, essentially prohibiting charge carriers from being generated from the LaAlO$_3$ [133].

Furthermore, the lattice parameter for LaAlO$_3$ is $a = 3.79$ Å which is ~0.2\% different from anatase TiO$_2$ and considerably a smaller mismatch than SrTiO$_3$. Figure 3.2 represents an overlay of the anatase (001) surface on top of the LaAlO$_3$(100) surface, noting the close match visually. Of course, this relationship should be demonstrated with characterizing techniques presented later in this investigation. The strong match of the LaAlO$_3$ substrate to the anatase TiO$_2$ film strongly restricts growth of other phases, in particular rutile TiO$_2$, at least initially. To preserve
the anatase film quality as growth extends from the substrate, deposition conditions are carefully controlled to favor proper growth including temperature, pressure, growth rate, and eventual cooling rates. To create a rutile TiO$_2$ film, we further investigate other substrates to establish a similar lattice match encouraging epitaxial film growth. Al$_2$O$_3$, more commonly known as sapphire, has provided an opportunity for rutile TiO$_2$ films. Initially desired for its wide popularity as a blue gem stone, it has found more common uses in recent technological improvements such as iPhone components including lenses, sensors, and displays to become widely commercially available. Its many natural colors originate from trace amounts of impurities. However, in its purest form without these impurities and as a single crystal, it can provide a superior substrate for growth of rutile TiO$_2$ [134-140]. Figure 3.3 is a ball and stick model of the $\alpha$-Al$_2$O$_3$ crystal with a trigonal crystal belonging to the space group R3c. This structure is characterized by 4-fold coordinated O atoms and 6-fold coordinated Al atoms. To closely match the unit cell of rutile TiO$_2$, we select the Al$_2$O$_3$ crystal with the r-plane (1-102) surface. The lattice constant of Al$_2$O$_3$ is a=4.758 Å. It has a lattice mismatch of +3.7% relative to rutile TiO$_2$. We see in Figure 3.4 the relationship between the rutile (101) crystal plane and the Al$_2$O$_3$(1-102) surface with half the surface covered by TiO$_2$ to more easily represent the relationship. Thus, given the relationship between the rutile crystal and the Al$_2$O$_3$ surface, we expect to obtain a similar relationship when film characterization is performed.
3.3 Film growth by PLD

Although several successful techniques exists for growth of metal-oxide thin films, pulsed laser deposition (PLD) was employed here based upon a few key advantages. The main motivation is its large versatility and variety of deposition source. Since the PLD targets can be easily prepared from widely available commercial powders, the components, concentrations, and dopants can easily be varied, even minimally, according to experimental necessity. Powders are pressed in hardened steel dye to match the diameter of the target requirements to pressures of ~20,000 psi. To then harden the target, it is sintered in an atmospheric furnace to approximately 1000-1300ºC depending on the target composition. Techniques including electron beam deposition require a metallic source, prohibiting some elemental components from being included directly in the source and must be supplied externally. Additionally, deposition rates can easily be controlled by varying laser fluence parameters including pulse frequency and power. Deposition rates can drastically affect the quality of the film as higher rates may higher certain phases [141, 142]. Also, the deposition rate can also be very influential in the epitaxial nature affecting the ultimate quality of the film. However, despite the distinct advantages PLD has over other deposition techniques, significant challenges do exist. The largest of which is the existence of particulates which usually occur at the surface of the film but can obviously add to many problems within bulk structures. These small clusters of target material are usually between 1 nm to 1 μm [143]. Often times, the existence and state of these particulates are linked to the target preparation conditions [144], lasing specifications [145], or target position [146]. Additionally, different elements can be preferentially deposited for different elements, especially for elements of much lighter mass. This can often times lead to large inconsistencies in film stoichiometry.

To better understand PLD, we explore the known physical principles related to its use. The obvious core element of PLD is the selection of a laser source of adequate energy and
power. There are numerous choices currently suitable for this application with solid-state lasers becoming a leading choice for their minimal loss in energy with age in contrast to gas lasers which may suffer large losses of intensity. These solid state lasers offer a consistency that is obviously beneficial to those who perform repetitive experiments requiring consistency between experiments. However, the choice of a particular laser is not necessarily important here but its power density onto the target certainly is. To simplify the steps to successful ablation here, we simplify PLD into three essential steps. The first is the contact of the laser spot with the desired target. Often times, the laser spot does not strike the target unimpeded from the laser but usually travels through mirrors and lenses first. These optics, of course, must be compatible with the wavelength being utilized to avoid being ablated as well. The mirrors enable optimal placement of the laser while the focusing lens, usually on the outside of the UHV chamber just outside the chamber window, provides an increased beam density necessary for proper ablation. At laser impact with the target, the laser’s pulse energy is quickly transferred to the electrons of the solid at the target’s surface [147]. After an equilibrium is established, heating of a pm size spot to thousands of degrees Celsius in mere picoseconds occurs [148]. Secondly, this small spot quickly expands, generating a plume normal to the surface. The ablated material continues to interact with the laser energy from same pulse, resulting in more energy absorption followed by ionization of a thin vapor layer on the target’s surface. When the laser pulse intensity disappears, the plume expands further away from the target surface. The shape of this expanding plume can vary widely according to different lasing conditions. Lastly, the plume’s contents makes contact with the desired substrate, establishing deposition. Once epitaxial deposition begins, it will likely proceed along one of three different growth mechanisms.

There are three main epitaxial growth mechanisms. The first is Volmer-Weber (VW) and is summarized as 3D island growth. The second, Frank-van der Merwe (FM), is layer-by-layer growth. The third, Stranski-Krastanow (SK), is essentially a mixture of 2D and 3D growth. VW
growth is the most common of the three modes. It occurs for heteroepitaxial growths and according to four main steps. The first step for this growth is nucleation, followed by growth of these nuclei into clusters, then coalescence of clusters, and lastly the disappearance of gaps between the clusters from further cluster coalescence [149]. The influential factor for this growth is characterized by the strong interaction of the film with itself, as opposed to the much weaker interaction of the film with the substrate. Conversely, the FM growth has a strong interaction of the substrate with the film resulting in a layer by layer growth. As FM growth begins, the adatoms are deposited onto the terrace sites of single crystals. Due to the strong interaction between the substrate and the film adatoms, the adatoms preferentially migrate from terraces to steps or kinks where they are stabilized. Eventually, all the substrate terrace sites are filled and layer by layer growth proceeds. As essentially a combination of the first two growth modes, SK growth proceeds as a layer plus island growth. Initially, adatoms proceed by layer by layer growth similar to FM growth. However, at a critical thickness, called the Stranski-Krastanov transition, 3D island growth proceeds. This critical point is often determined by the unique interaction of the substrate and the film. Early studies performed on \( \text{Al}_2\text{O}_3 \) (0001), (11-20), and (10-10) have suggested that VW growth occurs for rutile TiO\(_2\) on these surfaces [150]. Initially, 3D islands were observed for thicknesses less than 15 nm. However, the islands slightly enlarge for higher thicknesses consistent with the VW growth mechanism with island size apparently dependent on the different lattice mismatch of the different surfaces. Other studies of anatase TiO\(_2\) on SrTiO\(_3\)(001) have suggested SK growth utilizing MBE [122]. By utilizing STM, initial growth occurs with the evolution of two distinct structures of growth of islands on terraces and overlayers at step edges. In accordance with the SK growth mode, these two features eventually form a two monolayer wetting layer by which island growth continues.

To begin deposition, a custom stainless steel UHV capable chamber is evacuated to a minimum pressure of \(5\times10^{-10}\) Torr. Pumping is achieved with a combination of two pumps
working in series with a roughing pump providing a minimum vacuum of $3 \times 10^{-2}$ Torr for backing to a turbomolecular pump to a minimum pressure of $\sim 10^{-8}$ Torr. To remove the remaining water vapor within the chamber and on the chamber walls and components, the entire chamber and accessories are heated (baked) to a minimum of 150ºC. The additional heat gives additional mobility to the remaining water molecules so that they can be further removed with the turbomolecular pump. After baking is complete, an ion pump located within the base of the chamber can provide additional vacuum to the ultimate pressure. This ion pump functions by ionizing remaining particles in the chamber where they are exposed to a magnetic field provided by magnets external to the chamber. The ionized particles, as a result of the applied magnetic field, are accelerated into metallic plates where they remain indefinitely. A Ti sublimation pump is also utilized periodically to capture background gases by heating a Ti filament with $\sim 30$A of current, making the Ti highly reactive and capturing the remaining gases. A series of valves may isolate each pump depending on the operating pressures of the chamber.

To prepare the samples for deposition, they are ultrasonically cleaned in sequential baths of acetone and ethanol to remove any residual organic contaminates. Next, to ensure similar deposition conditions, a sample of each substrate is mounted side by side on a Mo sample plate attached with Ta wire across all corners to provide uniform thermal contact. The samples are placed into the vacuum chamber and moved into a vertical custom built sample holder mounted on a manipulator with the samples facing down onto the TiO$_2$ target. Outgassing of the samples and sample plate are performed by heating from within the sample holder. Heating is provided by a W filament behind the sample plate which is at a potential difference of 600V. The high potential extracts electrons from the heated W filament, generating electron bombardment to achieve higher temperatures compared to a traditional heating filament configuration. Heating is increased slowly to minimize outgassing rates and discourage changes in state to the substrates. Once 600ºC is achieved as determined by an optical
pyrometer, a background of ultra-high purity oxygen is supplied to a pressure of $2 \times 10^{-6}$ Torr, measure with a hot filament ionization gauge. Annealing with oxygen is performed for a period of two hours to remove any residual organic materials still remaining, after which deposition can begin. An Nd:YAG laser of ~170 mJ pulse energy, located above the UHV chamber, is focused onto an angled mirror to which the beam is directed onto a lens mounted on a UV-transparent window. The tightly focused laser spot strikes a previously prepared TiO$_2$ target within a water cooled Cu target holder mounted ~8 cm underneath the samples. The laser is maintained at 5-6 Hz pulse frequency to maintain a deposition rate of 0.8 angstroms/min. The deposition rate and final thickness is monitored with a quartz crystal microbalance calibrated to TEM thickness measurements and located adjacent to the sample. When the desired thickness for each experiment was attained, deposition was stopped and cooling at the rate of ~20°C/min to room temperature was maintained. After the sample had sufficiently cooled, the oxygen background was removed and the chamber returned to UHV vacuum. RHEED patterns corresponding to the anatase and rutile films were taken individually with a beam voltage of 13.6 keV. Figure 3.5 represents the core components of the deposition and characterization system part of the UHV chamber. An additional picture and diagram of the actual PLD chamber is given is Appendix 2.
3.4 Thin film characterization

To adequately characterize the newly deposited films onto their matching substrates, we explore several techniques capable of evaluating the phase, quality, and composition of the surface and bulk of the films. Because of the interaction of the surface and bulk of TiO$_2$ in relation to photocatalysis, we explore probe techniques that will conclusively demonstrate clear differences between the two popular phases, anatase and rutile, while also investigating any differences that may exist within the same phases themselves. Ideally, all characterizations performed will be in complete agreement with each other but also with previously performed published work of others. First, let us explore these techniques utilizing simple physical principles.

3.4.1 Reflective high energy electron diffraction (RHEED)

To begin, we evaluate a simple characterization technique that can easily be done during or quickly after deposition. Reflective high energy electron diffraction (RHEED) relies on simple electron diffraction principles to determine crystallinity of the top most layer. When used effectively on metal oxide surfaces, it can be used to determine sample orientation, lattice constant, relative roughness, and initial deposition rate. To obtain these measurements for this brief, the samples were analyzed in the same vacuum.

![Figure 3.6 FCC(110) real and reciprocal lattice. Diagram depicting the relation between the real lattice and reciprocal lattice of a face-centered cubic (FCC) (110) surface with the appropriate lattice constants and corresponding relationships.](image)
chamber and position as deposition was performed as described earlier. An electron gun mounted to the side of the chamber provides a beam of electrons with an energy of usually between 10-20 keV at a grazing incidence onto the surface of the sample usually between 4-7° off the horizontal to the sample. The beam is reflected off the sample surface as a diffracted beam. The resulting pattern strikes a phosphor coated glass window where a pattern will be displayed to the external viewer according to the reciprocal lattice and Ewald sphere. To understand how these patterns are created as a result of the surface interaction, we evaluate how the beam interfaces with the crystal lattice at the surface of the sample. Here, we define reciprocal space as the Fourier transform of the direct lattice. Figure 3.6 demonstrates a simple relationship between the direct lattice unit vector $a_1$ and the reciprocal lattice unit vector $a_1^*$ for a Face-Centered Cubic (110) surface. According to kinematical theory, the difference between the incident wavevector $k_0$ and the reflected wavevector $k$ is reciprocal lattice vector $G$ as

$$G = k - k_0 \tag{3.1}$$

Very simply, $G$ can be utilized to determine the separation between lattice planes in the crystal.

![Figure 3.7 Experimental RHEED setup.](image)

*Shown is a diagram depicting a side view (left) and a top view (right) of a sample with the resulting sample and Ewald sphere intersecting with the reciprocal lattice rods. The phosphor screen is also shown to depict how each of the resulting spots for the 0th, 1st, and 2nd Laue circles.*

To define the radius of the Ewald sphere, we use the equation
$$k_0 = \frac{2\pi}{\lambda} \quad (3.2)$$

where $\lambda$ is the wavelength of the electrons incident onto the sample surface. Figure 3.7 demonstrates the relationship between the sample, Ewald sphere, reciprocal lattice points and phosphor screen. Although most discussions regarding the construction of reciprocal lattices are of course in 3D, the diffraction limitations of RHEED require that the top 2D layer is relevant as diffraction will occur from lattice parameters perpendicular to the surface. Therefore, we only construct reciprocal lattice rods that extend from each reciprocal lattice point on the surface through the Ewald sphere. Diffraction spots will occur wherever the lattice rods intersect with the Ewald sphere and observed in Figure 3.7. From the figure, one can also easily see that the magnitude of the incident electron vector $k_0$ must be equal to the magnitude of the reflected vector $k$ so that

$$|k_0| = |k| \quad (3.3)$$

when scattering events are only elastic as is the case for kinematical scattering theory as we proposed earlier. This is known as the Laue diffraction condition. Therefore, diffraction spots for a well ordered crystal structure will lie on the Laue circles, starting with the 0th Laue circle with the specular spot at the top. Figure 3.8 shows a simple example of the diffraction spots along the Laue circle on the phosphor screen. Therefore, if changes are made to the azimuthal direction of the electron beam then changes will also be made to the orientation of the reciprocal lattice rods relative to the Ewald sphere. Certainly, these changes will result in a predictable manner to determine azimuthal direction of the electron beam relative to the known crystallographic

![Figure 3.8](image.png)
directions. For the most part, these directions are made along low index directions to minimize more complex diffraction patterns that arise from high index directions.

In addition to utilizing RHEED to determine crystallographic orientation, we can also determine the lattice constants of the lattice planes perpendicular to the sample surface. To do this, we use the simple principle provided by Bragg’s law as

$$2d \sin \Theta = n\lambda$$  \hspace{1cm} (3.4)

where \(d\) is the distance between planes, \(\Theta\) is the scattering angle, \(n\) is an integer number, and \(\lambda\) is the De Broglie wavelength of the incident wave given by the equation

$$\lambda = \frac{hc}{E}$$  \hspace{1cm} (3.5)

. Because the premise of RHEED relies on a very small scattering angles, we can easily use the approximation

$$2 \sin \Theta = \tan 2\Theta = \frac{S}{L}$$  \hspace{1cm} (3.6)

where \(S\) is the distance that is parallel to the sample surface and separates two similar diffraction spots on the same Laue circle and \(L\) distance between the phosphor screen and the origin of the Ewald sphere [151]. Therefore, the relationship can easily be found that

$$d_{\text{lattice}} = \frac{\lambda L}{S}$$  \hspace{1cm} (3.7)

. Thus, for constant electron wavelength, the lattice constant \(d\) is proportional to the ratio of the distance between the spot separation and the screen distance. For most experimental setups, \(\lambda\) and \(L\) are kept constant so that the lattice constant between the corresponding planes can be measured.

For the most part, many thin film depositions, at least performed on ordered substrates, will have films with predictable lattice constants based upon the known conditions. However, the surface morphology or roughness can often vary depending on a variety conditions such as
substrate temperature, deposition rate, and background pressure. Most measurements to determine the roughness related to film growth are microscopy probe based such as STM or AFM but require post growth analysis with long scan times.

Through the capabilities of RHEED, a qualitative measurement can also be made as to the approximate roughness of the film's surface. In addition, this technique also adds the ability to measure the initial deposition rate based upon these behaviors. To demonstrate this process, Figure 3.9 provides a diagram of how the RHEED primary spot intensity increases and decreases with surface roughness. If a well-ordered surface is present, either from the substrate or minimal film growth, a tightly focused primary spot will result on the 0th Laue circle as described earlier. As growth proceeds in sub-monolayer increments after a minimal thickness is achieved, usually 1-2 monolayers, the spot intensity will decrease. During this transition between monolayers, nucleation of isolated islands will proceed and yield a decrease in the spot intensity from the electron beam becoming diffracted from multiple layers. The ultimate method of layer-by-layer growth will ultimately depend upon the exact deposition technique and material used but will most likely proceed.
according to the principles presented earlier. When the surface of the film reaches a maximum roughness, the primary spot intensity will be at its minimum value. For most cases, this will be approximately ½ of a monolayer. As deposition continues from this point, the islands will coalesce to form larger islands thus reducing the roughness and increasing the spot intensity. Once one monolayer is reached, the spot intensity will reach close its maximum once again. As deposition proceeds further, the amplitude of each oscillation will ultimately decrease to a point in which oscillations no longer occur. Due to the relationship between these observed oscillations, which can ultimately be recorded on the phosphor screen by a CCD camera, and the layer-by-layer growth progression, an initial measurement of growth rate can be made. Provided these initial measurements are consistent with further deposition rates, an estimate as to the ultimate thickness of the film can thus be made, especially for very thin films. The eventual attenuations in amplitude are the result of the film eventually reaching an inherent roughness consistent with the material and/or conditions for growth.

