Surfaces and Epitaxial Films of Corundum-Structured Mixed Metal Oxides.

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Surfaces and Epitaxial Films of Corundum-Structured Mixed Metal Oxides

by

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A dissertation submitted in the partial fulfillment of the requirements for the degree of
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DEDICATION

To Kimli, my partner and wife who made it all possible, my father who showed me how and my children, who taught me why.
ACKNOWLEDGEMENTS

With the entirety of history as a backdrop, my experience as student and educator is nothing less than the most profound activity in which I have been engaged.

Those who played a part in any respect, as a teacher, a student, supporter, coach or critic, thank you.
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ABSTRACT

Throughout the last half century of materials science, significant motivations came from, and still do, the industrial applications of these materials. Whether it is electronic, thermal, tribological or chemical in nature, the study of metals, semiconductors and insulators eventually reveals that the surface plays a significant part in the properties of these materials. Understanding metal terminations reveals often that an oxide is the stable state of the metallic surface in an ambient atmosphere and the ability to predict and control these oxides has led to significant strides forward in not just the metallic bulk but the oxide as well.

Here we try to the understanding of the class of materials known as transition metal oxides by focusing on the structural and chemical nature of their surfaces. Vanadia, chromia and a new mixed metal oxide, VTiO₃, all of which form the corundum structure and have physical properties that need further study. Specifically, Cr₂O₃ has been at the center of much debate over how oxygen chemical potential influences surface terminations and top layer relaxation. Chromia is a wide band gap (~3.4eV) insulator with substantial ligand field interaction and measurements of the 3d states reveal these states split to t₂g and e₈ – consistent with the distorted octahedral.

V₂O₃ is known to be a Mott insulator and paramagnetic, properties that can be modified through dopants, stoichiometry and strain. In this work, solid solutions of V₂O₃ and Ti₂O₃ are studied. VTiO₃, has been synthesized in a corundum – like structure by epitaxial growth on an isostructural α-Al₂O₃ substrate.

Section I offers a review of corundum like transition metal oxides and their surface properties and motivations of continued research. In section II we describe in detail, the critical
components of PLD thin film growth and in the next section a review of the pertinent characterization techniques utilized in the process. Finally, the results are presented of the study of two transition metal oxide structures namely:

1) Novel VTiO$_3$ in a corundum structure has been grown via Pulsed Laser Deposition – Molecular Beam Epitaxy on a single crystal Al$_2$O$_3$(0001) substrate. The sapphire substrate with modest lattice mismatch was utilized in an effect to compel heteroepitaxial growth of the VTiO$_3$ film. Confirmation of the films structure & chemical state were performed by X-Ray diffraction, Transmission Electron Microscopy (HR), X-Ray Photo-electron Diffraction, Ultra-Violet Photo-Electron Diffraction and Reflection High Energy Electron expected that the metal ions exist in a 3+ charge state. While XPS clearly points to a V$^{3+}$ charge state and this suggests that Ti should as well, however there is also a strong Ti$^{4+}$ component present. EELS spectra support the existence of a mixed state Ti$^{3+}$ & $^{4+}$. Broadening of the valance band edge as revealed by UPS spectra indicate that the 3d orbitals are occupied and that the a$_{1g}$ molecular states are occupied. The conflict in diffraction data supporting corundum and PES/EELS data suggesting a mixed state implies that additional final state effects are present and/or an oxygen rich structure.
Additionally, corundum like Chromium(III) Oxide is formed on a Cr(110) surface and characterized with X-Ray Photoelectron Diffraction, Low Energy Electron Diffraction and XPS for the purpose of characterizing surface termination and terminating layer relaxation. Comparison of the XPD diffraction data with known and previously discussed terminations reveal the as grown film does not conform. Consequently, we propose a new, stoichiometric termination with oxygen termination and 1st layer chromium interstitials. Atop this structure was grown an ultra-thin film of V$_2$O$_3$ by vanadium e-beam evaporation in background oxygen. This final structure supports the previously proposed vanadyl structured surface.
1. INTRODUCTION

The corundum structure takes its name from the Tamil word *kuruntam* which specifically refers to the natural formation of $Al_2O_3$. It possesses alternating layers of oxygen and metal ions in the &lt;0001&gt; direction. Layers alternate in the form O-M-M-O and form an irregular octahedral with the metal cation off center coordinated with 6 nearest neighbor oxygen atoms. Therefore, the two in plane metal ions define the octahedrals with the third octahedral missing as can be viewed in 31. For XPD we plotted the intensity of both components summed.