3.4.2 Atomic force microscopy (AFM)

To further explore the quality of the epitaxial anatase and rutile TiO₂ films, we employ Atomic force microscopy (AFM). To further the advancements of technology in the last several decades, especially at the atomic level, a large number of microscopy technologies have been developed. Of course, some are much more complex than others. However, the benefits of the simpler AFM, as we will see, enable a unique perspective for its cost, ease of use, reproducibility, and time requirements. There are numerous probing techniques that are based upon the fundamental principles of AFM by adding additional capabilities including magnetic and electrical properties but are not relevant for the current discussion. Therefore, the discussion here only explores topographical and phase contrast modes that are the most helpful for the evaluation of the surface morphology.
The forerunner to the current AFM was the STM created by Heinrich Rohrer and Gerd Binnig in 1982 [152]. Gerd Binning, Christoph Gerber, and Calvin Quate later expanded upon these principles to create contact mode AFM by observing the deflection of a sharp probe across a sample surface in direct contact. Different from contact mode, Martin et al developed non-contact mode (NC-AFM) and relies on the tip lying in close proximity to the sample surface, usually a few nanometers [153]. The fundamental concept of this tip-surface interaction is the Van der Walls force. The Van der Walls force is an attractive force between atoms or molecules, resulting from the mutual interaction of their nuclei and electrons. However, the attractive force is balanced by the repulsive force from the resistance to share outer electronic shells for minimal distances [154]. We see in Figure 3.10 just how this relationship works, as the distance between 2 atoms or molecules decreases, the resulting sum force is attractive until a minimum distance is achieved at which point the forces become repulsive. This first regime, where distance is large, is ideal for non-contact imaging. In contrast, the second regime where the distance is minimum, is ideal for contact imaging. In addition, the attractive Van der Waals force can increase with increases in electron number per molecule, which is essentially proportional to atomic weight. Therefore, the development of NC-AFM technology was fundamentally based on exploiting all of these interactions. Thus, to image a surface in this mode, a cantilever made of silicon ~100 x 30 µm holds a sharp tip with a tip.
radius of <10nm. An image of a commercial AFM cantilever tip is shown in Figure 3.11. This cantilever is oscillated at a harmonic frequency, characteristic of each individual cantilever, and moved to approach the tip to the sample surface. As sufficient distance between the oscillating cantilever and stationary surface decreases to a minimum, the Van der Waals attractive forces will change the phase and amplitude of the cantilever [155]. A small laser spot is reflected through a series of mirrors off the back of the cantilever onto a photodetector where its position and intensity can be observed. A feedback loop then maintains this frequency or amplitude by moving a piezo in the up/down, or z-axis and recording this as a dataset. Simultaneously, the sample surface is rastered along the x and y axis so that a topograph can easily be made from these measurements. In addition, the changes in phases can be mapped as well to demonstrate significant changes in electron density based upon elemental differences on the surface. Figure 3.12 is a very simple diagram representing a common AFM setup. Of course, this design can also be used in contact and as well as tapping mode. Tapping mode can generally be considered to be a hybrid of contact and non-contact mode. Just as in NC-AFM, the cantilever and tip is oscillated in tapping mode also but with a few key differences. Instead of avoiding contact with the surface, the tip makes periodic contact so that adhesion to the surface is less likely. Typical cantilever oscillations are much larger in amplitude to achieve this. Thus, many of the challenges to maintain the narrow regime required for non-contact mode can be avoided. Certainly, very rough surfaces in a variety of disciplines would present difficulty in effectively maintaining uniform distances between the surface and the tip necessary for non-contact mode but not for tapping mode. However, the lateral resolutions for non-contact mode are generally considered superior provided a relatively flat surface is provided. Therefore, the epitaxial relationship suggested
earlier provided by sufficient growth conditions and substrates is expected to enable a highly resolved topography of the surface to ensure similar surface corrugations, minimizing any undesirable ambiguities.

3.4.3 Transmission electron microscopy (TEM)

Earlier in this section, we have provided techniques to properly characterize the surface structure of the rutile and anatase TiO$_2$ thin films. Although helpful in demonstrating the crystallinity and morphology at the surface, little characterization to the bulk of the films can thus be concluded besides evidence to suggest the surface is a direct result of the bulk structure. Obviously, a disordered bulk structure would not likely yield a well-ordered surface. As we suggested earlier, clear differences in photocatalytic behavior have been observed between the anatase and rutile surfaces but conclusive evidence has not been reported that explains these differences to be the result of the different bulk structures. Therefore, if any differences in photocatalytic behavior exist between the two phases of TiO$_2$ deposited here, a clear distinction must be made between the two underlying bulk structures. Ideally, a suitable technique would enable a careful analysis of the full width of the film thickness while also determining the lattice structure and constants consistent with known values. Transmission electron microscopy (TEM)
quickly became an excellent technique to provide these capabilities. Here, we investigate the physical principles behind this technique and its further relevance to the current investigation.

In order to effectively probe the bulk of the films so that a sufficient characterization can be made, each film must be oriented and further prepared to expose the film and substrate for analysis. As we will see later, the key to TEM is that the electron beam is focused and transmitted through the sample with the sample altering the beam to be collected and analyzed on the other side. Thus, the orientation of the sample is important to ensure the entire beam path does not traverse different phases or materials of the sample such as passing though the film and substrate in series but rather in parallel. In addition, each sample must be thin enough to allow the beam to traverse the sample but thick enough to allow for sufficient sampling. Therefore, each sample is prepared by what is known as the lift-out method, originally proposed by Overwijk et al [156].

To begin, a small area of interest on the sample is coated with a thin layer, usually a few microns thick of a metal such as W or Pt to protect the surface from damage and contamination. Next, a focused ion beam (FIB) is focused into the sample on both sides of the protective metal layer so that two trenches are created with the targeted sample being 2-4 µm in thickness between the two trenches. Additional trenches are created parallel and outward from the originals to create steps. Next, the sample is rotated to approximately 45° so that the FIB can be directed into the side of the thin sample area. Three penetration cuts are made, one along the bottom and two made vertically to the sides of the thin sample. The FIB is returned to the direction parallel to the thin sample to further thin the sample to about 50 nm. As the sample is becoming more and more electron transparent, the beam current is further reduced to
produce cleaner cuts. Lastly, the FIB is directed to sever the remaining structure on the surface of the sample, freeing the thin sample from the original. Figure 3.13 depicts the relationship between the FIB along the two directions and the cut-out created as a result of FIB directed from the side. To retrieve the sample for analysis with TEM, a glass tube with an end diameter of approximately 1µm is attached to the end of a micro-manipulator. The tip of the tube is moved to the thin sample where electrostatic forces attach the two [157, 158]. The thin membrane is transferred to a circular metal grid 3.05 mm in diameter, usually made of Cu or other highly conductive metal containing minimal or non-magnetic materials [159, 160]. From this point, the samples on the grids are loaded into the TEM where analysis begins.
There are essentially four core parts to a transmission electron microscope. The electron source, electron optics, the sample holder, and the detection apparatus. Of course, equipment will certainly vary with different equipment but here, we explore the JEOL 2100F that the samples were analyzed with for this investigation. The electrons are emitted from a field emission gun (FEG) from a W or LaB₆ source. Field emission guns are utilized to improve the energy dispersion, spot size, and increased brightness of the beam over thermionic emission from hot filaments [161]. Typical excitation energies for the electrons emitted is 100-300 keV. The first entry the electrons make after excitation is into the condenser lens coils as observed in Figure 3.14. Instead of relying on refraction in optical lenses to focus light, magnetic fields produced in coils to change the incoming divergent beam from the source to become converging as it enters the next stage. The now convergent beam enters the sample...
holder to transverse the electron transparent thin membrane sample described earlier. The transmitted beam makes entry into the objective lenses, also controlled with magnetic coils, followed by the objective aperture. The ultimate size of this objective aperture will determine what mode images will be produced, bright/dark field images or selected area electron diffraction (SAED) patterns. The main purpose of this aperture is to control the angle of the scattered electrons to only allow electrons of a maximum scatter angle. If the aperture is wide open or not present, the electrons with narrow or wide scattering angles will form a diffraction pattern on the back focal plane of the objective lens as a result of the focus of the intermediate lens. This is a direct result of the Fraunhofer conditions which requires that the Fourier transform of an image is created within the back focal plane from the lens [162]. For generation of diffraction patterns, the intermediate lens is focused to conjugate the object image from the projector lens with the back focal plane from the objective lens. The diffraction pattern is then transferred through the projector lens and onto the imaging system where it is collected for acquisition. For bright/dark field imaging, however, the aperture is inserted/reduced to absorb the wide scattered electrons. The objective lens produces an intermediate image with the narrow scattered electrons. Similar to diffraction conditions, the object image is conjugated from the projector lens with the image of the objective lens. The projector lens provides the last magnification onto the imaging system where it is collected for acquisition [163, 161]. The difference between bright field and dark field imaging is the source of electrons. Bright field imaging utilizes the objective aperture to select unscattered electrons. Thus, an electron that has little or no contact with the crystal structure of the sample will appear “bright” in the real image. Conversely, an electron that is scattered from contact with the crystal lattice will have its path disrupted and leave a dark contrast. In dark field real space imaging, the reverse is true with the source being scattered electrons. This is the direct result of the increase number of collisions scattered electrons have with the lattice of a crystal which is being collected in dark
field imaging. The background is otherwise dark without the scattered electrons which obviously have increased collisions.

### 3.5 Photocatalytic measurements

Lastly, we investigate the techniques associated with determining the photocatalytic activity of the anatase and rutile TiO$_2$ thin films. Ultimately, the purpose of these measurements is to determine the differences, if any, in the behavior of charge carriers between the anatase and rutile TiO$_2$ thin films and the relation to film thickness. There are numerous possibilities to obtain these measurements, certainly some more suited to the current brief than others. However, we present a novel design and implementation driven from established concepts to make these necessary comparisons. Previously, it was shown how electron-hole pairs can be generated in a photocatalyst such as TiO$_2$ with exposure to light of a minimum energy. Certainly, the diffusion of these charge carriers in photocatalysts has been heavily discussed including the very motivation for this investigation. However, significant challenges continue to exist in measuring these diffusion lengths, especially observing differences between two phases of TiO$_2$, anatase and rutile. Earlier, we explored in depth a number of different ways to properly characterize the thin films for their bulk and surface properties. However, similar measurements to directly characterize the charge carriers related to photocatalysis for the films created here provide significant challenges. The most significant of which is that such equipment is simply not readily available on the commercial market, although options obviously exist to build such instruments, it is beyond the scope of this brief provided other suitable solutions exist. Thus, we propose a technique here to achieve these measurements, either directly or indirectly, with instruments that are both easily accessible and supported by sound scientific principles.

Azo compounds are classification of a chemical group containing the chemical group R-N=N-R’ whereas R and R’ can be an aliphatic or aromatic functional group with the name
originating from the N=N called the azo group [164]. It is this azo connecting link between the aromatic groups that enables this compound to absorb visible light. Thus, this material makes an excellent dye for such uses in textiles. In fact, azo dyes account for the majority of dye use by both number and production volume [165]. However, these dyes have posed significant threats to the environment with reports indicating that as much as 15% of those produced contaminate the water supplies [166, 167]. The discoloration of these contaminated water supplies can become apparent with as little as 1 ppm for certain azo dyes [168]. More importantly, these dyes are considered very toxic and even carcinogenic [169-173]. Thus, large efforts have been taken to reduce their harmful effects by researching methods to reduce their toxicity. These methods include degradation using biological systems including microbes [174, 175], absorption utilizing high density sorbents [176, 177], and chlorination [178]. In addition, metal oxides such as TiO$_2$ have been successfully shown to act as photocatalysts in the degradation of the azo dyes [179-186]. Here is a summary of the reaction pathways for an azo dye and TiO$_2$ under illumination of UV light of sufficient energy:

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + e^- + h^+
\]

\[
\text{TiO}_2 + h^+ + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^-
\]

\[
\text{TiO}_2 + h^+ + \text{OH}^- \rightarrow \text{TiO}_2 + \text{OH}^-
\]

\[
\text{TiO}_2 + e^- + \text{O}_2 \rightarrow \text{TiO}_2 + \text{O}_2^-
\]

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2.
\]

\[
\text{Azo} + \text{OH}^- \rightarrow \text{degradation products}
\]

\[
\text{Azo} + h^+ \rightarrow \text{oxidation products}
\]

\[
\text{Azo} + e^- \rightarrow \text{reduction products}
\]
The photogenerated holes $h^+$ may oxidize the dye molecule to generate a $R^+$ group, or possibly with the $H_2O$ or $OH^-$ generating $OH\cdot$ radicals. Conversely, the photogenerated electrons $e^- \cdot$ react with the surface $O_2$ or dissolved in water to produce the superoxide radical anion $O_2^{2-}$, which in turn may react with the Hydrogen cation $H^+$ to yield a peroxide radical $HO_2$. [179, 187, 180]. The important note is that the $OH\cdot$ radicals have a very high redox potential of +2.8V [188, 189]. As a result, the $OH\cdot$ radicals are very reactive towards the azo compounds, reducing them to their degradation products. Lastly, direct oxidation or reduction may occur as the hole $h^+$ or electron $e^- \cdot$ respectively reacts with the azo compound directly to produce their characteristic products.

Now that there is an established reaction pathway for the degradation of azo dyes, we present how such reaction rates are evaluated. This decay can be effectively modeled according to the Langmuir-Hinshelwood (LH) kinetics model [190-194]. A Langmuir-Hinshelwood reaction is characterized by the following conditions [195]:

- Number of adsorption sites at the surface remains constant in equilibrium
- Restricted to one surface adsorbate to one surface site
- Each surface site cannot be irreversibly inhibited from binding adsorbates
- No interaction occurs between adjacent adsorbates
- Heat from adsorption is equal for each surface site
- Heat from adsorption is independent of amount of covered area
- Rate at which adsorption occurs is always greater than the rate of chemical reactions

Therefore, we can express the rate of the reaction $r$ as under illumination as

$$ r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (3.8) $$
where \( k \) is the rate constant of the system including the photocatalytic activity, the reaction medium, and the incident energy of the light source. Additionally, \( K \) is dependent on the adsorbates molecular structure and defined as equilibrium adsorption constant, \( C \) is the reactant’s concentration, and \( t \) is the reaction time \([196]\). However, this equation can be easily simplified to a first-order equation

\[
\ln \frac{C_i}{C_t} = kKt = k_a t
\]

(3.9)

when \( C_i \) is a very small initial concentration in the millimolar range and \( C_t \) is the concentration at time \( t \). Thus, it is therefore easy to obtain this equation in the simpler form

\[
\frac{C_t}{C_i} = e^{-k_at}
\]

(3.10)

with \( k_a \) being the product of \( k \) and \( K \) \([197, 179, 192]\). Thus, the ratio of the concentration at time \( t \) to the initial concentration can be effectively modeled with this first-order equation. As we have seen, the absorption of the azo dye is directly linked to the concentration. Thus, the ultimate photocatalytic activity can be also directly linked to the change in absorption \([198, 199]\). The absorption of the illuminated solutions/samples can easily be measured with a UV/Vis spectrophotometer which measures the intensity from wavelengths 200-800nm.

To accomplish the absorption measurements, a custom set-up was designed and constructed to accommodate the exact specifics and needs of the experiment. After proper characterization of the samples as described earlier, each sample of known thickness and phase was securely placed into a custom built sample holder. The holder consists of a Ta wire suspended from the top of the cuvet cover. The glass cuvet was filled with 3 mL solution of 0.1 millimolar solution of methyl orange, an azo dye. The sample was lowered into the cuvet containing the methyl orange solution. The sample and cuvet were illuminated from the side with a 100W Oriel Hg-arc lamp fitted with a lens and water cooled IR-filter. The incident light energy was measured at regular intervals between 200-700 nm in wavelength both before and
after the experiment to ensure uniform intensity between different sample measurements. A
UNICO 2800 UV/Vis spectrophotometer was utilized to obtain absorbance spectrum from 190-
800nm of the cuvet and methyl orange solution before illumination, at 30 minute intervals over a
period of 5 hours, and immediately after illumination was halted. From each spectrum, the area
under the curve between approximately 365-615nm, with a peak at 490nm, was calculated.
Each area was normalized against its initial peak spectrum area and recorded against
illumination time. Thus, this plot is then fitted to the first-order Langmuir-Hinshelwood (LH)
kineic equation (Eq. 3.10) where $k_a$ can be properly obtained from the fit. Finally, each $k_a$ value
was further plotted according to its known phase and film thickness. A picture of the cuvet
containing a 5x5 mm sample in a solution of methyl orange and the Hg arc lamp is given in
Appendix 3.
4. Conclusion

For this dissertation, planar single crystalline TiO_2 model systems were prepared. Their structural properties were characterized with several techniques. Lastly, the photocatalytic properties of these films were evaluated and correlated to the preparation and characterization results of planar TiO_2. The dissertation can be divided into approximately two core areas. The first of which is the investigation of under-coordinated sites on step edges. In order to investigate the influence of monatomic step edges, as a model for undercoordinated surface sites, we developed a new method for preparing a high density and crystallographically aligned stepped surfaces on single crystal rutile-TiO_2 samples. This proposition offered a new opportunity to generate aligned high density stepped surfaces on single crystal TiO_2. Such undercoordinated step-sites are expected to exhibit special chemical properties. This provides for the preparation of a well-defined model system, enabling the investigation of these step-sites properties in greater detail. For the second area, the focus is limited to planar epitaxial TiO_2 films consisting of individual anatase and rutile phases. To produce the TiO_2 structures, a pulsed laser deposition (PLD) system was designed, constructed, and optimized for growth parameters to yield high quality epitaxial thin film growth of TiO_2. From the construction of these films, a methodology was created to permit discrimination between photocatalytic activity originating from the surface and bulk of the TiO_2 film. This conclusively addresses the long-standing debate as to why the anatase phase is more photocatalytic active than the rutile phase of TiO_2. For the following, a series of conclusions are offered to support these two core areas.
4.1 **Surface modification of TiO$_2$**

By utilizing grazing incidence ion sputtering on rutile TiO$_2$(110) surfaces, the surface can be modified to produce a series of functional interfaces. For low energy ions ~ 1keV and at an angle of incidence to grazing >80° relative to the surface normal, a large majority of impinging ions on the terraces will be reflected with minimal kinetic sputtering occurring on these terraces. However, the suggested grazing incidence angle provides high kinetic energy transfer to steps perpendicular to the beams direction. These steps edges, with their faces directed toward the ion beam, are impacted both directly and from ions reflected from the nearby terraces resulting from the ions reflected from the defect free terraces. This results in an increase in the sputter yield of step edges relative to the sputter yield of terraces. This property provides an opportunity to produce unique structures and terminations on TiO$_2$ and other oxides.

Rutile TiO$_2$(110) surfaces prepared by annealing in vacuum have step edges that are predominantly directed along the <001> and <1-11> directions visible with STM [47, 3, 200]. However, absent from the reports are step edges directed parallel to the <1-10> direction. The absence of these steps is fundamentally based upon the high formation energy such a low-index step would have. Thus, by low energy ion sputtering at a grazing incidence angle of 83° and an elevated temperature of 400° C at an azimuthal direction parallel to the <1-10> step edges, these high energy step edges are created. The existence of these step edges is supported by atomic scale STM measurements. By further annealing the sample >600° C, the <1-10> step edges disappear, replaced by more stable <1-11> and <11-1> step edges in their place. Thus, demonstrating the meta-stable nature of the <1-10> steps. To correctly resolve the STM measurements taken along this high energy step edge, a structural model was created to establish the atomic configuration while maintaining proper Ti and O ratios. This model was determined to contain both <1-10> and <11-1>/<1-11> step constructions including four-fold and five-fold coordinated Ti atoms at the edge with two-fold O edge atoms. Additionally, this
model was further corroborated by DFT calculations by evaluating the atomic relaxations and formation energy. The calculations suggested a 0.09 eV/Å lower value for the model presented above compared to the unreconstructed <1-10> step edge. Finally, the same reconstructed model was subjected to simulated STM measurements and compared to experimental STM measurements and found to be in agreement [201].

Although the principles behind low energy grazing incidence sputtering of step edges at low fluences have been explained, evidence conclusively showing preferential sputtering at step edges on a metal oxide has not been shown. Additionally, nanoripple patterning at high fluence is the result of, at minimum, a contribution from the increased sputter yield at step edges for grazing incidence. In addition, a comparison of the sputter yield for two low-index directions of rutile TiO₂(110) for terraces and steps were derived from experimental STM studies.

4.2 Photocatalytic activity of anatase and rutile thin films

A novel technique was proposed and utilized to determine why differences in photocatalytic activity is observed between the anatase and rutile phases of TiO₂, even differences between different crystallographic orientations of the same polymorph. To do this, a series of epitaxial anatase and rutile films of different thicknesses were deposited on lattice matched single crystal LaAlO₃(100) and Al₂O₃(1-102) substrates respectively under identical conditions. Details of the film preparation and characterization are given in the attached publications. To evaluate the photocatalytic activity of the films, a novel experimental setup was constructed to evaluate the well-known decomposition of methyl orange, as described in the experimental section of this dissertation. A difference in the photocatalytic activity was observed between the anatase and rutile TiO₂ films. For the rutile phase, the degradation rates did not reveal appreciable rate increases for thicknesses greater than ~2 nm while the anatase film revealed rate increases for thicknesses larger than 5 nm. The different thicknesses at which
maximum degradation is achieved is attributed to the collection of excitons at greater distances from the surface for the anatase film versus the rutile film. This is further supported by developing a model to reflect the relation of charge carrier length to degradation rate. This is done by fitting the increase of the photocatalytic activity to the increase in film thickness with the relation

\[ k = C \left( 1 - e^{-\frac{d}{\lambda}} \right) \]  \hspace{1cm} (4.1)

where \( k \) is the rate of dye degradation proposed earlier, \( d \) is the film thickness, \( C \) is a fitting constant, and \( \lambda \) as the charge diffusion length normal to the surface. A value of \( \lambda \) for the anatase phase was found to be \( \lambda_{\text{anatase}} = 3.2 \pm 0.6 \) nm while a value of the rutile was found to be \( \lambda_{\text{rutile}} = 1.6 \pm 0.4 \) nm. Clearly, this suggests different changes in photocatalytic activity for film thickness increases for anatase and rutile TiO\(_2\). For the thickest films of 20nm, the rates of degradation of the anatase films are approximately twice the rates of similar rutile films. This is in direct agreement with a multitude of published reports indicating a higher photocatalytic activity of the anatase phase. Consequently, our studies show that the difference in charge diffusion lengths in the bulk of the material, and not only surface properties, are mainly responsible for the observed differences in the photocatalytic properties of anatase and rutile. The longer charge diffusion in anatase may be associated with its indirect band gap compared to the likely direct gap of rutile. Our finding substantiates importance of the bulk charge (exciton) transport for the photocatalytic properties of TiO\(_2\). In addition, it may also explain dependences of photocatalytic properties as a function of crystallographic orientation. In this case, crystallographic anisotropies in charge diffusion may yield such observations. Generally, the results suggest that a careful evaluation of exciton bulk diffusion is needed for the design of better transition metal photocatalysts.
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Appendices

Appendix 1: UHV ion sputter chamber

Pictured is the Omicron UHV ion sputter chamber with variable temperature STM with supporting electronics below.
Appendix 2: UHV PLD chamber

Pictured is the UHV PLD Chamber with Nd:YAG Laser 355 nm.
Appendix 3: Photocatalysis of methyl orange

Pictured is Cuvet with suspended 5x5 mm sample with 3 mL solution of methyl orange

Pictured is illuminated cuvet containing sample and methyl orange solution
Appendix 4: Published results for surface modifications of TiO$_2$

First-author peer-reviewed journal article citations are listed below followed by the corresponding reprinted publications related to the second chapter of this dissertation, Surface Modifications of TiO$_2$.


New Directions for Atomic Steps: Step Alignment by Grazing Incident Ion Beams on TiO$_2$(110)

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(Received 21 January 2009, published 22 April 2009)

Grazing incidence low energy ion beams preferentially erode steps with directional components normal to the azimuthal direction of the beam, thus generating step edges aligned along the beam direction. With this kinetic method, the fabrication of thermodynamically metastable low index step-edge orientations is demonstrated on TiO$_2$(110). The (110) step edge is prepared, enabling its atomic structure determination by scanning tunneling microscopy and density-functional theory. A reconstructed atom configuration is revealed, which is reminiscent of the structure of the rutile-TiO$_2$(001)$(2 \times 1)$ face.

DOI: 10.1103/PhysRevLett.102.166103

PACS numbers: 68.47.Ch, 61.80.Jb, 68.35.B—, 68.35.Md

The properties of monatomic-height steps are central for many processes at surfaces, such as etching [1], nucleation [2], and chemical reaction [3]. Step edges with different crystallographic orientations exhibit specific electronic [4] and chemical properties [5]. Consequently, controlling step edge orientations enables tuning of interface functionalities. Although any step orientation can be theoretically constructed, energy minimization during heat treatment prevents formation of most step orientations.

Low energy ion beams have been successfully employed for the preparation of thin films with a preferred texture [6]. In this method, the ion beam destabilizes grains with high sputter yield resulting from unfavorable crystallographic orientation relative to the ion beam. Here, this principle of creating a texture by preferential removal of structures with a high sputter yield is extended from 3D films to 2D surfaces. In particular, variations in the sputter yield of step edges as a function of their orientations relative to a grazing incident ion beam are exploited to form step-edge textures with a preferential alignment of steps parallel to the beam. More importantly, we show that with this technique, steps that are thermodynamically disfavored can be kinetically stabilized. We demonstrate this method by preparing and characterizing the thermodynamically metastable (110) step on rutile-TiO$_2$(110).

All the experiments were performed in an ultra high vacuum (UHV) chamber equipped with a commercial low energy ion gun and a variable temperature STM. All samples were irradiated at a polar angle of $83.0 \pm 0.5^\circ$ measured from the surface normal with an Ar$^+$ ion beam of 0.8 keV along low index azimuth-directions of the substrate. The TiO$_2$ substrates were oriented in the (110) orientation and STM images of freshly prepared samples showed terraces 10–30 nm wide. During irradiation, the sample temperature was kept at 400°C if not noted otherwise. Empty-state STM measurements were performed in situ with a bias voltage of 1.5 V and tunnel current of $\sim 1$ nA.

For assessing the stability of step-edge structures and to interpret STM images, total energy density functional theory (DFT) calculations have been carried out within the generalized gradient approximation (GGA) using the PWSCE code included in the QUANTUM-ESPRESSO package [7]. Electron-ion interactions were described by ultrasoft pseudopotentials [8], with electrons from O 2s, 2p, and Ti 3s, 3p, 3d, 4s shells explicitly included in the calculations. Plane-wave basis set cutoffs for the smooth part of the wave functions and the augmented density were 25 and 200 Ry, respectively. The (110) steps at rutile TiO$_2$(110) were modeled with vicinal rutile TiO$_2$(441) surface, which contains (110) terraces and monatomic (110) steps. A periodic slab with 4 layers of oxide was used and the vacuum between slabs is $\sim 10$ Å. In order to model the $2 \times 1$ reconstructed structure (see below), we also used a $(2 \times 1)$ surface cell with corresponding $2 \times 2 \times 1 \Gamma$-point mesh. All the atoms within the slab were allowed to move in structural optimization (force threshold is 0.05 eV/Å). Simulated STM images were calculated within the TerraeI-Hamann approach [9], under empty-state conditions with a 1 eV energy window and a fixed distance of $\sim 2$ Å above the terrace twofold coordinated O atoms [the cut plane is parallel to the (110) facet].

It has been previously shown that the sputter yield of a grazing incidence low energy ion beam varies largely at flat terraces compared to defect sites such as step edges [10]. For low ion energies ($\sim 1$ keV) and large incidence angles (larger than $\sim 80^\circ$), ions may reflect from a terrace without penetrating the surface layer, and thus only limited kinetic sputtering of surface atoms occurs. Ions impacting close to a step edge, on the other hand, experience a locally steeper impact angle and thus cause sputter damage. Thus, ion sputtering at grazing angles is fundamentally different from sputtering at steeper angles. At steeper angles, the ions deposit their energy deeper in the bulk, and surface-curvature dependent sputter yields cause surface instabilities and pattern formation [11]. Figure 1(a) illustrates the localized nature of sputtering at step edges for a grazing
incident ion beam on a TiO$_2$(110) sample irradiated at room temperature. Sputter damage is mainly located along step edges that are facing the ion beam (step-up), thus demonstrating strong sputter-yield anisotropy under these experimental conditions. From the analogy of ion beam assisted film growth, it is thus expected that the surface arranges in a step texture that reduces the overall sputtering. This is accomplished by minimizing steps with a directional component normal to the ion beam. If sputtering was only limited to step edges, this would result in the erosion of all steps and eventually a stepless surface. Such a scenario is unrealistic though. Some sputtering at terrace sites will occur, e.g., at point defects, and ions impacting at step edges will induce sputter damage also at lower terraces and creating vacancies away from the step edge [10]. Agglomeration of these vacancies leads to nucleation of “holes,” causing formation of new step edges and thus a roughening of the surface with longer sputter time. Therefore, combination of preferential sputtering of step edges exposed to a grazing incidence ion beam together with the nucleation of new step edges will give rise to a self-formation of a nanostructured surface [10].

In this Letter, we explore to what extent control can be exerted over step-edge orientation by a low energy grazing ion beam. Of particular interest is the possibility of creating steps that are only metastable and thus do not withstand high temperature treatments necessary in other preparation methods.

Rutile TiO$_2$(110) single crystals were used as the substrate for these studies. TiO$_2$(110) is a model system for transition metal oxide surfaces [12,13]. At room temperature, complex sputter defects will form, and the surface becomes disordered, the onset of which can be seen in Fig. 1. In addition, the lighter oxygen atoms are preferentially sputtered, resulting in a Ti-enriched surface. For rutile TiO$_2$, it is established that Ti-cations easily diffuse. Thus, at elevated temperatures, local sputter damage can heal, and excess Ti diffuses into the bulk. Studies on sputter reduced surfaces have shown that a temperature of 400–700 K is sufficient to reestablish a stoichiometric surface [14]. In addition, atom mobility at elevated temperatures allows forming low energy constellations at step edges. Consequently, the combination of preferential sputtering of steps exposed to the ion beam and formation of low energy step constellation results in a stepped surface with steps preferentially oriented along the ion beam azimuth as is shown in Figs. 1(c) and 1(d). While the formation of thermodynamically favored step edges, i.e., step-edge orientations that are part of a 2D Wulff construction of terraces [15], may be generally useful for nanostructuring of surfaces, the main goal is the fabrication of low index step edges that have a higher formation energy and thus are not present in a thermodynamic equilibrium terrace structure.

TiO$_2$(110) samples prepared by annealing in vacuum exhibit terraces that are bound by step edges along (001) and (111) directions [15,16]. Steps along the low index (110) direction are not observed. Figure 2(a) shows a STM image of this typical surface morphology. The prevalence of certain step orientations is a consequence of free energy minimization. Especially in ionic and covalent materials, the formation energy for step edges is strongly orientation dependent. An estimate of the relative formation energies for different low index step edges can be obtained from viewing step edges as microfacets of low index surfaces; i.e., low index step edges should correlate to the surface energy of the extended faces. Surface energies have been calculated for TiO$_2$, and therefore we can categorize the different step-edge orientations. The (001) step edge can be viewed as a [110], the (111) as a [101], and the (110) as a [001] microfacet [see Figs. 2(b)–2(e)]. The surface energies for TiO$_2$ increase in the order of [110] < [101] < [001] [17], and consequently this indicates that the (110) step edge has the highest step energy among the low index steps on TiO$_2$(110). This is in agreement with the absence of (110) steps on annealed TiO$_2$(110). Furthermore, the (001) facets of rutile TiO$_2$ are known to reconstruct in a 2 x 1 structure consisting of [101] facets [18]. This raises the question if the analogy between step edges and microfacets can be extended to reconstructed surfaces; i.e., does the (110) step have a
FIG. 2 (color online). Low energy step-edge structure on TiO$_2$(110). (a) STM image of a typical surface structure of clean TiO$_2$(110) surface, (b) orientations of the step edges on the surface (top view), and (c)-(e) illustrative structures of the different step edges (side views). In (c)-(e), the shaded area represents microfacets of an extended low index crystallographic plane corresponding to the step edge. Ti and O atoms are represented by small and big balls, respectively.

similar reconstruction as the extended [101] face? In order to prepare and characterize the atomic scale structure of this high energy step edge, the grazing incident ion beam method is used. Figures 3(a) and 3(b) show STM images after grazing incidence ion irradiation along the (110) azimuth. The majority of the step edges are now aligned with the direction of the ion beam. The thermal stability of this step orientation can be tested by annealing the sample for 5 min at ~900 K. After this heat treatment, the (110) step edges convert into zigzagging steps with (111) orientations, shown in Fig. 3(c). Although this increases the overall step-edge length, the small angle (24°) between the (111) and the (110) direction [see Fig. 2(b)] results in a length increase of only 10%. This increase in length has to be compensated for by an at least 10% lower formation energy for (111) steps.

The preparation of high energy step edges enables the analysis of their atomic scale structure. A step-edge model is constructed from the measured periodicity of the step edge [twice that of the surface unit cell, see Fig. 3(b)] and invoking of charge counting arguments [19], i.e., creating a step edge that does not change the ratio of Ti/O atoms and thus allowing the cations and anions to retain their preferred nominal charges of +4 and -2, respectively. Such a step-edge model is shown in Figs. 4(a) and 4(b). This model consists of step segments with both [110] and [111]/[111] orientations and the step-edge Ti atoms are fourfold and fivefold coordinated compared to the sixfold bulk coordination. All the step-edge O atoms are twofold coordinated. To confirm this model, we performed ab initio DFT calculations to assess stability and atom relaxations at the step edge. We also calculated the reconstructed (110) step edge [Fig. 2(c)] for comparison. By assuming that their step-step interaction energies per unit area are identical, the step-edge formation energy was estimated to be 0.09 eV/A lower for the reconstructed step shown in Fig. 4. Moreover, the Tersoff-Hamann [9] plot of this step-edge structure is in excellent agreement with the experimental STM images as can be judged from Figs. 4(c) and 4(d). Therefore, the computational analysis corroborates this step-edge structure. The simulated STM images also reproduce the known fact that on terraces, the fivefold coordinated Ti (Ti$_{5c}$) atoms are imaged bright [12]. At the step edges, however, the twofold coordinated bridging oxygen atoms (O$_{Br}$) appear brighter under empty-state imaging conditions, indicating a variation of the tunneling probability for O$_{Br}$ atoms on terraces compared to step edges. A similar effect has been observed for bridging twofold coordinated step-edge oxygen species on anatase TiO$_2$(101) surfaces [15]. In both cases, the step-edge O$_{Br}$ are coordinated to more under-coordinated Ti atoms. Apparently, this change in the local coordination environment of the O$_{Br}$ has a pronounced effect on the empty orbitals and thus the STM contrast.