The experimental XPD patterns superimposed on their corresponding EDAC simulations for O-1s and V-2p are shown in Fig 6(c) and 6(d) respectively. These XPD patterns can only be satisfactorily simulated with the vanadyl terminated surface, illustrated in Fig. 1 (f). For the optimized structures we find the lowest R values of 0.22 and 0.24 for V-2p and O-1s, respectively. The relaxations and atom separations of the optimized model are illustrated in Fig. 7 and can be compared to those reported from DFT simulations56, also shown in Figure 1 (TopL) Corundum [0001] plane, (Left), and View normal to the [1-210] plane. Coloring clarifies metal ion position and red shading distinguishes oxygen layers. Colors and shading correspond from top to bottom. (TopR) Octahedral coordination.
Fig. 7 for comparison. Using the reported DFT values for the vanadyl structure for calculating the XPD pattern with the EDAC code the R values are slightly worse (R = 0.31 and 0.16 for V and O, respectively), than those of our optimized structure, as shown in the supplement. Other models, suggested in Fig. 1, give much worse R factors and are not further considered here. Thus our results indicates that the vanadyl termination is the preferred surface structure also for ultrathin vanadia films heteroepitaxily grown on another corundum oxide substrate.

1.1.1. Conclusions

Corundum structured oxides are common for many sesquioxides and combinations of them may form solid solutions\(^1\). In theory, one distinguishes terminations of this structure perpendicular to the \(<0001>\) direction that introduce the possibility of a non-stoichiometric surface, if terminated immediately before or after the oxygen layer, or a stoichiometric surface if truncation occurs between two metal ions. Termination however, is achieved by either cleaving a single crystal, through the growth process of an epitaxial film or through surface treatment that is self-organizing. As such, one can distinguish between
the mechanisms that affect the final surface structure. Simultaneous with the termination process is the surface structures response to the creation of dangling bonds and propensity to minimize the surface energy. In the absence of pathways that allow an influx or outflow of atomic species, the surface will minimize the surface energy by creating new bonds that may lead to various reconstructions as seen in Figure 2, without a change in composition.

Simultaneously, surface and near surface layers undergo a relaxation due to removal of a semi-infinite section of the original crystal and the influence of those forces on the new surface.

Alternatively, in an environment of oxygen chemical potential that may take the form of an oxygen atmosphere, for example, or diffusion pathways that allow of a change in composition of both metal and oxygen, equilibration will also affect the surface structure and stoichiometry. It is the case of many transition metal oxides that even under low oxygen chemical potential, a well ordered metal rapidly forms a metal-oxygen superstructure. At low temperatures and in many cases, this process is self-limiting by the ability of the metal ion to diffuse upward towards the surface thereby maintaining a gradient in potential and/or the ability for oxygen to diffuse downward. Under energetic conditions such as higher temperature or ion (O\(^+\)) bombardment, the process can produce thicker films. In the case of chromium metal\(^2\), the oxide layer is primarily Cr\(_2\)O\(_3\) and film growth and thickness is best described in terms of substrate temperature and ion diffusion. The diffusion kinetics of the higher temperature growth is then rate limited buy the formation of
metal-oxide layer defects. Defects provide an active diffusion pathway for cation migration towards the surface and correspondingly, the oxygen potential dictates the nature of these defects. We can see the effect of low temperature growth in that the thin Cr$_2$O$_3$ film reaches equilibrium at about 10 Angstroms. Thickening of the oxide film at elevated temperatures involves electron tunneling from the metal/oxide interface through to the surface oxide layer resulting in an electric filed that further promotes migration of chromium metal to the surface and oxygen towards the interface.

With regards to this work, an important question to answer is the nature of surface energy and how it relates to ad layers. The surface terminations discussed above are revealed in detail in work from Jonayat$^3$ et al. The mechanism in play is surface oxygen chemical potential and the response of the surface to the introduction of a metal ad layer. In one case vanadium (in an oxygen background) is deposited on a pristine Cr$_2$O$_3$ surface and then annealed. The chromia surface, prior to vanadium deposition, was annealed in oxygen to determine the nature of the surface reconstruction/relaxation. Deposition, on the relaxed chromia surface, of vanadium reveal a monotonic increase in vanadium with respect to chromium XPS peak area implying that during deposition (at RT and in oxygen) vanadium prefers to remain at the surface. Temporal (XPS) scans of the annealing process show a constant peak area ratio demonstrating that again vanadium prefers the surface or alternatively, oxygen selectively binds with chromium over vanadium.

Alternatively, DFT calculations of the surface energy of oxygen terminations of Cr$_2$O$_3$ (is the case with our sample discussed above) confirm that the surface potential energy of O terminated is lower than that of chromium termination of the same film, for $-0.5 < \mu_0 < -1.30$ which corresponds to $\sim 1 \times 10^{-8}$ Torr oxygen partial pressure for temperatures between 300-700K.
Further calculations show that energy difference between surface vanadium and subsurface Cr₂O₃ layers (Δε) show a positive Δε = 0.26 indicating the chromium prefers to stay subsurface.

This discussion demonstrates the role surface energy plays on the surface environment and the need for further study especially in light of the interaction of oxygen chemical potential and surface termination.

1.2. Motivations and Background

Transition metal oxide (TMO) have become a subject of interest due to a wide range of properties and structures. This is a result of the d – orbitals that comprise the valence electrons involved in bonding. These bonds can vary in nature and crystal structure spans well known hexagonal, perovskite, spinel among others. Electronic properties range from the metallic LaNiO₃ and In₄Sn₃O₁₂ to a number of wide gap insulators like BaTiO₃. There are metal oxides exhibiting magnetic properties like FeO (ferromagnetic) and antiferromagnetic NiO. It is the nature of the d-block metal oxides that produce metal – oxygen overlap of orbitals that are small resulting in narrow electronic bands. These typically scale on the order of a few eV compared to metallic bands that range ~5-15eV.

Some of the group 4 transition metal oxides are stable in the corundum structure. These sesquioxides have been studied in varying degrees for their magnetic, electronic, optical and structural behavior and have found broad use as catalysts⁴ ⁵ (Cr₂O₃, Fe₂O₃) and as magnetic recording medium (Fe₂O₃) and anticorrosion coating. Still, the prospects of engineering stable forms of the structures remain a motivation to study them in full detail.

Mixed metal oxides have been utilized as a method to tune the known properties of simple binary metal oxides. SnO₂ is a rutile structured insulator. It is used as a white colorant
and polishing agent. In$_2$O$_3$ forms in the corundum structure and has specialized use as a battery anode and thin film reflective coating. Formation of In$_2$SnO$_5$ produces a widely used optically transparent and electrically conductive thin film for touch screens and other applications. Conversely, Cr$_2$O$_3$ is an insulator as well but introducing In produces a magnetic semiconductor In$_{2-x}$Cr$_x$O$_3$

$\alpha$-Cr$_2$O$_3$, once used pervasively as a color pigment in paints and gained the infamous moniker *intuitional green* is a hard, Mohs scale 8, naturally occurring mineral that is antiferromagnetic to $T_N$ 307° and paramagnetic above. The magnetic properties$^6$,$^7$ have been attributed to oxygen defects as a result of strain. Punugupati$^7$ et al. demonstrated that there is a high correlation between films thickness (and consequently strain) and magnetization in addition to studies that show reduced ferromagnetism for high oxygen annealing temperatures.

Vanadia, V$_2$O$_3$ is particularly interesting as a Mott insulator. Insulators, in general, are classified as in thermal equilibrium in the presence of a (relatively) weak electric field. That is, in terms of the net motion of electrons in the system, there is no migration as a response to the applied field. As such, we can assign causality to either the electron – ion interaction or to electron – electron interaction as a reason behind it’s insulating properties. In the former case, the interaction is due to completely filled highest bands or the electron’s interaction with lattice deformation or disorder/impurities. Conversely, to understand the behavior of a Mott insulator we look to the electron – electron interaction.

A Mott insulator is characterized by the electron – electron interaction. A gap in the band structure is formed when the repulsive potential $U$ is large. The Mott – Hubbard model of this insulating state describes kinetic tunneling or hopping between neighboring interacting ions of a lattice in the presence of a local, on-site potential. This works sufficiently well at low
temperatures, short range interaction and periodic (simplified) potentials. The two competing concepts at play are on-site potential and the transfer integral. The former is a result of the mentioned columbic repulsion between nearest neighbor electrons and the latter which is scaled by direction as well as distance between ion centers. Through this competition, a description of the metal – insulator transition can be achieved. As the temperature of the metal oxide increases, so goes the mean interatomic distance and consequently the on-site potential dominates over a weakening transfer (Hopping) integral.

What is lacking in the prior model is long range order. The Mott – Heisenberg model considers this in the form of exchange interaction of localized spins. The result is a thermodynamic phase transition whereby ordering below the critical Néel temperature is allowed and above which, transition to a paramagnetic state further characterized as a correlated metal or Mott- Hubbard insulator occurs. Ultimately, we remain cognizant of the fact that as the complexity of real materials increases from an ideal simplified binary metal oxide, one soon realizes that insulating materials need descriptions involving more than just one interaction.

Modifications to the Vanadia structure could result in useful magnetic materials and any number of sensing or control applications.

Both Cr2O3 and V2O3 have been studied for growth properties as thin films to determine firstly, bulk properties and more recently surface termination and surface layer relaxation. Conceptually, terminating a bulk corundum-like metal oxide abruptly may result in a surface that must relax in response. The structure dissipates this energy for more favorable structures that may include an atomic reorganization of the surface by producing bonds that may or may not be bulk-like. V2O3 is known to reorganized, for example, its (0001) surface by ensuring the
terminating layer is composed of vanadyl species. Much like \( \text{31} \). For XPD we plotted the intensity of both components summed.