FIG. 3 (color online). Step edges fabricated by directing an ion beam along the [110] azimuth. The sample was irradiated with 0.8 keV Ar$^+$ ions with a total ion flux of ~5.6 x 10$^{16}$ ions/cm$^2$. (a) Ridges formed on the surface along the ion beam azimuth, (b) atomic resolution of step edges along the [110] direction, and (c) the same sample as in (a) after annealing for 5 min at 900 K.
stronger adsorption sites. Finally, the success of directing surface features along an ion beam may point to a larger utility of grazing incidence low energy ion beams in surface preparation. For instance, symmetry breaking of multiple rotational domain structures (facets or reconstructions) by directing the beam along one domain symmetry direction seems possible.

The ECUST group acknowledges the financial support from National Natural Science Foundation of China (20703017) and the 111 project (B08021).

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Nanoripple formation on TiO$_2$(110) by low-energy grazing incidence ion sputtering

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(Received 22 April 2010; revised manuscript received 15 June 2010; published 8 July 2010)

The self-formation of metastable nanoripples by low-energy Ar$^+$ ions impacting at a grazing incidence angle on a TiO$_2$(110) surface has been investigated by scanning tunneling microscopy. Ripple formation is a consequence of preferential sputtering of monatomic step edges with a directional component perpendicular to the ion-beam azimuth. The combination of preferential erosion of step edges and ion-beam-induced surface roughening results in a surface morphology with nanoripples aligned parallel to the ion-beam azimuth. We investigate the surface-structure evolution as a function of ion fluence for two ion-beam azimuth directions. Analysis of the formation and evolution of sputter-induced vacancy islands shows that under the conditions employed here (0.8 keV Ar ions, 8° grazing incidence angle) the sputter probability at step edges is significantly enhanced compared to sputtering at flat terraces. Although the initial vacancy island morphology can be strongly influenced by the step-edge formation energies for different crystallographic orientations, both investigated azimuth directions form similar ripple structures at high ion fluences. This study demonstrates that grazing incidence ion beams can be employed to pattern oxide substrates with quasi-periodic nanoripples with ripple spacing of tens of nanometers.

DOI: 10.1103/PhysRevB.82.035408 PACS number(s): 79.20.Rt, 68.47.Gh, 68.37.Ef

1. INTRODUCTION

Patterned surfaces with nanostructures can modify their chemical and physical properties. Furthermore, nanostructuring of thin-film substrates will affect film growth and may enable relaxation of lattice misfits in heterostructures. In addition, by patterning the surface with lateral anisotropic features, such as ripples, films with artificial anisotropic properties can be grown. Large-scale patterning of surfaces with feature sizes in the ≤10 nm range requires self-formation mechanisms. Here we discuss the use of low-energy, grazing-incidence ion beams for patterning single-crystal surfaces with nanoripple structures. Sputtering by low-energy ions can be applied to a wide range of materials and thus the mechanisms discussed here may be applied to many single-crystal substrates. The material used in this study is a rutile TiO$_2$(110) wafer, as a model system for transition-metal oxides, an important class of materials for thin-film substrates.

Ion-sputtering-induced surface instabilities can result in nanostructure formation at surfaces. Two fundamentally different ion irradiation regimes can be distinguished: (i) ions impinging at the surface at incidence angles and ion energies large enough to penetrate the surface layer causing collision cascades in the subsurface region which subsequently result in ejection of surface atoms and (ii) grazing incidence ion irradiation, where the surface normal kinetic energy of the ions is too small to penetrate the surface layer and thus most ions are reflected from the surface, introducing only few defects at atomically flat terraces. The first regime has been studied extensively and it is understood that under these conditions the sputter yield becomes dependent on the surface curvature and this causes ripple formation or other nanostructures such as quantum dots. With increasing ion-incident angle (measured from the surface normal) the sputter yield initially increases because the ion energy is deposited closer to the surface and thus collision cascades cause the ejection of more surface atoms. As the ion incident angle approaches a grazing angle the sputter yield decreases sharply due to the fact that the incoming ions cannot penetrate the surface layer anymore and are reflected from the surface.

Furthermore, for low-energy ions the momentum transfer to the surface during the reflection is too small to induce lattice defects. This is the grazing incidence regime which is the focus of this paper. Compared to (close to) normal incidence ion bombardment, grazing incidence ion beams have been studied less by the scientific and engineering community. Recent studies, however, have demonstrated the utility of grazing incidence sputtering in surface “polishing” and aiding alignment of molecules. It has also been shown that irradiation of a single-crystal surface with grazing incidence ions results in the formation of nanoscale ripple structures parallel to the projection of the ion-beam direction on the surface. The formation mechanism of this ripple structure is fundamentally different from the ripple formation at nonglancing angles. At glancing angle the ripple formation is a consequence of higher sputter yields at monatomic step edges compared to atomically flat terraces. Consequently, it has been shown that step edges parallel to the ion beam are stabilized while step edges that have a directional component perpendicular to the ion-beam azimuth are preferentially eroded. This results in step arrays parallel to the beam and subsequent formation of ripples whose separation tends to increase with irradiation duration.

The studies reported here on TiO$_2$ are the first studies of this kind on a metal oxide. Previous studies of structure formation by grazing ion beams concentrated on metal surfaces and ionic crystals such as CsF(111) and KBr(001). While the studies on Pt(111) by the Michely group are comprehensive, the main question this present study addresses is if the same processes are applicable to more complex materials such as covalent/ionic bonded oxides, i.e., materials for which single-crystal wafers have potential applications, such as thin-film substrates.
Prior to the investigation of structure formation due to ion sputtering, ion-scattering experiments of grazing incident ions on metal single-crystal surfaces have shown that the (quasidiffusional) reflection of the ion beam depends on the surface crystallographic orientation, i.e., the azimuth incident angle of the ion beam relative to low-index crystallographic surface directions.

For low-index crystallographic directions a higher ion-beam reflection has been observed which was attributed to surface channeling. This demonstrates that grazing incident ions interact differently in surface-channeling and nonchanneling directions and consequently a difference in surface sputtering events may be expected in addition to sputtering at step edges and other surface defects. Furthermore, investigations of step-edge sputter yields on metal surfaces have indicated that subsurface ion channeling affects the sputter yield. More open step-edge structures exhibit a lower sputter yield and incident ions may channel between the surface and the second atomic layer for low-index azimuth directions.

Metal oxides are more complex in their surface structure than metals and therefore a more pronounced directional dependence may be expected. Also, preferential sputtering of oxygen can change the surface composition. In the particular case of TiO$_2$ a surface reduction is known to trigger a local surface reconstruction which may affect the ion-surface interaction. Therefore some TiO$_2$ specific properties need to be taken into account which is briefly discussed next.

II. STRUCTURAL CONSIDERATION OF THE TiO$_2$(110) SURFACE FOR GRAZING INCIDENCE ION SCATTERING

Rutile TiO$_2$(110) is the best studied transition-metal oxide surface and thus a wealth of details regarding its properties is known. In this section a brief summary of some surface phenomena of this system relevant for this study are given.

Figure 1 shows a model of the surface structure of TiO$_2$(110). The (110) surface exhibits twofold coordinated bridging oxygen atoms that protrude from the surface plane and are closely spaced (0.30 nm) along the (001) direction and are far apart (0.65 nm) along the (110) direction. This gives the surface a large corrugation and a strong structural anisotropy. This structural characteristic of the TiO$_2$(110) surface has implications for grazing incidence ion bombardment. Ions impinging at the surface are deflected through Coulomb interactions between the atom cores giving rise to a shadow cone behind the scatter atom in which no ions can penetrate. The size and shape of this shadow cone has been discussed extensively for applications in structural determination of surfaces by low-energy ion scattering spectroscopy. A shadow cone of 0.8 keV Ar$^+$ ions incident at 8° grazing angle and interacting with surface oxygen atoms extends ~2 nm behind the scatterer before the cone intersects the surface plane. It is apparent that under these conditions a bridging oxygen atom is lying within the shadow cone of its neighbor atom in the direction of the ion beam for both azimuths and therefore forming an envelope that prevents direct head-on ion impact on the surface atoms. This is the reason for the strongly reduced sputter yield at grazing incidence conditions. The shadow cone extends in three dimensions so that the in-plane shape of the shadow cone also needs to be considered. In the (001) direction, the rows of bridging oxygen atoms are further apart and the oxygen atoms are closer spaced. This provides a better ion channeling than along the (110) direction. From these arguments a smaller terrace sputter yield for the (001) azimuth compared to the (110) direction may be anticipated. However, a more detailed binary collision simulation would be needed for a thorough theoretical analysis.

At step edges, surface atoms are not “protected” by the shadow-cone envelope and therefore direct ion impact results in higher sputtering rates. In addition, ions reflected from the lower terrace onto the step-edge atoms may cause sputter events at steps. Therefore step-edge atoms are expected to experience a much higher sputter yield under grazing incidence conditions compared to terrace atoms. Comparing the crystal structure along (001) and (110) directions gives information about the atom densities for step edges along these directions, which is expected to correlate with the sputter yield. Both directions exhibit open structures with cations and anions aligning in columns perpendicular to the planes. The density of anion and cation columns gives a rough measure for the expected step-edge sputter yield differences for the two azimuth directions with denser packed step edges having a higher ion-impact probability compared to more open structures. For the (110) step orientation the column density is 28.4 atoms/nm$^2$ while for the (001) step orientation the column density is 41 atoms/nm$^2$. Thus this simple estimate suggests a 1.4 times higher step-edge sputter yield for grazing ions impinging on the (001)-oriented steps, i.e., for ions beams along the (110) azimuth, than for the (110)-oriented steps, i.e., for an ion-beam azimuth along the (001) crystallographic direction.

In addition to the bulk-truncated surface and step edges, the TiO$_2$(110) surface may also exhibit local 1×2 reconstructions. This surface reconstruction forms on TiO$_2$(110) if it is reduced. From STM simulations an about four times higher sputter yield for the lighter O atoms compared to Ti atoms is calculated. Therefore oxygen is preferentially sputtered and the sample is reduced during ion irradiation. Thus regions of high sputtering, e.g., along step edges the surface may be prone to form this 1×2 reconstruction. This structural change, in turn, will affect the ion-beam interaction at step edges. Although the exact structure of the 1×2 reconstruction is controversial, a recent high-resolution, cross-sectional transmission electron microscopy study has visu-
alized Ti-interstitial atoms in $\{11\}$ octahedral sites.\textsuperscript{32} This implies that the otherwise open channels along (001) and (110) directions are (partially) blocked by the Ti-interstitial atoms in the $1\times2$ reconstructed phase. This should result in an increased step-edge sputtering compared to the unreconstructed surface, but should affect both azimuths in a similar manner.

Here we report experimental studies that verify the increased step-edge sputtering on TiO$_2$(110) surfaces under grazing incidence ion bombardment and show that the higher sputter yield at step edges is responsible for nanoripple formation at the surface. We compare nanoripple formation with the ion-beam azimuth direction aligned along the (001) and the (110) azimuths.

III. EXPERIMENTAL METHODS

All the experiments were performed in an UHV chamber with a base pressure in the low $10^{-10}$ Torr range. The chamber was equipped with an Omicron variable temperature scanning tunnel microscope (STM), a commercial ion sputter gun (LK technologies), and a sample manipulator that allowed polar rotation relative to the ion gun. For change in the azimuthal orientation, the sample had to be removed from the vacuum chamber and remounted onto the sample plate. The azimuthal orientation of the sample relative to the ion beam was judged to be better than $\pm 3^\circ$. All the measurements shown here were taken at a polar incidence angle of $82^\circ$, i.e., $8^\circ$ glancing angle. In addition the sample temperature, ion energy, and ion flux was kept constant at 400 °C, 800 eV, $1.3\times10^{12}$ ions/(m$^2\times$s), respectively. The elevated sample temperature during irradiation is necessary to provide enough thermal energy to heal sputter defects and to reform a crystalline, stoichiometric surface.\textsuperscript{33} On the other hand the sample temperature was chosen low enough to avoid large-scale reorganization of the surface.

The rutile TiO$_2$(110) single crystal was obtained from MTI Corporation and was epipolished. The crystal was cleaned in situ by repeated Ar sputtering and annealing (700 °C) cycles.

IV. RESULTS

STM images of the surface evolution for short sputter times (low ion fluence) with irradiation along the (001) and the (110) azimuths are shown in Fig. 2. Sputter-induced vacancies agglomerate and excess Ti dissolves into the bulk forming vacancy islands at the surface. Initially at low fluences the density of these vacancy islands increases until they coalesce to form larger islands. Comparing the two azimuths shows that surfaces irradiated along the (110) direction exhibits a higher density of vacancy islands at low fluences compared to the (001) azimuth direction. This behavior can be more clearly seen in Fig. 3(a) which shows a plot of the island density versus sputter time. For both ion-beam directions the vacancy-island density increases at first and then drops off at longer sputter times as the individual islands merge. Also the shape of the islands is distinctively different for the two irradiation directions. It is obvious from visual inspection of the Fig. 2 that for the ion beam directed along the (001) azimuth the vacancy islands are elongated in the (001) direction, while for irradiation along the (110) direction there is no obvious anisotropy of the vacancy island shape for low ion fluences. The differences in the aspect ratios of the vacancy islands can be obtained by plotting the total width of all islands, i.e., the sum of the width of all the vacancy islands in a $200\times200$ nm$^2$ STM image, against the summed lengths of all islands. This is shown in Fig. 3(b). In this plot the length and width are measured parallel and perpendicular to the ion-beam direction, respectively. The different data points in Fig. 3(b) are obtained for different sputter times. From a linear regression through these data points it can be seen that for the (110) azimuth the islands grow almost uniformly in width and length while for the (001) azimuth the length of the islands are on average more than twice their width.
FIG. 3. (Color online) STM image analyses for surface properties as a function of sputtering time for ion beams directed along the (001) direction and the (110) azimuth. (a) Shows the evolution of the vacancy island density with sputtering time. (b) Shows the total island lengths versus widths. Each data point corresponds to a different sputtering time. The total number of sputtered atoms derived from the total vacancy island area as a function of sputtering time is shown in (c). The solid lines in (c) are the best quadratic fit to the data points while the dashed lines are fits restricting the linear term by predefined terrace sputter yields (see text).

To evaluate the sputter yield, the number of sputtered surface atoms per unit area, measured from the size of the vacancy islands, is plotted versus the sputtering time (ion fluence). This is shown in Fig. 3(c) for the two azimuth directions. This plot shows a decrease in the rate of sputtered atoms, i.e., the sputter yield is increasing with sputter time. Such a behavior is expected if the sputtering yield is larger at step edges than on terraces. In this case, the total sputter yield from the surface is increasing as the step-edge density increases, i.e., as the surface becomes rougher. Therefore the increase in sputter yield with increased step-edge density, or vacancy-island density, is a direct validation for the higher sputter yield at step edges. Furthermore, Fig. 3(d) shows a larger sputter yield for the (110) azimuth compared to the (001) azimuth direction. This directional dependence in the sputter yield was expected from the strongly anisotropic surface structure of the TiO2(110) surface and may be attributed to variations in the terrace sputter yield for the two azimuth directions.

The higher sputter yield at step edges exposed to the ion beam compared to the sputter yield at terraces or steps oriented parallel to the beam can also be clearly appreciated from the structure of pre-existing step edges after ion irradiation. Figure 4(a) shows an STM image after 80 min irradiation. Step edges exposed to the ion beam (ascending steps) are much more "rugged" than steps parallel to the ion beam or descending steps. Although we cannot measure how much of the step edge was eroded by the ion beam the roughening of the step is a clear indication of stochastic removal of atoms by sputtering of the exposed step edge. In addition, the formation of 1 × 2 reconstruction islands is observed along these exposed step edges and within newly formed vacancy islands. This is evidence for the preferential O sputtering at step edges, which causes a local enrichment with Ti interstitials and consequently the formation of the reconstruction. This can be seen in Fig. 4(b). The localization of 1 × 2 reconstruction islands close to step edges indicates the reduction in titania by preferential O sputtering from step edges and thus is an additional confirmation of the higher sputter yield at step edges compared to terraces.

Anisotropic structure formation as observed for grazing incidence ion irradiation along the (001) azimuth could also be partially influenced by a strong anisotropic diffusion of ion-beam-induced vacancies. To exclude this possibility we examine the vacancy island formation at normal incidence sputtering. If anisotropic diffusion was to contribute to the elongated vacancy island shape then some elongation of vacancy islands should be observable independent of the ion-beam direction. Figure 4(c) shows a surface bombarded with normal incidence ions but otherwise identical conditions as for the grazing incidence experiments. The vacancy islands that formed do not exhibit any preferential orientation and therefore anisotropic defect diffusion can be excluded as a major formation mechanism for elongated vacancy islands. Furthermore, the normal-incidence-sputtered surface exhibits subatomic height protrusions of nanometer dimension. These protrusions may be associated with formation of subsurface Ar bubbles due to Ar implantation. This effect also suggests that grazing ion-beam irradiation is much more surface sensitive and avoids subsurface damage and Ar accumulation and therefore is better suited for surface modifications.