The experimental XPD patterns superimposed on their corresponding EDAC simulations for O-1s and V-2p are shown in Fig 6(c) and 6(d) respectively. These XPD patterns can only be satisfactorily simulated with the vanadyl terminated surface, illustrated in Fig. 1 (f). For the optimized structures we find the lowest R values of 0.22 and 0.24 for V-2p and O-1s, respectively. The relaxations and atom separations of the optimized model are illustrated in Fig. 7 and can be compared to those reported from DFT simulations\(^{56}\), also shown in Fig. 7 for comparison. Using the reported DFT values for the vanadyl structure for calculating the XPD pattern with the EDAC code the R values are slightly worse (\( R = 0.31 \) and 0.16 for V and O, respectively), than those of our optimized structure, as shown in the supplement. Other models, suggested in Fig. 1, give much worse R factors and are not further considered here. Thus our results indicates that the vanadyl termination is the preferred surface structure also for ultrathin vanadia films heteroepitaxially grown on another corundum oxide substrate.

1.2.1. Conclusions

Corundum structured oxides are common for many sesquioxides and combinations of them may form solid solutions\(^{18}\), the final layers include a full oxygen layer topped by a half vanadium layer but with a double bonded additional oxygen atom atop each terminating vanadium. Structurally, this effects not just the terminating profile but the interlayer spacing as well. The corundum structure is characterized, by an O–M–M–O profile that repeats in \(<0001>\) direction but terminates as O-M-M-O-M=O with the double bonded M=O as the exposed surface
and the interlayer spacing takes on much relaxed dimension to compensate. This surface is preferred provided sufficient oxygen chemical potential is met that is affected by the nature of the oxygen molecule (i.e. monoatomic vs. diatomic or other reactive oxide composites), pressure of the atmosphere and surface temperature. The chemical potential as a growth parameter has been manipulated to affect the surface termination and relaxation of Cr$_2$O$_3$. In light of the introductory discussion on oxygen chemical potential above, it is worth further mention here that the chemical potential effects surface energy insomuch as the presence of very low oxygen chemical potentials (reducing atmosphere) the metallic termination is stable and preferred over oxygen termination.

The focus here is twofold; one, on a novel corundum structure VTiO$_3$ and two, a previously studied Cr$_2$O$_3$ with conflicted reports as to surface termination and the response to ultra-thin films of V$_2$O$_3$ deposited on the surface. The goal of the work is to determine, in the case of VTiO$_3$, the effect the corundum substrate has on not just the epitaxial heterostructure, but the chemical state, reproducibility of growth and stability of the structure. Chromia is well known to be stable under a multitude of conditions and there has been some DFT attempts at predicting the surface relaxations of both and the behavior of ad layers of V on Chromia. The DFT process is does not stand alone with respect to transition metal oxides as it relies heavily on experiment incorporation of the effects of crystal field and on-site potentials. Understanding the structure can further help to support modifications to the DFT assumptions.
2. THIN FILM GROWTH

2.1. Growth Chamber

Pulsed laser deposition (PLD) growth of VTiO$_3$ thin films is achieved in an Ultra High Vacuum (UHV) chamber. UHV conditions are achieved in stages by way of a mechanically backed turbo-molecular pump, an ion pump and intermittently employed titanium sublimation pump. The chamber is also fitted with a sample e-beam heater capable of heating substrates to 900°C. Immediate characterization of the as grown film can be performed by an in-situ reflection high-energy electron diffraction (RHEED) system. Transfer of the sample to an attached XPS chamber is possible without breaking vacuum.

2.2. ND: YAG Laser

Thin films are grown by pulsed laser ablation of material from a solid ceramic target with an externally mounted solid state Nd: YAG laser. The optically pumped laser provides 430mJ focused to a spot size of approximately 0.9mm at 355nm wavelength and 5Hz repetition. Optical emission of the laser occurs by excitation of the highest electron energy levels of the Nd ions via a broad-spectrum flash lamp. The optical excitation provides energy for excitation of electrons to states well above the upper transition level. This inversion of states allows for the controlled rapid de-excitation/emission without total depletion of the same states. The photon energy released corresponds to 1064nm and through frequency tripling, emission is of $\lambda=355$nm.

There are three transitions$^8$ from the 4F3/2 to lower (4I) energy states that are useful for photoemission due in part to the long lifetime that yields a total emission rate of approximately
4350 Hz. Since the quantum efficiency of this transition is about 0.56 the true rate is nearer to 2440 Hz. The upper level is affected by a hyperfine splitting of nearly 10 meV so, considering the radiative efficiency (4F3/2upper / 4F3/2 total ~ 0.135) of only this upper most level of the hyperfine splitting we find a net radiative frequency of 820 Hz or 1.2 ms.

2.3. Ceramic Target

The laser described above is tasked with the sole purpose of ablating material from the ceramic target to deposit an epitaxial thin film on the chosen substrate. Reflection and transmission optics focus the beam onto the target within the chamber through a quartz window. The incident laser irradiates the target and due to the coherent, high energy nature of the electric
field produced, electrons are allowed to oscillate within the target transferring some of their thermal energy to the bulk.

For the VTiO$_3$ film growth, a pressed target of V$_2$O$_5$ and TiO$_2$ was prepared with a metal ion ratio of 1:1. The appropriate weights of each powder, with purities of 99.99%, were mixed well and pressed within a hardened steel die. The die has a cylindrical cavity of diameter 25 mm and variable height. A linear hydraulic press is used to apply a total pressure of 25 kN for 24 hours. The target is then removed from the die and annealed in a high temperature tube (amorphous-Al$_2$O$_3$) furnace at 650°C for 10 hours in an ambient atmosphere. The final pressed target is a metal oxide composite with approximately 25% void space as determined by density calculation. Observations of a cleaved target reveal the exposed surface to be darker in color compared to the core and although no analysis has been performed it is assumed that the surface is chemically modified to some degree.

Bound oxygen is plentiful within the target, however not all is readily available for film growth through the development of the plume above the target and even less so on the surface of the substrate at elevated temperature. To compensate for the oxygen necessary at the surface for recombination and stoichiometric growth of the film, and to assist in film formation, a background pressure of 10$^{-6}$ Torr of ultra-pure molecular oxygen is introduced into the chamber during growth.

Proper conditioning of the target is also required to ensure reproducible and homogeneous films. To ensure uniformity during lengthy depositions, the target is exposed to the emission of several thousand laser pulses. This ablates the surface layer to a certain degree but more importantly provides for thermal and chemical stability. Consideration is also paid to the formation of a deep “W” shaped trench profile as deviation from a flat target can lead to
splashing and slow growth rates. As a consequence of the above, the useable lifetime of particular path along the surface of the target is limited to the equivalent of a few tens of nm of film thickness on the substrate.

2.4. Deposition

The mechanisms of PLD that comprise the system of laser pulse though film deposition are not simple. The transformation is termed normal vaporization and describes the incident pulsed electric field generating a coupled electron-phonon process. The electric field induces excited electronic states that mature, in short time, to thermal/mechanical/chemical energies characterized by (local) temperature changes in the realm of $10^{11}$ K/s and pressure (gas) of tens to hundreds of atmospheres. The nature of the electric field/plume composite is driven, in large part by the photon energy of the laser. It will determine such characteristics as penetration depth of the electric field through the Beer-Lambert law $I(z) = I_0 e^{-\alpha z}$ where the attenuation constant $\alpha = 2/\delta$ and $\delta$ is the penetration or optical skin depth. Energy of the excited electronic states quickly transforms the local environment to a plasma after the dislocation of material from the target. The plasma forms a plume at and above the target surface and due to the ridged nature of the plasma/target interface, reflects the plume in a direction largely normal to the interface towards the substrate. In consideration of these parameters, low penetration of the electric field and low thermal conductivity assist in containing the thermomechanical energy to the surface. This prevents expansion of the material at depth that would, in turn, explode or splash the surface material in large grains producing an irregular film.

Finally, oxygen, target/substrate distance, substrate temperature all need be considered when optimizing growth rates and stoichiometry. Specifically, available oxygen can be a limiting
condition if monatomic species are not in sufficient supply either through surface reaction or other reactive sources as O$_3$ and NO$_2$.

While the target is typically stoichiometric in its assembly, the nature of its homogeneity is promptly modified even after a few pulses. Characteristics akin to, as well as unique from mechanical atomic sputtering can be observed. In the case of the former for example, one can detect the formation of trench profiles of conic cross section that are indicative of momentum transfer lateral as well as normal to the surface. In the case of the later, desorption rates vary in the PLD process for different elements in say complex oxides. Some early evidence was observed in the cone formation from PLD pulses of a YBCO stoichiometric target. This feature characterized by SEM and neutron scattering revealed a stable Yttrium-Oxide surface complex after several hundred pulses that prevented further evaporation of either Ba or Cu contained within the subsurface. The interior (central) portion of the cone then contained undisturbed stoichiometric YBCO. This implies that one must account for the change in composition of the target as the target is modified during deposition.

Further controls are necessary in matching pulse energy and duration to the target material. Excitation of the initial formation stage of the plume can be heavily affected by these parameters and hence the characteristics of the plume on arrival to the substrate surface. Non-uniform heating of the plume often produces undesirable results since the masses of particles propagating in the plume can vary wildly and heavier neutral particles can act to sputter the substrate of newly grown film.

Control of the substrate temperature is achieved through a simple e-beam heater. The substrate is mounted on a clean Ta sample plate with the aid of thin Ta foil straps spot welded to the plate. The plate is electrically isolated and held at high potential relative to a nearby tungsten
filament. Current through the filament and emission current to the plate is regulated by a feedback loop that maintains the latter as constant. Knowledge of the substrate temperature is gleaned from prior calibration of emission current to sample temperature. In the calibration configuration, a K-type thermocouple was sandwiched between two sapphire single crystals and emission current was stepped at regular intervals, allowing the temperature measurement to stabilize. In this way, the substrate temperature is correlated to e-beam emission current from 50-900°C.