With increasing ion fluences the differences in the surface morphologies for the two ion-beam azimuths become less pronounced. Figure 5 shows the evolution of the surface morphologies for "intermediate" ion fluences. Along the (110) azimuth direction a transition of vacancy island shapes from "compact" to elongated islands with the long axis along the ion-beam direction is observed [Figs. 5(e) and 5(f)]. For both azimuthal directions the surface becomes rougher as vacancy islands are nucleated and grow at the bottom of previously formed vacancy islands. Importantly, however, the surface does not evolve into a randomly rough surface.
NANORIPPLE FORMATION ON TiO$_2$(110) BY LOW-... PHYSICAL REVIEW B 82, 035408 (2010)

FIG. 4. (Color online) STM images of TiO$_2$(110) surface after various ion irradiation procedures (a) 200×200 nm$^2$ image after grazing ion irradiation along the (001) azimuth. In this image increased sputter damage on “step-up” edges is observed while steps parallel to the ion beam and “step-down” edges are not altered by the ion beam. (b) 10×10 nm$^2$ showing the formation of 2×1 reconstruction within the vacancy island. (c) 400×400 nm$^2$ image after ion irradiation at normal incidence. The formed vacancy islands do not exhibit any preferential orientation, thus excluding anisotropic vacancy island shape due to anisotropic diffusion. Also several nanometer wide subatomic height protrusions are visible which are attributed to subsurface Ar bubbles.

Instead, nanoripples with the ridges and troughs aligned in the direction of the ion beam and with a ripple separation exhibiting a characteristic separation of ~10 nm perpendicular to the ion-beam azimuth direction are formed. The ripple structures become clearly visible in Figs. 5(c) and 5(d) for the (001) azimuth and Figs. 5(g) and 5(h) for the (110) azimuth. At lower fluences there exists no clear preferential separation between elongated vacancy islands. However, the widths of adisland and vacancy island that evolve into ridges and troughs at higher fluences have a fairly uniform characteristic width. The island widths do not change significantly throughout the surface evolution. As the surface is covered with more and more islands, the preferred width of the islands causes a close-to-uniform separation and nanoripple formation.

At the highest ion fluences used in this study, the surfaces consist of ripples with similar spacing and corrugation for the two azimuths. Representative STM images of such surfaces are shown in Fig. 6. The (001) azimuth appears somewhat more regular which may have its origin from the elongation of the vacancy islands from the outset of the sputtering.

V. DISCUSSION

The higher initial density of vacancy islands for ion beams impinging at the surface along the (110) azimuth compared to the (001) azimuth suggests that the sputter yield at terraces is higher for the former. Also the strong elongation of the vacancy islands in the ion-beam direction for the (001) azimuth suggests that step-edge sputtering is the favored sputter mechanism.

In order to be more quantitative about the sputter yield differences for the two ion-beam orientations we estimate the number of sputtered atoms from the total vacancy island size as a function of sputter time shown in Fig. 3(c). If we differentiate between atoms sputtered from step edges and atoms sputtered from terraces the total number of sputtered atoms is given by

$$N_{\text{tot}} = N_{\text{tep}} + N_{\text{terrace}}. \quad (1)$$

The step-edge sputtering per unit area, $N_{\text{tep}}$, is a function of the step length per unit area, which is sputter time dependent, and therefore the sputter rate (sputter yield) of the surface becomes time dependent. Figure 7(a) shows the increase in steps perpendicular to the ion beam, i.e., steps that are “exposed” to the ion beam with sputter time for the two azimuths. In this plot we only counted the step edges of vacancy islands and not the pre-existing steps at the surface. This has been done because the erosion of the pre-existing steps is difficult to evaluate from the STM images and the sputter yield is only measured from the size and density of the vacancy islands. Thus, by not measuring sputtering from pre-existing steps we also must not take the length of these steps into account for evaluating the step-edge sputter yield. The estimates we obtain here are therefore consistent with hypothetical perfectly flat surfaces without any initial step edges. The increase in step-edge density for low ion fluence can be approximated with a linear increase. As the vacancy islands merge, step edges are being annihilated and the step-edge density decreases again. Therefore this analysis is only valid for short sputter times.
The number of sputtered atoms due to step-edge sputter events, \( N_{\text{step}} \), is given by the step-edge sputter yield, \( Y_{\text{step}} \), times the number of ions impinging in an area close to the step edge where they can induce step-edge sputtering. Thus the number of atoms sputtered from step edges per unit area can be expressed as

\[
N_{\text{step}} = Y_{\text{step}}S_L(t)dFt,
\]

where \( S_L(t) \) is the step length per unit area [determined from Fig. 7(a)], which is a function of sputter time, \( d \) is an effective distance away from the step edge at which the impinging ions are inflicting damage at the step edge, \( F \) is the ion fluence at the surface, and \( t \) the sputter time. The effective distance, \( d \), away from step edges is estimated from geometrical considerations.

**FIG. 5.** (Color online) STM images of TiO\(_2\) (110) (200×200 nm\(^2\)) after irradiation times of (a) 320 minutes, (b) 640 minutes, (c) 1600 minutes, and (d) 3250 minutes along the (001) azimuth, and of (e) 320 minutes, (f) 640 minutes, (g) 1600 minutes, and (h) 3250 minutes along the (110) azimuth.

**FIG. 6.** (Color online) STM images (400×400 nm\(^2\)) of the surface morphology after extended periods of grazing incidence irradiation in (a) (110) azimuth and (b) (001) azimuth directions. Nanoripples are formed that are aligned parallel to the ion-beam directions. The corrugation of these ripples is ~4 nm as can be judged from the shown cross-sections.

**FIG. 7.** (Color online) The step-edge length perpendicular to the ion beam is plotted as a function of sputter time for the (001) and the (110) azimuths in (a). The lines indicate a linear fit for these data points. (b) shows the geometric argument for estimating the “effective step width,” \( d \).
terrace sputtering events and thus a higher vacancy island density suggests a higher terrace sputtering. Assuming a critical vacancy island size for which vacancy islands are stable of three atoms, which is the smallest vacancy island observed, allows estimating the terrace sputter yield for the two azimuths directions by the following expression:

\[
Y_{\text{terrace}} = \frac{\text{(density critical island size)/ion fluence \times sputter time)}}{N_{\text{tot}}}.
\]  

(5)

With this method the terrace sputter yield is estimated to be 0.03 and 0.008 for the (1\(\bar{1}\)0) and the (001) azimuths, respectively. These numbers indicate a significant larger terrace sputter yield for the (1\(\bar{1}\)0) azimuth than the number derived from the quadratic fit and reconciles the surface structural argument that the terrace sputter yield should be higher with ion beam directed perpendicular to the bridging oxygen rows. Using these new values for the terrace sputter yield for restricting the linear term in the quadratic regression in Fig. 3(c) new values for the step-edge sputter yield of 0.09 and 0.14 are obtained for the (1\(\bar{1}\)0) and the (001) azimuths, respectively. This new fit to the experimental values is shown in Fig. 3(c) as dashed lines. Although the yields are quite different from those of the direct quadratic regression to the data points (Table I) the new quadratic fits are still close enough to the data points to be within the margin of error of the experimental data. Therefore we conclude that within the accuracy of this analysis the step-edge sputter yield is about the same for both azimuths but the terrace sputter yield varies, with approximately two to three times higher terrace sputter yield for the (1\(\bar{1}\)0) azimuth. The higher terrace sputtering along the (1\(\bar{1}\)0) direction is therefore primarily responsible for the higher total sputter yield for this azimuth direction, which causes the nucleation of more vacancy islands on terraces and thus an accelerated step-edge sputtering per unit area. This leads to the significantly larger total sputtering with the ion beam directed along the (1\(\bar{1}\)0) direction compared to the (001) direction as is evident from Fig. 3(c).

These variations in the terrace and step sputter yield are not sufficient to explain the strongly different vacancy island shapes for the two azimuth directions. Instead we propose that thermodynamic stability of vacancy islands play an important role in the initial shape. All the sputtering experiments have been conducted at 400 °C as a necessity to maintain crystallographic order in the surface during the experiment. In addition to short-range rearrangement of atoms, the elevated temperature also activates surface diffusion and thus the rearrangement of surface features into thermodynamically more stable configurations. In particular, undercoordinated step-edge atoms are easier rearranged than terrace or bulk atoms. This means that vacancy islands will form shapes that minimize the step-edge energies of the island. The equilibrium island shape is determined by the step-edge energies and step directions in a 2D equivalent of the Wulff construction.\(^\text{34}\) The exact values for the step-edge energies of the TiO\(_2\)(1\(\bar{1}\)0) surface are not known, but experimental investigations of the surface structure show that only (001) and (1\(\bar{1}\)1) step edges are present at the surface but no step edges
have been observed along the (110) direction, see Fig. 8. This implies that the (110) step direction is unstable and terraces cut along this direction will rearrange to form steps with the {111} directions. In previous studies we showed that this is indeed the case, i.e., the directed ion beam can be used to stabilize steps along the (110) direction but these steps are unstable and restructure upon heat treatment into the energetically favored {111} steps. This observation has implications for describing the vacancy island morphologies. For sputtering with the ion-beam azimuth along the (001) direction, step edges parallel to the ion beam are formed by an anisotropic erosion of the surface. These (001) step edges have a low formation energy as is evident from their presence in equilibrium island shapes. Therefore, although strongly elongated islands are not equilibrium shapes, the step edges are stable in the temperature range of the experiment. For the ion-beam direction along the (110) azimuth, on the other hand, the step edges parallel to the ion beam direction are unstable and can easily transform into {111} steps. This transformation is further aided by the small angle (24.5°) that is included between (111) and (110) crystallographic directions. Consequently, even for the grazing ion beam directed along the (110) direction small vacancy islands do not initially exhibit steps parallel to the ion beam but reorganize into vacancy islands with a more stable step-edge structure which necessarily involves formation of compact island shapes. As the vacancy islands grow in size, the (110) step edges become more frequent because it would require a larger mass transport to reshape the larger islands into equilibrium shapes. It appears that in the temperature regime and on the time scale of the experiment, there is not enough atom mobility to allow for such a significant material transport.

The ripple formation by grazing incidence ion sputtering is due to local variations in the sputter yield. Atomically flat surfaces exhibit a smaller sputter yield compared to defects, in particular, step edges under grazing incidence irradiation. This gives rise to preferential erosion of step edges that are exposed to the ion beam. As a consequence of structure-dependent sputter yield, surface features with high sputter yield are eroded faster causing self-organization of the surface into a morphology that reduces the overall sputtering.

Step edges "facing" the ion beam are preferentially sputtered at the surface while step edges parallel to the ion-beam azimuth do not experience a higher erosion rate. Because sputtering at terraces is not entirely suppressed, new vacancy islands are constantly nucleated and thus a roughening of the surface is observed. As a consequence of the lower sputter yield of steps aligned parallel to the ion-beam azimuth and the tendency of surface roughening, ridges are formed that are aligned with the ion-beam azimuth. While the ion sputtering plays the central role in the alignment of the step edges parallel to the ion beam and causes surface roughening, the ion-beam effects by themselves cannot explain the formation of ripples with a characteristic separation. For this to occur, a self-regulating mechanism must be present that causes troughs to maintain a preferred separation. For nanoripple formation on metal surfaces, it has been shown that the diffusion of adatoms generated by the ion impacts plays a crucial role in regulating the ripple separation.\(^1\)\(^3\) The presence of adatoms on the TiO2 surface is not obvious, however, since excess O atoms will desorb from the surface at the temperature of the experiment and Ti adatoms are diffusing into the bulk. On the other hand, the mobility and diffusion of vacancies generated by sputtering is clearly present at the surface as is evident from the clustering of vacancies and formation of vacancy islands. Also the arrangement of vacancy islands with low-energy steps indicates step-edge diffusion. Therefore, under the experimental conditions, significant atom mobility exists at the surface. In covalent materials, step-step interactions can be strong and it has been shown, for example, for anatase TiO2 that step separation on the order of nanometers can significantly lower the energy of stepped surfaces.\(^34\) Repulsive step interactions would explain that vacancy and adislands always exhibit a minimum width in the STM measurements. Surfaces with enough atom mobility will arrange to lower their free energy. On a rough surface, the step-step interaction energy will contribute to the surface energy and therefore this energy contribution will regulate the average step-step separation leading to fairly uniform distribution of ripples as observed in the experiments.

Nanoripple formation by grazing incidence ion sputtering has been observed on very different materials systems, ranging from metals, to purely ionic, and now metal oxides. This indicates that the formation mechanism for ripple formation is robust. Preferential step-edge sputtering has been shown as the main mechanism responsible for directing the nanoripples in the direction of the ion-beam azimuth for all these systems. The mechanism, by which a regular pattern is formed, on the other hand, may have different origins for different systems or several mechanisms are acting together. One may differentiate self-regulating mechanisms driven by kinetics such as barriers for diffusion at step edges and other diffusion-driven mechanisms that would allow an equilibration of ripple widths, and energetic arguments that would lower the energy of the system by formation of roughly equally spaced step separation and thus cause a uniform ripple structure. In both cases, diffusion of vacancies or adatoms is crucial for establishing the ripple structure and thus the temperature can affect the ripple structures.

The fact that similar ripple structures can be formed on metals as well as on TiO2(110) indicates that special proper-
ties of TiO$_2$ such as strongly anisotropic step-edge energies, easy bulk diffusion of Ti, preferential erosion of oxygen, and the directional formation of 2 × 1 reconstruction strands on reduced TiO$_2$ does not fundamentally affect the ripple-formation mechanism. Therefore, the process of grazing incidence sputtering appears to be a widely applicable method for nanopatterning of single-crystal substrate materials.

VI. CONCLUSION

Grazing incidence ion beams have been used to pattern a transition-metal oxide surface with nanoscale ripple structures by directing the ion beam along the (110) or the (001) crystallographic directions. Ripple formation is induced by preferential step-edge sputtering by grazing incident ion beams along the low-index azimuth directions. The sputter yield was deduced from sputter-induced vacancy island sizes measured with STM as a function of ion fluence. This indicated a dependence of the sputter yield on the surface morphology under grazing incidence conditions. The dependence of the sputter yield on the step-edge density enabled a detection of sputter yields for step edges and flat terraces. Under the ion-beam conditions used in this experiment a higher step-edge sputter yield compared to terrace sputtering has been observed for both the (110) and the (001) azimuth directions. The terrace sputter yield appeared, however, to show a strongly azimuthal dependence which can be understood on the basis of the strongly corrugated surface structure of TiO$_2$(110). The directionality of the ion-beam and the higher sputter yields at step edges exposed to the ion beam causes a preferential removal of those step edges. In addition stochastic ion sputtering from terraces causes a surface roughening. These two effects combine to cause nanripples aligned with the ion-beam azimuth. A self-regulating mechanism, such as energy minimization of step-step interaction energies, is responsible for the formation of a narrow distribution of ripple separations.

The ion-beam interaction with the surface is dominated by binary collision effects that are largely independent for the sputtered elements. Therefore this method of patterning large scale areas with nanripples is expected to be of universal applicability if ion-beam-induced structural and compositional changes can be avoided.

ACKNOWLEDGMENT

This material is based upon work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Grant No. DE-SC0001508.

30. srim simulation package is available at: http://www.srim.org
Appendix 5: Published results for photocatalysis of thin films of anatase and rutile TiO$_2$

First-author peer-reviewed journal article citations are listed below followed by the corresponding reprinted publications related to the third chapter of this dissertation, Photocatalysis of Thin Films of Anatase and Rutile TiO$_2$.


Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO$_2$ films

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The prototypical photocatalyst TiO$_2$ exists in different polymorphs, the most common forms are the anatase- and rutile-crystal structures. Generally, anatase is more active than rutile, but no consensus exists to explain this difference. Here we demonstrate that it is the bulk transport of excitons to the surface that contributes to the difference. Utilizing high-quality epitaxial TiO$_2$ films of the two polymorphs we evaluate the photocatalytic activity as a function of TiO$_2$-film thickness. For anatase the activity increases for films up to $\sim 5$ nm thick, while rutile films reach their maximum activity for $\sim 25$ nm films already. This shows that charge carriers excited deeper in the bulk contribute to surface reactions in anatase than in rutile. Furthermore, we measure surface orientation dependent activity on rutile single crystals. The pronounced orientation-dependent activity can also be correlated to anisotropic bulk charge carrier mobility, suggesting general importance of bulk charge diffusion for explaining photocatalytic anisotropies.

Tetania (TiO$_2$) is the most widely used photocatalyst$^{1-5}$ for decomposition of organic pollutants because it is chemically stable and biologically benign. The band gap of TiO$_2$ is larger than 3 eV (3.0 for rutile and 3.2 for anatase), thus making pure TiO$_2$ primarily active for UV light. The most common commercial photocatalyst is the Degussa P-25, a powder consisting of both rutile and anatase crystallites$^1$. The phase mixture of different polymorphs is known to have synergistic effects and an increased photocatalytic activity is observed compared to pure phases$^1$. However, for pure phases it is generally accepted that anatase exhibits a higher photocatalytic activity compared to rutile TiO$_2$. Furthermore, not only do the two polymorphs show varying photocatalytic activity, but the different crystallographic orientations of the same material may exhibit different activities$^{5,6}$. Despite the intensive study of TiO$_2$, there is no generally accepted explanation for the differences of photocatalytic activity of different polymorphs or surface orientations. Possible explanations may be categorized as follows:

- Anatase has a larger band gap than rutile TiO$_2$. While this reduces the light that can be absorbed, it may raise the valence band maximum to higher energy levels relative to redox potentials of adsorbed molecules. This increases the oxidation ‘power’ of electrons and facilitates electron transfer from the TiO$_2$ to adsorbed molecules$^{7}$. This explanation has also been expanded to explain surface orientation dependent activities by suggesting that different surfaces exhibit different band gaps$^{7}$.
- Surface properties may play a role in the adsorption of molecules and subsequent charge transfer to the molecule. The surface properties may not just be polymorph dependent but may differ largely for the same material for different surface orientations or reconstructions$^{8,9}$ and consequently may contribute to the observation of pronounced surface effects in photocatalytic activities. Surface properties may again be subdivided into (i) chemical effects, e.g. coordination structure of surfaces that controls adsorption of molecules$^{3}$; (ii) electronic structure of the clean surface$^{9}$ or defects and adsorbate (e.g. hydroxyl)-induced states that may be crucial for charge trapping and separation at the surface$^{10}$, (iii) interaction of molecules with surface defects$^{8,9}$, and (iv) surface potential differences (such as work function differences measured in vacuum or flat band potentials in aqueous solution)$^{11,12}$ may affect charge transfer from the photocatalyst to molecules. It should be mentioned that the relative position of the conduction band minimum (CBM) in rutile and anatase is still controversial, while the large band gap of anatase might suggest the CBM in anatase to be higher than for rutile, and this has been so far the general perception$^{13}$, recent results are suggesting that conduction band of anatase is actually lower than that of rutile$^7$. 

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Received 23 August 2013
Accepted 24 January 2014
Published 10 February 2014

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Anatase exhibits an indirect band gap that is smaller than its direct band gap. For rutile, on the other hand, its fundamental band gap is either direct or its indirect band gap is very similar to its direct band gap. Semiconductor with indirect band gap generally exhibit longer charge carrier life times compared to direct band gap materials. A longer electron-hole pair life in anatase than in rutile would make it more likely for charge carriers to participate in surface reactions. One evidence for longer charge carrier lifetime in anatase than in rutile comes from transient photocurrent measurements on single crystal samples.  

Charge transport may differ for different polymorphs. In addition to the exciton lifetime the exciton mobility needs to be taken into account. Only excitons that efficiently diffuse can reach the surface within their lifetime. Preferential diffusion of excitons along certain crystallographic directions has been proposed for other photocatalysts to be important to explain surface orientation dependencies in their oxidation/reduction behavior. One measure for exciton mobility is the polaron effective mass. Although contradicting values for effective masses are reported, a generally higher effective mass is reported for rutile than for anatase. The polaron effective mass for rutile is ~7-8 m0 (where m0 is the electron mass) while anatase exhibits a polaron effective mass of ~3-5m0. In addition, in rutile a strong anisotropy for the effective electron masses exists and consequently, its charge mobility is reported, with values ~2-4 m0 along the [001] direction and ~1-15 m0 along the [100] direction. No values are reported for other crystallographic directions. Here we demonstrate that bulk charge carrier transport indeed explains the difference between rutile and anatase and furthermore is consistent with orientation dependent activity variations in rutile.

One main obstacle that has prevented a better fundamental description of titania photocatalysis is the masking of bulk properties by complex surface effects. Here we describe a new approach that enables separating surface effects from bulk effects in describing the photocatalytic activity and to compare photocatalytic on rutile and anatase TiO2. Utilizing thin epitaxial films of anatase and rutile we evaluate the photocatalytic activity as a function of film thickness. Since the surface properties are the same for any film thickness of the same material any change in the photocatalytic activity can be solely ascribed to the increased bulk volume. The increase in the photocatalytic activity with film thickness is thus a consequence of more excitons, generated by photo-absorption in the bulk, reaching the surface. In this case the photocatalytic activity increases for TiO2 films that are thicker than the layer that contributes charges for surface reactions, i.e. when the film becomes thicker than the maximum exciton diffusion length. Consequently, this approach enables us to measure for the first time quantitatively the surface region that contributes to photocatalytic reactions. We demonstrate that this surface region is larger for rutile than for anatase and this difference contributes to the different photocatalytic performances of these two TiO2 polymorphs. Furthermore, we investigate different crystallographic orientations for rutile and find that the orientation dependency may also be correlated to bulk anisotropies in exciton diffusion.

Results

We first describe the structure and morphology of the thin rutile and anatase TiO2 films. This is followed by measurements of the thin film photocatalytic activity and the dependence of it on the film thickness. The relationship between photocatalytic activity and film thickness contains information on the bulk exciton diffusion length in the two different TiO2 polymorphs. In order to connect the findings on the morph dependence of photocatalytic activity of TiO2 with crystallographic anisotropies we subsequently performed measurements on rutile single crystal samples with different crystallographic orientations. Structure and properties of TiO2 films. Epitaxial rutile and anatase TiO2 films have been grown by a variety of physical vapor deposition methods including (oxygen plasma assisted molecular beam epitaxy (OPA-MBE)) and sputter deposition. Rutile TiO2(101) has been grown on r-cut sapphire (r-A12O3 (1-102)) while anatase TiO2(001) has been previously synthesized on SrTiO3 or LaAlO3 (100) substrates. For anatase TiO2 on LaAlO3 the crystallographic relationship is [001] || [1-10] and for rutile TiO2 on sapphire the crystallographic relationship is [1-11] || [1-11]. For rutile TiO2(101) grown on r-cut sapphire it is known that it forms twin domain structures with coherent boundaries in [101] planes. In the studies reported here mainly LaAlO3 and A12O3 are used, because these substrates (contrary to SrTiO3) are wide band gap materials and do not exhibit any photocatalytic properties by themselves. Furthermore, the large band-gap of the substrate prevents charges to be transferred to the substrate.

Central to the success of measuring photocatalytic activity as a function of film thickness is the growth of well-defined TiO2 films and thus we briefly present key characterizations of the prepared films. Fig. 1 shows characterization of anatase films and Fig. 2 for rutile films. Reflection high energy electron diffraction (RHEED) patterns of the as prepared films are shown in Fig. 1 (a) and (2a) for the anatase (001) and rutile (101) samples, respectively. For the anatase sample a 4 X 1 superstructure is observed in the RHEED pattern. This is the typical surface reconstruction for the anatase (001) surface in vacuum35,36 and the fairly sharp diffraction pattern confirms a good surface quality of the film. For the rutile (101) surface no superstructure spots are observed despite the fact that the rutile (101) surface is known to reconstruct into a 2 X 1 superstructure37,38. Absence of surface superstructure spots is consistent with the diffraction pattern exhibiting bulk-like diffraction and thus may indicate a somewhat larger surface roughness.

The surface roughness has been characterized by atomic force microscopy (AFM) for every sample. Fig. 1(b) and 2(b) show typical images for anatase and rutile films, respectively. On the anatase films, flat terraces with mono-atomic steps are observed indicating a well-defined crystalline surface quality in agreement with the RHEED pattern. The rutile samples exhibits slightly higher surface roughness, with some ~40 nm wide ‘grains’ with roughness ~2 nm for a 12 nm thick film. The ‘grains’ have a slightly rectangular shape and two kinds of rectangular grains oriented 90° to each other are observed. These are due to the before mentioned twinning of the film39. As the zoomed-in image in Fig. 2(b) shows the individual ‘grains’ are flat and atomic-height step edges can be imaged. 

Transmission electron microscopy (TEM) imaging and selected area electron diffraction (SAED) of 25 nm thick films further corroborate the high crystalline order and epitaxial relationship between substrate and film. Fig. 1(e), (f) and 2(e), (f) show TEM images and corresponding diffraction patterns (DPs) for electron beam along the <0-10>SAED || <100>SS and <110>SAED || <110>SS for anatase and rutile films, respectively. The SAED were taken with a ~500 nm aperture at several points along the film. In addition a 20 nm diameter electron beam was scanned along the film and the diffraction pattern monitored. No other phases were detected in the diffraction patterns, in particular the anatase films were phase-pure and formation of any rutile inclusions can be excluded. X-ray photoemission spectra (XPS) of the films are compared to those of rutile single crystal samples and no discernible difference is observed indicating the formation of stoichiometric TiO2 within the sensitivity of XPS.

Photocatalytic activity of rutile(101) and anatase(001) films. The photocatalytic activity of the films is measured by photocatalytic decomposition of an organic dye (methyl orange). Fig. 3 (a) and (b) illustrate a typical measurement of the methyl orange...
Figure 1 | Characterization of anatase (001) films. (a) and (b) RHEED pattern along the <101> and <110> azimuths, respectively. Note the superstructure streaks in (a) indicating the 4 x 1 surface reconstruction. (c) and (d) show areal AFM images, indicating atomically flat terraces. (e) cross-sectional TEM of the LAO/anatase interface, with (f) showing the diffraction pattern of the interface indicating the epitaxial alignment of the anatase film.

Concentration versus reaction time for a TiO₂ film. From the rate of Methyl orange decomposition the photocatalytic activity for different TiO₂ films is determined and this information is plotted in Fig. 3(c) as a function of the film thickness. For thick films, it is apparent that the photocatalytic activity for the anatase films is about twice the activity of rutile in agreement with the general notion that anatase is the photocatalytically more active material. Important for this study is, however, the dependence of the photocatalytic activity with film thickness. For the rutile films, the photocatalytic activity does not change significantly for films thicker than ~2.5 nm. Only for the very thinnest films the activity drops. This suggests that for thick films excitons generated deeper than ~2.5 nm from the surface do not reach the surface, i.e. they recombine before reaching the surface, and thus do not contribute to photocurrents. For anatase films, on the other hand, the photocatalytic activity increases to film thickness larger than 5 nm. This indicates that in anatase charge carriers from deeper in the bulk reach the surface compared to rutile.

Dependence of photocatalytic activity on surface orientation and sample preparation conditions of rutile single crystals. High quality epitaxial thin films may only be grown with a few surface orientations. Thus, in order to investigate the variation of the photocatalytic activity as a function of surface orientation, we resort to studies of single crystal rutile TiO₂. No anatase single crystals of large-enough size are available to investigate surface dependence of the photocatalytic activity on anatase with our approach. However, it should be mentioned that there does exist some interesting investigations on surface engineered powder samples that exhibit preferential surface orientations.

Figure 2 | Characterization of rutile (101) films. (a) and (b) RHEED pattern along the <010> and <−101> azimuths, respectively. (b) and (c) show areal AFM images, indicating two crystal orientations due to twinning in the film. (d) cross-sectional TEM of the Al₂O₃/rutile interface, with (f) showing the diffraction pattern of the interface indicating the epitaxial alignment of the rutile film.

Figure 4(a), shows the measured photocatalytic activity for rutile samples with different surface orientations for different surface preparation methods. For all sample preparation procedures, with exception of HF-etched and tube furnace annealed samples, the activity follows the order (101) > (110) > (001) > (100) for photocatalytic degradation of organics. For HF-etched and tube furnace annealed samples the (001) orientation exhibited a slightly higher activity than the (110) sample. Remarkably, the photocatalytic activity of the ‘as-received’ samples are as much as 30% higher than the samples after HF-etching and tube furnace annealing, which results in a much better defined surface as indicated in the AFM images shown in Fig. 4(b) and (c). Formation of surface defects has been discussed in several publications to affect surface charge trapping and charge transfer to adsorbates and/or water. Our observation of a variation of the overall activity of the single crystals on the surface preparation is in agreement with such an influence of the surface morphology. This further underlines the challenge in separating bulk from surface effects for photocatalytic measurements and illustrates the need of identical sample preparation to enable quantitative comparisons.

Importantly, the single crystal studies on rutile (101) show very similar photocatalytic activity as those of the rutile (101) films. The same photocatalytic activity of the films and the single crystal demonstrates that the films are of single-crystal quality in terms of photocatalytic activity. In particular, this implies that the twin-boundary structure and the slightly increased surface roughness of the rutile films compared to the single crystal surfaces does not adversely affect the photocatalytic activity of the films. We also point out that the (101) surface is the most photocatalytically active surface.
of all the rutile surface orientations studied, in agreement with previous reports. This is important for comparing the overall photocatalytic activity of the rutile and anatase films. The fact that the most active rutile surface is significantly less active than the anatase (001) surface (which according to some reports is only the second most active anatase surface) further validates the fact that anatase is photocatalytically more active than rutile.

**Discussion**

The general perception that anatase has a higher photocatalytic activity compared to rutile TiO$_2$ is confirmed by our measurements on extended planar epitaxial thin films. The anatase (001) films (in the thick-limit: $\sim$20 nm) exhibit around twice the activity for photocatalytic decomposition of organic molecules than the rutile (101) films grown under identical conditions. Importantly, the film thickness-dependence of the photocatalytic activity demonstrates that this difference in the photocatalytic activity is at least partially a bulk property of the two forms of TiO$_2$. In particular, the measurements show similar activity (or slightly higher activity for rutile) for very thin films (less than 2 nm) but while the activity for rutile films remains almost unchanged for films thicker than 2 nm the activity for anatase films keeps increasing and only saturates for films thicker than $\sim$5 nm. This behavior indicates that charge carriers for photocatalytic reactions can originate from much deeper in the bulk for
anatase than for rutile. The film thicknesses are much smaller than the absorption depth of light and thus light absorption cannot be responsible for the saturation of the photocatalytic activity. Also, the film thickness is smaller than typical depletion regions in oxides, which excludes band-bending effects for charge separation. The studies reported here also compare favorably with previously reported work on photocatalytic activity as a function of film thickness for rutile films using photoreduction of Ag ions as a measure of the photocatalytic activity. In these studies a sharp increase in the photocatalytic activity for thin films up to less than 10 nm thickness was reported which then plateaued. This is very similar to the results presented here, however, different to the studies shown here a further increase in the activity at a lower rate has also been observed. The two different rates of increase in photocatalytic activity suggest two different mechanisms at work. In studies reported here the increase for much thicker TiO₂ samples could not be observed and the photocatalytic activity truly saturates at less than 10 nm. This difference in the two investigations is likely a consequence of the different photocatalytic properties studied. In particular Ag clusters that formed during photoreaction in previous work will modify the photocatalyst and this can give rise to additional phenomena.

In order to quantify the charge diffusion length normal to the surface of our macroscopically planar samples, we fit the increase in photocatalytic activity with increasing film thickness by an exponential dependence of the form: \( k = C \cdot (1 - \exp(-d/\lambda)) \), where \( k \) is the photocatalytic activity of the films (equivalent to the measured decomposition rate constant) and \( d \) is the film thickness. \( C \) and \( \lambda \) are fitting parameters, where \( C \) corresponds to the activity for very thick films (or bulk samples). The best fit parameters give a value of \( C_{\text{bulk}} = 0.0033 \pm 0.0003 \), \( \lambda_{\text{rutile}} = 3.2 \pm 0.6 \) mm, and \( C_{\text{anatase}} = 0.0618 \pm 0.0001 \), \( \lambda_{\text{anatase}} = 1.6 \pm 0.4 \) mm, for anatase and rutile respectively. The parameter \( \lambda \) may be interpreted as the surface-normal charge diffusion length and its value indicates the distance from the surface at which a generated charge carrier has a probability of \( 1/e \) to reach the surface. The films studied here differ from pure TiO₂ by the presence of an interface with a substrate. Consequently it may be important to consider how this interface may affect our observations. There are three main potential contributions by which the interface could distort the measured photocatalytic properties compared to a hypothetical ideal case of a ‘free’ TiO₂ sheet. Firstly, charge carriers may be trapped and recombine at the interface and the rate of this process may be different for the LaAlO₃ or Al₂O₃ substrates. Secondly, the lattice matching at the interface will induce some strain in the film that could affect the exciton diffusion to the surface. Thirdly, the lattice mismatch will facilitate point-defect formation in the film that varies with film thickness. All three of these effects are likely present.
to some extent but we argue that they do not obscure the main conclusion of a twice longer excitation length in anatase compared to rutile. The observation that rutile films, only 5 nm thick (a thickness where substrate induced strain is expected to be still present), exhibit a photocatalytic activity that is identical as that for rutile single crystal samples, indicates that strain in the films does not significantly alter the photocatalytic properties. In terms of charge trapping and recombination at the interface, it is important to realize that this effect can only modify the photocatalytic activity for films appreciably thinner than the charge diffusion length \(d < \lambda\) and any influence from charge recombination at the interface diminishes as the film thickness approaches \(\lambda\). Thus excitation recombination at the interface may only contribute to a deviation from the ideal exponential-functional dependence used to describe the behavior of the photocatalytic activity versus film thickness, but it will not change the film thickness at which the photocatalytic activity saturates. In order to assess the general possibility of lattice mismatch induced variation in the film properties, including formation of point defects, we compared the activity of anatase films grown on LaAlO\(_3\)(001) with those grown on SrTiO\(_3\)(001). These substrates exhibit large varying lattice mismatch with respect to anatase films of 0.1% and 3.1%, respectively\(^{10}\). Despite this large misfit for SrTiO\(_3\), we measure the same (within 5%) photocatalytic activity as for anatase films on LaAlO\(_3\), if the films thicker than 5 nm. For thinner films charge carriers generated in the photocatalytically active SrTiO\(_3\) substrate can contribute to the photocatalytic reactions and thus a slightly larger activity is measured compared to LaAlO\(_3\) substrates for very thin films. Thus from these arguments and test-studies we conclude that interface effects will not affect the key result of a larger \(\alpha\) than anatase than rutile and consequently our measurements show, for the first time conclusively, that the material-volume that contributes to the photocatalytic activity is significantly larger for anatase than for rutile.

The charge diffusion length \(\lambda\) is a convolution of charge carrier life time and charge carrier diffusivity. Arguably, it is the diffusion length \(\lambda\) that is the important property for characterizing the efficiency of a photocatalyst. The difference in the charge diffusion length between rutile and anatase may have its origin in the longer life-time of charge excitations and/or higher charge carrier mobilities in anatase than in rutile. Both properties have been previously reported\(^{12}\) but could not be unambiguously linked to photocatalytic activity differences between polynorphs.

Our determination that bulk properties are important to explain differences in the photocactivity of different polynorphs of TiO\(_2\) can also be applied to the measured surface orientation dependence for the rutile samples. The known bulk anisotropy in the effective masses and charge mobility in rutile along and perpendicular to the c-axis, i.e. (001) and (100) surface orientations, respectively, correlates well with the observed photocatalytic activity measurements. Independently from the surface preparation, we consistently measure higher photocatalytic activity for the (001) direction than for the (100) direction for which room temperature mobilities of \(\mu_{\text{room}} = 8 \text{ cm}^2/\text{V s}\) and \(\mu_{\text{room}} = 1.4 \text{ cm}^2/\text{V s}\) are respectively reported\(^{16}\).