Pulse energy/rates correspond to a film growth rate of approximately 1.0Å/min. The duty cycle and frequency of the Q-switch control signal is adjusted to achieve the proper film growth rate. Film thickness is monitored by a quartz micro-balance located near the substrate. The microbalance operates by monitoring the change in resonant frequency of a quartz crystal. An unadulterated quartz (thin film) crystal is driven at resonance and exposed to the deposition plume during film growth. The addition of material on the crystal changes the mass of the system thereby changing the resonant frequency. Since film thickness is dependent on density this parameter must be provided to the micro-balance controller. A tooling factor is also required to compensate for the crystal’s placement with respect to the sample and the fact that growth conditions on the quartz crystal do not match that of the substrate surface. Ultimately, a correlation to the microbalance reported thickness and the actual film thickness then must be established. As a coarse test, this can be done by XPS scans at increasingly larger grazing emission angles and equating the inelastic mean free path of the ejected electrons to the thickness of the film. More accurate measurements are made of optically thin films through the use of the optical technique ellipsometry and finally, if available, cross sectional imaging from TEM produces reliable data.
A detailed description of relevant growth parameters and methodologies of the samples used in this work are reported in the following Results sections.
3. MATERIALS CHARACTERIZATION TECHNIQUES


Reflection High Energy Electron Diffraction (RHEED) is an in-situ surface sensitive technique that is used in determination of solid state surfaces. Among such determinations are its crystalline/poly-crystalline ordering, step edge formation, surface atomic reconstruction, surface atomic spacing and surface roughness.

Functionally, the process involves the introduction of a highly collimated electron beam incident at grazing angles (a few degrees) to the sample surface as pictured in Figure 7. The electron scattering from ion centers is elastic as well as inelastic. In the half sphere above the sample plane that is projected upon a phosphor or CCD screen aligned opposite to the electron gun and normal to the e-beam, one can record the pattern of diffraction spots caused by the superimposed intensities of the elastically scattered and diffracted electrons. Electron emission energies from the gun typically range from 10-30keV although energies up to 100keV have been utilized, although the higher electron kinetic energy spectrum can become damaging to the sample surface.

The fundamental concept is the scattering process. An incident wave scatters off a regularly spaced periodic array of atoms, identical in the simplest case, with spacing between adjacent atoms of a (See Figure 4). The incident (scattered) wave is at the angle $\theta_i$($\theta_r$). For
integer multiples of wavelengths $n\lambda$. Constructive interference occurs by

$$a \cos \theta_i - a \cos \theta_r = n\lambda. \quad (3.1.6)$$

In terms of wavevectors, $k = 2\pi/\lambda$ and reciprocal lattice constant $B_n = 2\pi n/a$, (3.1.6) becomes

$$k \cos \theta_i - k \cos \theta_s = B_n. \quad \text{(3.1.6)}$$

The projection of each of these circles, spaced at intervals dependent onto a plane represent Laue zones. With parallel distributions of lines of atoms onto a periodic plane each with orthogonal spacing of $a$, we now can construct the simplest of 2D projections of reciprocal space onto the phosphor screen by the overlap or constructive interference created by many lines of atoms that produce the Laue zones described above.

Vertical stacking of atomic planes introduce a modification to the ideal image – that of streaking. Crystal steps with lateral dimensions smaller that the coherent length of the electron beam interact to, in the sense of their Fourier relationship, to creat streaking. Provided the step
sizes are large in comparison to the coherence length then the streaking is not evident and bright diffraction spots are visible.

Surface morphologies impact RHEED. Features that cannot maintain coherence of the beam relative to the ideal surface scattering produce superimposed pattering whereas features that can maintain coherence tend to streak. Rough surfaces that project crystalline material normal to the surface and mean height with dimensions large in comparison to the e-beam present as transmission diffraction patterns and not grazing angle diffraction. In Figure 6 are the zeroth and 1st Laue zone circles and the diffraction spots in the zeroth Laue zone as described above that are streaked by crystal steps. Also visible in the same diffraction pattern is the straight through e-beam spot (at bottom center) that has penetrated the sample in direct line from the source. From a RHEED diffraction pattern the horizontal spacing is related to the surface 2D lattice spacing. Referencing a known sample (see Figure 22) allows one to compare reciprocal space dimension and hence real space lattice constants. All taken together, RHEED is a surface sensitive tool that can report the quality of a crystalline surface.

![Figure 6 RHEED schematic. (Left) The device is assembled so that the sample remains in vacuum. An electron gun produces a collimated electron beam scattering from the sample surface and generating the diffraction pattern on the far screen. Typical setups include a CCD camera outside of the chamber to view the diffraction patterns on the phosphor screen. (Right) RHEED diffraction pattern taken at 13.6keV of V$_2$O$_4$(0001) single crystal surface grown on R-cut Sapphire. Visible are the (1x1) reconstructed surface Zeroth Laue zone and 1st Laue zone circles.](image)
3.2. Low Energy Electron Diffraction: LEED.