Unfortunately, to the best of our knowledge, no charge mobility data for the (110) or (111) direction are known.

In conclusion, this investigation demonstrates the importance of bulk properties for the production of more efficient photocatalysts. For TiO\(_2\) films it appears that a surface region of only a few nanometer depths contributes charge carriers to photo-reactions. Higher activity in e.g. ZnO\(_2\) may be attributed to higher charge mobility in ZnO and thus the search for better photocatalysts should take charge mobilities and excitation life times into account. Finally, the approach described here for determining the active surface regions may not only be applied to pure materials but also to bulk dopant modified photocatalysts. This may enable future studies to extract information on the influence of dopants on the overall photocatalytic performance.

**Methods**

**Epitaxial TiO\(_2\) film growth and characterization.** LaAlO\(_3\)(100), SrTiO\(_3\)(100), and Al\(_2\)O\(_3\)(1102) (c-cut) substrates (MTI Corp.) were used for TiO\(_2\) growth. The substrates were ultrasonically cleaned in acetone and ethanol to remove any residual surface contaminants. To ensure identical growth conditions and identical film thicknesses a LaAlO\(_3\)(100) and an Al\(_2\)O\(_3\)(1102) substrates were mounted together and the TiO\(_2\) film was grown on both substrates at the same time. Before growth the samples were heated in the growth chamber at 600°C in a 2 X 10\(^{-8}\) Torr O\(_2\) atmosphere for 3 hours. TiO\(_2\) films were grown by pulsed laser deposition (PLD). The PLD ultra high vacuum (UHV) chamber was equipped with quartz-micro balance for calibrating and monitoring the deposition rate and a reflection high energy electron diffraction (RHEED) optics. A long target-to-substrate distance (8 cm) reduces the growth rate and eliminated the deposition of particulates from the ablation process. The target was ablated with a 330 nm Nd:YAG laser (SpectroSonic Ti) The TiO\(_2\) films were grown with the substrates at 600°C and an oxygen background pressure of 2 X 10\(^{-7}\) Torr. The deposition rate was in the range of 0.07 to 0.09 nm/min. The TiO\(_2\) films thicknesses from the morphological balance readings was checked on selected samples by ellipsometry and compared to cross-sectional TEM images for one sample. Ambient atomic force microscopy (AFM) (Park Scientific XE-70) characteristics were performed on all samples to ensure comparable surface morphologies and the measured rms roughness was used to estimate the uncertainty in film thickness.

TEM characterization was conducted at the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory, Upton, NY. Thin sections for TEM were prepared by focused ion beam milling. High-resolution TEM (HRTEM) imaging and selected area electron diffraction were performed in a JEOL-2100F at 300 kV.

**Rutile single crystal preparation.** In addition to thin epitaxial films we also conducted studies on rutile single crystals with (111), (110), (100), and (001) orientation. Epi-polished crystals were obtained from MTI-corp. and their orientations were checked with x-ray diffraction. The as received crystals were faceted but did not exhibit a clearly defined step structure as the AFM images in Fig. 4 show. To improve and obtain better defined surface morphology a slightly modified method of a previously reported procedure\(^{13}\) was used. The samples were polished in 10% HF for 30 min, cleaned in ethanol and rinsed with DI-water, and subsequently annealed in 200 mTorr O\(_2\) at 800°C for 1 h. This procedure resulted in well-defined stepped surfaces.

We also measured the activity of the samples after annealing in ultra-high vacuum at 600°C for 30 min. This causes a slight reduction of the samples as was evident from a change in color from transparent (slight yellowish) to a blue hue.

**Photocatalytic activity measurement and analysis.** The photocatalytic activity of different samples has been evaluated by measuring the photocatalytic decomposition of methyl orange using UV illumination. A 105 W Hg arc lamp (Osram) equipped with a water-cooled IR filter was used as the light source. The 5 x 5 mm square samples were suspended within a closed glass cuvette in a methylene orange (Fisher Scientific) solution. The glass cuvette has a transmission rate of \(\sim 95\%\) at 350 nm (3.54 eV) that only the near UV portion of the spectrum of our UV-lamp was transmitted and reached the sample. At regular time intervals the sample was taken out of the cuvette and the transmission of the methyl orange solution was measured with UV-Vis spectrometer. The intensity of the orange absorption of the solution at a wavelength of \(\lambda = 499\) nm is a direct measure of the decomposition of the dye and thus of the photocatalytic activity. A base line of the decomposition of the methyl orange without a photocatalytically active sample, e.g. a bare LaAlO\(_3\) substrate, shows a very small decrease in the orange absorption with irradiation time (see Fig. 3b). This base-line has been subtracted from all other measurements in order to only monitor the methyl orange decomposition due to photocatalytic action only. The intensity of the absorption peak is plotted as a function of irradiation time and the decrease is fitted with an exponential decay function (see Fig. 3b) in order to measure the rate constant. The rate constant of the decomposition has been used as a measure for the photocatalytic activity of the films and single crystal samples. Since all the samples have identical exposed surface area, the decay time is directly used for comparing the photocatalytic activity of different samples. For TiO\(_2\)-films this photocatalytic activity value was plotted as a function of film thickness to derive information on the volume of the TiO\(_2\) that contributes to the photocactivity.

Uncertainties in the measured photocatalytic activity are determined from the standard deviation in the photocatalytic of the samples thicker than ten nanometers, i.e. samples in the thick limit where the activity does not increase. The error bars for the film thickness shown in Fig. 3c) are the rms-roughness of the films measured by AFM.

Photocatalytic activity of anatase and rutile TiO$_2$ epitaxial thin film grown by pulsed laser deposition

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Abstract:

Epitaxial rutile-TiO$_2$(011) and anatase-TiO$_2$(001) films have been grown by pulsed laser deposition on Al$_2$O$_3$(-1102) and LaAlO$_3$(100), respectively. For low growth rates of $\sim0.0012$ nm/s and growth temperatures of 600 $^\circ$C high quality films are obtained. In particular the anatase films exhibit 100 nm wide flat terraces for 10-15 nm film thickness. Atomic steps of both $\sim0.25$ and $\sim0.5$ nm are measured, suggesting the existence of two different terminations, although only a 4×1 reconstruction is observed in RHEED. The rutile films exhibit coherent twin domain boundaries which is likely the reason for smaller terrace sizes compared to anatase films. Photocatalytic activity of the films is measured by decomposition of methyl orange solution under UV-irradiation. The anatase films are about twice as active as the rutile films. For both films the activity does not change significantly for films of 10 nm and thicker. For rutile films the activity is also compared to that of single crystal rutile TiO$_2$(011) samples. Both rutile-films and single crystals exhibit very similar activity, indicating the good quality of the films. Post-growth annealing of the films in air at 600 $^\circ$C decreases the photocatalytic activity of the films. On the other hand, reduction of thin films by vacuum annealing to 800 $^\circ$C does not change the photocatalytic activity of the films significantly compared to the as grown films. This is in contrast to single crystal rutile samples whose photocatalytic activity almost doubles after reduction by high-temperature annealing in vacuum compared to the stoichiometric bulk-samples. The differences between films and bulk samples may hint differences in defect formation due to the substrate interface.

Keywords: TiO$_2$; rutile; anatase; epitaxial films; metal oxides; pulsed laser deposition; photocatalysis
1. Introduction:

High quality anatase TiO$_2$(001) epitaxial films have been grown on LaAlO$_3$(001) or SrTiO$_3$(001) by reactive sputter deposition$^1$, reactive or oxygen plasma assisted molecular beam epitaxy (MBE)$^{2,3}$, and laser MBE or pulsed laser deposition (PLD)$^4$. On the other hand, the synthesis of rutile TiO$_2$(011) (equivalent to (011) for tetragonal unit cell) was demonstrated on r-cut, (-1102)-oriented Al$_2$O$_3$ substrates$^{4,12,13}$. For anatase TiO$_2$ on LaAlO$_3$, the established crystallographic relationship is (001)[1-10]$_\text{anatase}$ // (001)[110]$_\text{LAO}$ and for rutile TiO$_2$ on r-cut sapphire the crystallographic relationship is (101)[1-111]$_\text{rutile}$ // (-1102)[20-2-1]$_\text{sapphire}$. The same crystallographic relationship is also found for other rutile-structured oxides.$^{14}$ For rutile TiO$_2$(011) grown on r-cut sapphire, it is known that twin domain structures form with coherent boundaries in {101} planes.$^{15}$ While most studies have focused on the bulk structure of the films, several studies have also investigated optimization of film growth to obtain good surface properties for anatase TiO$_2$(001), i.e. atomically smooth terraces with well-defined monoatomic step-structures. In oxygen plasma assisted MBE, well defined surface structures are obtained for low growth rates (0.003-0.011 nm/s) and growth temperatures between 550-650 °C.$^{15}$ Under these conditions, a characteristic 4×1 reconstruction of the anatase TiO$_2$(001) surface$^{16,17,18}$ has been observed in reflection high energy electron diffraction (RHEED). Furthermore, RHEED-oscillations could also be observed during growth thus indicating a layer-by-layer growth mode, subsequent to an initial growth period without oscillations. It was shown that one full-period RHEED-oscillation corresponds to the formation of two atomic layers of TiO$_2$, which has been rationalized by the atomic structure of anatase in the (001) direction. In the (001) direction, the anatase structure consists of alternating crystal planes with distinct bonding structures so that two planes form one crystal building block (see e.g. Figure 4 below). STM studies of the growth of anatase on Nb:SrTiO$_3$(001) suggested that a crystalline wetting layer forms. In agreement with RHEED-oscillation measurements, the STM studies also showed that the growth proceeds in a bilayer growth mode resulting in 0.5 nm height bilayer steps. Furthermore, the 4×1 reconstruction has been observed to develop for films thicker than 3nm.$^{19}$
TiO$_2$ films are also widely used to study the effects of material modifications by dopants. In particular, the anatase films were used to demonstrate dilute ferromagnetism$^{20,21,22}$ by doping with Co,$^{23,24,25,26,27,28}$ Mn,$^{29}$ Cu,$^{30}$ V,$^{31}$ Cr,$^{32,33,34}$ Fe, Ni$^{35}$ or transparent conducting properties by doping with Nb$^{36,37,38,39,40}$ or Ta$^{41,42}$. Furthermore, TiO$_2$ is the prototypical photocatalyst$^{43,44,45}$ and therefore pure and doped films may be used to learn about the fundamental aspects of dopant incorporation and their influence on photocatalytic properties.$^{46,47,48,49,50,51}$ In this article, we also suggest that photocatalytic activity of these films may be evaluated in order to determine a quantitative difference in the photocatalytic activity between rutile and anatase. It is generally accepted that anatase is the more photocatalytic active phase of TiO$_2$ compared to rutile.$^{52}$ However, due to differences of the morphology in common powder photocatalysts, it may be difficult to assess by how much the two polymorphs differ in their activity. Using planar epitaxial films, morphology differences can be excluded and therefore the difference in photocatalytic activity may be measured directly.

This article has two main objectives: (i) characterization of the growth of TiO$_2$ films grown by laser MBE for rutile (101) and anatase (001), and (ii) characterization of the photocatalytic activity of these films for the decomposition of organic compounds in an aqueous solution under UV irradiation. For films thicker than 10 nm we measure constant photocatalytic activities suggesting that for thicker films charge carriers excited deeper than 10 nm do not contribute to photocatalytic reactions at the surface. A similar initial saturation of photocatalytic activity was also found for previously conducted similar thin film experiments.$^{53}$ In our studies, we find that the as-grown anatase films are about twice as active as rutile. To ensure that the films are good model systems for bulk TiO$_2$, we also compare the activity of rutile films with that of single crystals, which we demonstrate to have very similar activity. Finally, the effect of post-growth annealing in an oxygen atmosphere for anatase and rutile films in addition to reduction of the films and rutile single crystals by vacuum annealing are studied and compared.

2. Methods:

The thin films were prepared by pulsed laser deposition with a Nd:YAG laser (Symphotic Tii, $\lambda=355\text{nm}$, repetition frequency 5 Hz). TiO$_2$ ablation targets were made
of anatase and rutile TiO₂ powder with 99.995% purity. The powder was pressed into 1”
round targets to 23,000 psi and sintered for 8 hours at 1300°C. The deposition ultra-high
vacuum (UHV) chamber was evacuated to a base pressure of 5×10⁻¹⁰ Torr utilizing a
turbo molecular pump and ion-getter pump. During deposition, ultra-high purity oxygen
was supplied to a pressure of 2×10⁻⁶ Torr. A long sample-to-target distance of ~ 8cm
reduced the growth rate to 0.0011-0.0013 nm/s. As apparent from the AFM data
presented below for these growth parameters we did not observe deposition of particulates from the ablation process.

For growing rutile-TiO₂(101) and anatase-TiO₂(001) films, Al₂O₃(-1102) and
LaAlO₃(100) substrates were used respectively. The standard substrate preparation
methods used for the films discussed in this paper involved ultrasonic cleaning in acetone
then ethanol for 10 minutes each. Both substrates were subsequently mounted side-by-
side on a tantalum plate and placed into the UHV deposition chamber through a load-
lock. These substrates were then annealed at 600°C in an atmosphere of 2×10⁻⁶ Torr
oxygen for a period of 2 hours immediately before deposition. AFM images of the
substrate morphology after this preparation is shown in Fig. 1 (a) and (b) and compared
to substrates prepared by annealing in a tube furnace at atmospheric pressure O₂ at
1000 °C for 2 h, shown in Fig. 1 (c) and (d). While the tube furnace annealed substrates
exhibited a better organized step-structure compared to the vacuum annealed substrates,
the ultimate quality of the grown TiO₂ films did not show any dependence on the
substrate preparation and thus in the following only low-pressure (UHV) oxygen
annealing was employed for substrate preparation.

The structure of the as-grown films was evaluated in-situ by RHEED and ex-situ
with non-contact atomic force microscopy (NC-AFM). High-resolution transmission
electron microscopy (HRTEM) measurements were performed at the Center for
Functional Nanomaterials (CFN) at Brookhaven National Laboratory with a JEOL JEM-
2100F at a beam voltage of 200kV. The TEM samples were prepared by “lift off” using
focused ion beam milling. The crystallinity and epitaxial relationship between the film
and the substrate were investigated with selected area electron diffraction (SAED) with
large aperture (~500 nm). Electron diffraction from the film alone was performed in
nano-beam mode. This has been used to characterize super-structure spots due to periodic planar defects in the anatase films.

The photocatalytic activity of different samples has been evaluated by measuring the photocatalytic decomposition of methyl orange under UV illumination. A 100 W Hg arc lamp (Oriel) equipped with a water-cooled IR filter was used as the light source. The 5×5 mm square samples were suspended within a closed glass cuvette with a 0.1 mM solution of methylene orange. The glass cuvette has a transmission cut-off at ~350 nm (3.54 eV) so that only the near UV portion of the spectrum of our UV-lamp was transmitted and reached the sample. At regular time intervals the sample was taken out of the cuvette and the transmission of the methyl orange solution was measured with a UV-Vis spectrometer. The intensity of the orange absorption of the solution at a wavelength of ~489 nm is a direct measure of the decomposition of the dye and thus of the photocatalytic activity. A base line of the decomposition of the methyl orange without a photocatalytically active sample, e.g. a bare LaAlO₃ substrate, shows a very small decrease in the orange absorption with irradiation time. This base-line has been subtracted from all other measurements in order to only monitor the methyl orange decomposition due to the photocatalytic action of the samples. The intensity of the absorption peak is plotted as a function of irradiation time and the decrease is fitted with an exponential decay function in order to measure a rate constant. The rate constant of the decomposition has been used as a measure for the photoactivity of the films and single crystal samples. Since all the samples have identical exposed surface area, the decay time is directly used for comparing the photocatalytic activity of different samples.

3. Results

The result section is divided into two sub-sections. First, we discuss the film-structure of rutile and anatase TiO₂ as a function of film thickness and with an emphasis of the surface structure. In the second sub-section we present photocatalytic activity measurements for these films and compare them to rutile single crystals.

3.1 Thin film growth
To evaluate the quality of the anatase and rutile thin films grown by PLD, in-situ RHEED patterns were taken immediately following deposition onto each substrate for different film thicknesses. Fig. 2 shows the RHEED patterns for the anatase and rutile thin films grown on LaAlO$_3$(100) and Al$_2$O$_3$(1-102), respectively. The thicknesses of the films are from 0.5 nm to 20 nm. The left hand column shows RHEED patterns of the bare LaAlO$_3$(100) substrate and the anatase films with increasing thickness with the electron beam parallel to the $<101>$ azimuthal direction. The RHEED patterns of the same anatase samples along the $<110>$ azimuthal direction are shown in the center column. The right column depicts the RHEED patterns of the bare sapphire substrate and the rutile films with increasing thickness with the electron beam parallel to the $<010>$ azimuthal direction.

For the 0.5 nm films of anatase and rutile TiO$_2$ (a-c), the RHEED patterns exhibit an attenuated diffraction spots of the substrate spots and no diffraction from the film can be identified. An initial decrease in the RHEED reflection intensity was also observed in MBE growth of anatase.$^{15}$ Diffraction spots originating from the TiO$_2$ films are observed for a film thickness of 1.5 nm, see Fig. 2 (g)-(i), however, substrate spots are also still visible. NC-AFM images, discussed below, show that the entire substrate is uniformly covered by TiO$_2$ for this film thickness and thus the substrate diffraction spots must originate from the interface. For the anatase (001) film, faint 4×1 superstructure spots (3 spots between the primary (intensity) spots on the 0th Laue circle) become visible in Fig. 2(j) for 2.5 nm thick films. This is in agreement with STM studies on anatase films on SrTiO$_3$, where well-defined terraces with 4×1 reconstructions are reported for films in excess of 3 nm thick.$^{19}$ For even thicker films the RHEED pattern and in particular the 4×1 diffraction spots become more pronounced. For the thinnest film studied here of 20 nm thickness, shown in Fig. 2 (s), the diffraction spots become streakier, possibly indicating a roughening of the surface.

For the rutile (011) films the diffraction spots also become more pronounced with film thickness. It is known from bulk single crystal samples that the rutile (101) surface reconstructs into a 2×1 superstructure.$^{54,55}$ However, no half-order diffraction spots are observed with the exception of faint spots for the thickest 20 nm film, shown in Fig 2(u).
The challenge of detecting these spots may be related to the larger surface roughness of the rutile films compared to the anatase films as the AFM studies which we discuss next.

NC-4 AFM images are shown in Fig. 3 for the anatase films. Very thin films of 0.5 nm (Fig. 3(a)) show the largest surface roughness, with height variations of 0.8 nm. For 1.5 to 2.5 nm (Fig. 3(b) and (c)) the surface morphology is similar to that of the substrate. Thus, the TiO$_2$ film seems to uniformly cover the substrate. For films 5-10 nm thick (Fig. 3(d) and (e)) the films exhibit the best surface structure, with large atomically flat terraces of the order of 100 nm wide, i.e. much wider than the terrace width of the substrate. In Figure 4, the step structure of these films can be observed in greater detail. Clearly, two preferred step directions in the crystallographically equivalent (100) and (010) direction are observed. Previous reports suggested that predominantly two atomic-layer height steps of 0.5 nm exist. On our samples, we also observe these step heights. However, we often measure half-height steps of ~0.25 nm. As the ball-and-stick model in Figure 4 suggests, the crystal structure of anatase (001) is made up of bi-layer units and thus to obtain a surface with uniform truncation, bilayer step heights of 0.5 nm should form. Our observation of the frequent existence of steps with half this height suggests that the surface exhibits two truncations. These two truncations should have different surface structures, i.e. only one will exhibit the generally observed 4×1 reconstruction. It is also apparent from the AFM image in Fig. 4 that the terrace widths corresponding to the different step heights are different, indicating that one of the two truncations is favored over the other. It is possible that these two truncations have not been previously observed because our terrace-widths are much larger than in other reports on this surface. The existence of 0.25 nm steps also has implications on the growth mechanism. It implies that growth does not proceed via step-flow of bilayer TiO$_2$, but rather by formation of one atomic layer at the time. Still, the apparent difference in population of the two truncations at the surface, does not exclude the possibility that a full bilayer is completed first before the next layer is nucleated and thus giving rise to RHEED oscillations with periods corresponding to bilayers as has been previously reported. This may be particularly true for surfaces with narrower terraces. For the 20 nm thick films (Fig. 3(f)), the terrace sizes appear to shrink and the roughness of the films increases. This is consistent with the above reported RHEED patterns that become streakier for thicker films.
For rutile TiO$_2$(011) on sapphire, NC-AFM images are shown in Fig. 5. The substrate step-structure can still be discerned for 0.5 nm thick films (Fig. 5(a)). With increasing film thickness the surface develops two terrace orientations that are rotated 90° with respect to each other. This is a consequence of the existence of two twin structures in the film that form coherent boundaries along the {101} planes, as previously described.\textsuperscript{12} Possibly as a consequence of the twinning in the film, the resulting terraces are significantly smaller than for the anatase films. Nevertheless, terraces of 5-50 nm wide are observed for the 20 nm thick films (Fig. 5(f)).

In order to examine the morphology, phase purity and the bulk defect structures in the films we also performed high resolution TEM and electron diffraction, shown in Fig. 6 (a) and (b) for anatase films and Fig. 6 (c) and (d) for rutile films. The images and diffraction patterns of substrate and films confirm the known epitaxial relationships between these substrates and TiO$_2$ films, i.e. LaAlO$_3$(100)/A(101) and Al$_2$O$_3$(1-12)//R(-101). Furthermore, for the TiO$_2$ films on sapphire and LaAlO$_3$ detailed electron diffraction investigations detected only rutile and anatase, respectively, i.e. both films are phase-pure without inclusions of secondary phases. The rutile films are highly crystalline but show the presence of stacking faults, as shown in Fig. 7(a). These stacking faults originate at the substrate step edges and propagate through the entire film. The as-grown anatase films on LaAlO$_3$ are single-crystalline and do not contain extended structural defects. Despite their good crystalline quality a ‘wavy’ contrast can be seen in the TEM images. This can be clearly seen in Fig. 7 (b) for anatase films additionally annealed in oxygen atmosphere, discussed below in more detail. Similar wavy contrast was reported in an earlier work where it was associated with oxygen deficient shear planes,\textsuperscript{56} similar to the well-known Magnéli phases in rutile TiO$_2$.\textsuperscript{57} Briefly, these phases form by condensation of O-vacancies onto defined crystallographic planes in sub-stoichiometric TiO$_2$. For the anatase films, crystallographic shear planes (CSP) with removed O-atoms on the (103) and (101) planes were identified.\textsuperscript{56} The TEM studies of our samples indicate identical shear planes. According to ab-initio thermodynamics computations these Magnéli phases become energetically favorable under low oxygen chemical potentials at which they should form spontaneously.\textsuperscript{56,58} Such low oxygen chemical potential conditions may be encountered under the growth conditions at 600 °C in a low oxygen
pressure of $10^{-6}$ Torr and thus their formation is a reasonable proposal. To test the
stability of these CSP, we cleaved an as-grown film and exposed one half of the anatase-
film to atmospheric pressure $O_2$ at 600 °C for 2h in a tube furnace and let it cool down in
the oxygen atmosphere. The expectation for this study was to observe a decrease of the
CSP in the film after the sample treatment at high oxygen chemical potential. However,
the exact opposite was observed, i.e. the density of CSP dramatically increased covering
the entire sample (see Fig. 7 (b)). The increase in CSP can also be clearly seen by
comparing the electron diffraction patterns shown in Fig. 6 (e) for the as-grown films and
Fig. 6(f) after additional atmospheric pressure oxygen annealing. Superstructure spots
due to periodic planar defects along the (103) and (101) planes are seen in both samples.
However, the superstructure spots are much more pronounced after oxygen treatment and
defect planes are more frequent in real-space TEM. Currently, we have no explanation
for this behavior that appears to contradict the prediction of ab-initio thermodynamics
computations. Clearly, further studies are needed. For the photocatalytic activity,
discussed next, it is important to recognize that tube furnace annealing in oxygen may
increase defect concentration in the TiO$_2$ films.

3.2 Photocatalytic measurements

We determined the photocatalytic activity for ~10-20 nm thick films deposited on
5×5 mm substrates by measuring the rate of decomposition of methyl-orange organic dye
under UV irradiation. Figure 8 shows the comparison of a rutile and anatase film. Fitting
of the decrease with an exponential decay function allows us to extract a rate constant
that is a measure of the photocatalytic activity of the films. These measurements give a
rate constant of $(3.88 \pm 0.09) \times 10^{-3}$ min$^{-1}$ for anatase and $(2.35 \pm 0.04) \times 10^{-3}$ min$^{-1}$
for rutile. Thus, these thin films reproduce the known effect that anatase is more active than
rutile for photocatalytic reactions and moreover show that the difference is about a factor
of two for the decomposition of organic molecules for these two specific surface
orientations. Well-known orientation dependent variations of photocatalytic activities$^{39}$
may alter this result slightly for multi-faceted powder samples.

It is conceivable that interface-effects, such as interface charge trapping, epitaxial
or thermal stresses in the film induced during growth, and/or defects in the film induced
due to lattice mismatch or twinning affect the photocatalytic activity. Therefore, in order to verify that the thin films are good model systems for photocatalysts, we also compared the activity of the rutile thin films with that of a rutile TiO$_2$(011) single crystal of the same lateral size. For TiO$_2$ single crystals we measure an photocatalytic rate constant of $2.2 \times 10^{-3}$ min$^{-1}$ of the as received crystals and this value drops to $1.5 \times 10^{-3}$ min$^{-1}$ after etching with HF and annealing in O$_2$ at 800 °C in a tube furnace. Thus the photocatalytic activity of the single crystals is similar to those of the rutile films indicating that the films are reliable models of TiO$_2$ bulk materials in terms of photocatalytic activity. Unfortunately, no commercial anatase samples exist to perform a similar test for the anatase films.

Interestingly, we observe a strong dependence of the photocatalytic activity of the rutile single crystal samples on their vacuum treatment. It is well known that annealing in vacuum reduces TiO$_2$ which leads to formation of O-vacancies and Ti-interstitials. Formation of color centers also results in visible change of the initially transparent TiO$_2$ (with a slight yellow hue) to turn blue and eventually opaque and even showing a metallic shine.$^{60}$ Figure 9 shows the photocatalytic activity together with photographs of the crystals after annealing for 30 min at increasingly higher annealing temperatures in UHV. Surprisingly, the photocatalytic rate increases with reduction of the crystal. Up to an annealing temperature of 700 °C the activity is remaining roughly constant, but once the crystal is becoming almost opaque, at annealing temperatures of higher than 800 °C, the photocatalytic decomposition rate for methyl orange increases sharply to a value almost twice that of a stoichiometric sample.

The dependence of the photocatalytic activity for single crystal samples also motivated us to measure the photocatalytic activity for rutile and anatase films as a function of post-growth processing. For samples annealed in atmospheric pressure oxygen at 600 °C, the rate constant for methyl orange decomposition drops from $3.88 \times 10^{-3}$ min$^{-1}$ and $2.35 \times 10^{-3}$ min$^{-1}$ for the as grown anatase and rutile films respectively to $1.52 \times 10^{-3}$ min$^{-1}$ and $0.85 \times 10^{-3}$ min$^{-1}$ for anatase and rutile respectively after oxygen annealing. In contrast to the results for single crystal samples, vacuum annealing at 800 °C and thus presumably reduction of the samples did not change the photocatalytic activity significantly.
4. Discussion and conclusions

We investigated the growth of rutile and anatase epitaxial films by pulsed laser deposition. For low growth rates and growth temperatures at 600 °C, we obtain flat films with clearly defined crystallographic step structures on both surfaces. Especially for the anatase films terraces of ~100 nm wide are obtained for films 5-15 nm thick. On these flat surfaces step heights of 0.25 nm and 0.5 nm are observed implying the presence of two different surface terminations as a result of the bilayer crystallographic structure of anatase. This suggests that another metastable surface structure, beside the well-known 4×1 reconstruction exist and further atomic-scale scanning tunneling microscopy investigation are planned to verify this.

The photocatalysis studies on rutile films and single crystals showed that 10 nm thick films are sufficient to obtain the same photoactivity as in bulk single crystals. This implies that no charge carriers from deeper than 10 nm away from the surface are contributing to photocatalytic reactions at the surface. For the anatase films we also did not observe any further increase in photocatalytic activity with film thickness for films thicker than 10 nm. Furthermore, the photocatalytic activity of anatase was about twice the activity of rutile, consistent with the general notion of higher photocatalytic activity of anatase compared to rutile.

Finally, the effect of oxidation and reduction of TiO$_2$ on its photocatalytic activity has been investigated. For rutile single crystals, a close-to-double the activity is observed for crystals reduced in vacuum by high temperature annealing at 800 °C compared to stoichiometric samples. Under these conditions, the crystals become opaque indicating strong reduction of the crystal. This increase is measured under UV plus visible-irradiation. Previous reports on reduced TiO$_2$ showed an increase in visible light photocatalytic activity. Our measurements also demonstrate that the photocatalytic activity does not just increase for visible light on the expense of overall photocatalytic activity, as is often the case of impurity doped samples, but shows an overall increase in photocatalytic activity. The increased activity for reduced samples may be associated with an increase in charge carrier generation due to increased visible light absorption. This result is somewhat surprising since defects in TiO$_2$ are often considered charge trap
and recombination sites, resulting in diminished photocatalytic activity. The observation of the opposite effect suggests that defects induced by reduction are not strong charge trapping sites.

For the thin film samples, on the other hand, no noticeable increase in the photocatalytic activity by high temperature vacuum annealing has been observed. This may be a consequence of the as-grown films already being reduced, or instability and increased interface induced defect formation that compensates for increased light absorption in reduced samples. Thin TiO₂ films annealed in atmospheric pressure oxygen, on the other hand, showed a decrease in photocatalytic activity. This may also be attributed to defect formation in the films. High resolution TEM and SAED show an increased density of periodic planar defects for anatase samples. These defects may be one reason for the decreased activity upon oxygen annealing.

Acknowledgement: Financial support from DOE-BES under grant no. DE-FG02-09ER1608 and from NSF under award CHE-0840547 and CBET-1033000 is acknowledged. The TEM characterization of the TiO₂ films was performed at the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. The authors thank Kim Kisslinger for technical support.
Figure 1: Non-contact AFM images of oxide substrates. 2μm x 2 μm non-contact Atomic Force Microscopy images of (a) LaAlO₃(100) and (b) Al₂O₃(1-102) after 2 hours annealing in the growth chamber in 1x10⁻⁶ Torr oxygen at 600 °C. Substrates prepared by atmospheric pressure oxygen annealing in a tube furnace at 1000 °C are shown in (c) for LaAlO₃(100) and in (d) for Al₂O₃(1-102). Atomic steps are visible in all images with slightly better defined terraces obtain by high temperature and pressure annealing in a tube furnace.
Figure 2: RHEED images taken along low index crystallographic directions of anatase and rutile TiO$_2$ thin films with thicknesses of 0.5 nm (d-f), 1.5 nm (g-i), 2.5 nm (j-l), 5.0 nm (m-o), 10 nm (p-r), and 20 nm (s-u). For the anatase thin films, electron beam is parallel to the $<101>$ in the left column while parallel to $<110>$ in the center column. For the rutile film, the electron beam is parallel to the $<010>$ direction in the right column. Corresponding RHEED patterns of the clean substrates before growth are shown in (a-c).
Figure 3: Non-contact atomic force microscopy images of anatase TiO$_2$ on LaAlO$_3$(100) with thicknesses of 0.5 nm (a), 1.5 nm (b), 2.5 nm (c), 5.0 nm (d), 10 nm (e), and 20 nm (f) with corresponding cross-sections along the indicated lines shown below each image.
Figure 4: Detailed non-contact atomic force microscopy step-analysis of a 10 nm thick anatase film. The cross-sections indicate the presence of ~0.25 nm as well as ~0.5 nm steps. The ball-and-stick model of the anatase TiO$_2$(001) orientation shows two possible bulk truncations giving rise to the two possible step-heights.
Figure 5: Non-contact atomic force microscopy images of rutile TiO$_2$ on Al$_2$O$_3$(1-102) with thicknesses of 0.5 nm (a), 1.5 nm (b), 2.5 nm (c), 5.0 nm (d), 10 nm (e), and 20 nm (f) with corresponding cross-sections along the indicated lines shown below each image.
Figure 6: High-resolution transmission electron microscopy of 25 nm thick anatase and rutile TiO$_2$ film. A well-ordered real space atomic structuring can be seen for (a) anatase TiO$_2$ on LaAlO$_3$(100) and (c) rutile TiO$_2$ on Al$_2$O$_3$(1-102) with the lattice planes for the substrates (red) and thin films (yellow) appropriately labeled. Additionally, the SAED patterns depict the epitaxial relationships between (b) anatase and (d) rutile TiO$_2$ and their corresponding substrates. (e) and (f) show electron diffraction patterns for an as-grown and after ambient pressure oxygen annealing at 600 °C, respectively. Superstructure spots corresponding to periodic planar defects along the (101) and (103) planes are observed. After oxygen treatment these defect structures are much more pronounced.
Figure 7: High resolution TEM of rutile (a) and anatase (b) films. Stacking faults are apparent in the rutile films. Two stacking faults are highlighted by the two arrows in (a). The anatase films exhibits ‘wavy’ superstructures, which likely originate from almost periodic oxygen-deficient crystallographic shear planes, similar to Magnéli phases.
Figure 8: Photocatalytic decomposition of methyl orange for rutile films (blue triangles) and anatase films (red circles). The black square data points indicate the test experiment without photocatalyst. Plotted is the normalized light absorption of the orange dye in the solution as a function of irradiation time.
Figure 9: Variation of photocatalytic activity measured as a function of annealing temperatures in vacuum. In between every reduction the sample is made stoichiometric by annealing at 900 °C in ambient pressure O2 (first data point). Subsequent reduction is performed by annealing in UHV at the indicated target temperatures for 30 min. Similar reduction can also be achieved by prolonged (5 h) annealing at lower temperatures, e.g. 700 °C (last data point).
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About the Author

Timothy Luttrell graduated with a B.S. in Physics in 2004 from the University of South Florida. He enrolled in the Doctoral program for Applied Physics in 2007, quickly joining the interface and surface science laboratory (ISSL) in 2008. With the guidance of Dr. Matthias Batzill, Timothy has pursued research interests related to catalytic reactions on metal oxides. Specifically, the modification, characterization, and improvement of TiO\textsubscript{2} surfaces and thin films for photocatalytic activity. At the time of dissertation defense, he has six publications in peer-reviewed journals which includes three first author as well as one additional first author publication submitted for peer-reviewed publication. Additionally, he has presented at four major peer-reviewed conferences including the APS March Meeting and the AVS International Symposia. He is a 2011 Duckwall Graduate Fellowship recipient. He has further shared his experiences by mentoring two undergraduate students from the REU program for summer internship.