LEED imaging exploits the low penetration depth effected by low energy electrons (<200eV) in a scattering process, similar to that described above for RHEED, to produce a reciprocal space diffraction pattern of the sample surface. In this technique, the electron gun is placed at normal incidence to the sample surface resulting in a backscattering and diffraction of electrons that form a very surface sensitive diffraction pattern.

Penetration depth of the electron beam is $\Lambda(z) \left| \frac{I(z)}{I_0} = e^{-\frac{z}{\Lambda}} \right.$ where $\Lambda$ is the inelastic mean free path defined as the average distance an electron travels without engaging in inelastic collisions. The penetration depth dictates the effective surface that influences the diffraction pattern and is limited to 5-10Å in the case of functional electron energies utilized by the technique.

![Figure 7 LEED Image of C2O3r(001). Primitive translation vectors of the 2D surface reciprocal space are notated. The electron gun (small disk) can be seen in the foreground center.](image-url)
A LEED system (Figure 9) will employ filters to selectively reject inelastically scattered electrons by providing a steering potential to electrons in flight towards the phosphor screen with lower kinetic energy. Adjustment of this potential modifies the S:N ratio of the diffraction pattern but also attenuates the desired signal. Other mechanisms are also employed at the output of the electron gun to focus and filter the incident electron beam. Figure 7 depicts the reciprocal lattice diffraction pattern created from a LEED instrument of a Cr$_2$O$_3$ (0001) single crystal surface. Spots are labeled with their reciprocal space translations. Based on this information, one can infer a structure of the surface and the degree to which the surface is single/poly crystalline, the nature of ad atoms/layers or the ordered nature of sublayers.

In Figure 8 the diffraction pattern of a dirty chromium (110) metal sample is shown with two notable characteristics. The surface reconstruction is such that, in at least one direction, there is not the expected (1x1) order but since the placements of the diffraction spot is of integer fraction (1/n) the reconstruction is of n multiples of the (1x1) reconstruction or (1xn) are imaged.
It has been previously established that chromium is known to easily absorb nitrogen carbon and oxygen and the low intensity, but well ordered, diffraction spots indicate that interstitial nitrogen or other absorbates are indeed present. In Figure 10 we see the ideal BCC(110) surface and the primitive real space translation vectors along with the LEED diffraction of a (1x1) reconstructed surface with interstitial contaminants. The interstitials fill the void space between chromium ions and that the LEED diffraction pattern indicates commensurate placement about the main diffraction peaks indicates that they are regularly spaced in the real latticec surface. Comparing the LEED diffraction patterns of Figure 8 and Figure 10 we see the effect of two surface reconstruction of the same sample as described above.

3.3. X-Ray Photo-electron Spectroscopy: XPS.

Photo-electron spectroscopy (PES) encompasses the photon energy specific techniques of X-ray and ultra violet (discussed in the next section) spectroscopies. The photo electric effect
describes the relation between the incident photon energy \( E_p = h\nu \) and the ejected electron’s kinetic energy. Incident photons, (see Figure 11), on a sample impart the total of their energy on valence and core electrons losing an amount equal to the binding energy \( E_B \) of the electron. Having lost an additional fraction, the work function \( \phi \), of the remaining kinetic energy to escaping the material surface, BE can be characterized in terms of the remaining kinetic energy \( KE \). The technique seeks to quantify the \( E_B \) through the relation 

\[
E_B = h\nu - KE - \phi. \quad (3.2.1)
\]

Measurement of the electron \( KE \) is the heart of data acquisition while correlation of the acquired \( KE \) is at the heart of data analysis. Through backfilling of electrons from a higher level, a secondary emission event occurs concurrently. The release of the energy difference can occur in the form of a photon or as an ejected electron (also detectable with the analyzer).

The ejected Auger electron \( KE \) is not dependent on \( h\nu \) from (3.2.1) but (Figure 11) from the difference in energy between the backfilled electron and the energy level of the emitted Auger electron or \( KE = (E_{1s} - E_{2p}) - E_{2p} \). More generally, \( KE_A = \Delta E_{bf} - E_A \).
### 3.3.1. Data Acquisition

Several configurations of analyzer are in use for PES. We will focus on the hemispherical analyzer that is used throughout this work. The PES process begins with the production of a photon that, in these experiments is either created by electron-excitation of either an Aluminum, $h\nu = 1486.6eV$ or Magnesium, $h\nu = 1253.6eV$ anode in the case of XPS or a, monochromatized synchrotron light source $2eV < h\nu < 2E9eV$ in the case of synchrotron XPS/XPD. In all cases the light source is fixed relative to the UHV chamber housing the sample, as is the analyzer itself. The sample is allowed to rotate and translate for purposes of aligning the incident photon and scattered electron beams in an appropriate geometry. Once this alignment is achieved, polar and azimuthal angles can be selected as needed.

Not unlike J. J. Thompson’s original experiment to measure the electrons charge ($q$) mass ($m$) ratio, the analyzer is designed to exploit the relation $m\vec{a} = q\vec{E}$ that is Coulomb’s law and centripetal force on the electron $m\vec{a} = m\frac{v^2}{r} = \frac{2}{r}KE \Rightarrow KE = \frac{qr}{2}|\vec{E}|$. If we fix the path radius ($r$) and its orientation with respect to the electric ($\vec{E}$) field, then there is a direct relation between the kinetic energy ($KE$) and the field within which the electron moves. This is a selection process; choose $|\vec{E}|$ to select any narrow band of K.E. or $d|\vec{E}| \propto dKE$

![Figure 12 Schematic of XPS components mounted on a UHV chamber. The angle between the EEA and the X-Ray source if fixed while the sample is mounted on a 5-axis sample mount.](image)
Figure 13 characterizes the electron’s path. Once ejected from the sample, the solid angle of current is narrowed by the acceptance angle of the entrance aperture and lensing system that channels the beam to the input segment of the hemispheres. This structure is constructed by two electrically isolated hemispheres of mean radius \(r\) that, with an applied potential, produce a uniform electric field to guide and select energy specific electrons towards the detector. Those electrons satisfying the expression \(KE = \frac{qr}{2} |\vec{E}|\) are counted by the detector.

The detector fitted in the laboratory configuration is constructed of an array of cascading electron multipliers (CEM) is a surface coated with a semiconductor material that relies on an amplified current produced by means of inelastic electron-electron interaction to detect the selected emission current. Free electrons to be counted collide with the inner surface of doped silicon coated glass fashioned in a semi-toroidal tube with an enlarged acceptance flange. The initial collision produces multiple (1-3) ejected electrons that in turn eject additional electrons. In this way the photo-emission current is correlated to the measured current.
and electron count rate (CPS). The electric field magnitude of the analyzer is stepped at regular intervals and a CPS vs. BE plot is created much like Figure 15.

Ultimately, it is necessary to calibrate the system. Since the analyzer, specifically the CEMs, have a work function of their own, this must be determined along with the sample under study. A standard technique is to reference both the sample and the analyzer at the same (0eV) ground potential which allows the sample and analyzer to share the same Fermi level. A potential difference ($\Delta \phi = \phi_s - \phi_a$) is then created. Accounting for this contact potential, (3.2.1) becomes $E_B = h\nu - KE - \phi_s - \Delta \phi$ or $E_B = h\nu - KE - \phi_a$. This implies that all one needs to know is the analyzer work function of the analyzer.

Considering the above discussion on surface modification and keeping in mind that XPS is surface sensitive, the final XPS spectra is that of the sample surface that may not represent the bulk.

![Figure 15 XPS spectra of a clean single crystal Cr(110) using photon energy of 690eV. Cr 2p spin-orbit splitting evident at high end of spectrum.](image)
3.3.2. Data Analysis

While the instrumentation is straightforward, the analysis can be cumbersome. Peak profiles manifest themselves on a multitude of parameters. Provided the light source has been monochromatized, emission from metallic samples of core states produce largely a symmetric Gauss/Lorentzian main line peak as the wave vector is interpreted as localized and the broadening of the peak then, for these core metallic states, is attributable to the core-hole lifetime convoluted with the analyzer response. Alternatively, if the light source is broad as well, then this will contribute the peak width. These emitted photo-electrons then must travel to the surface and other pathways are possible. First, there may be no interaction at all with the solid and the emission then is, as earlier describe, directly related to the KE and deemed a ‘main line’ peak. Secondly, in the excited state during photo-ionization, where there is a core hole that must be considered, the upper levels feel a higher potential due to the screening loss from the PE and in that state inelastic electron-electron interaction with the VB electrons in highly correlated systems produce electrons with KE less than the main line, hence higher BE. If the material is an insulator, then these satellite peaks have discrete energy levels and for metals the continuous band reveals itself as a main line peak tail towards high binding energy. Visible in the inset spectrum of Figure 15 is the spin-orbit splitting of Cr 2p. For the 2p orbital, the expected ratio of areas is 1:2 the energy splitting, along with the peak

![Figure 16 Chromium 2p 3/2 spectra. The peak is fitted with a main line emission peak (Violet), metallic peak (Blue) and shake up peaks at higher BE (Indigo & Red).](image)
profile and position of the peaks all report on the local environment of the chromium atom. The peak position (BE) is predominantly affected by the charge state and local environment of the bound electron however the crystal field and multiplet splitting also plays a part. The chromium metal sample spectra show the 3/2 peak position where expected ~574.4eV but with a broadening at the base, the latter due to lifetime broadening \( \Delta E \geq \frac{\hbar}{\tau} \) and instrumentation resolution. Ultra-pure chromium surface would depict a line shape more consistent with a Gaussian function, but the presence of nitrogen and carbon contribute to the chemical shift of these effected chromium atoms of a small but measurable secondary peak towards the higher BE representative of a higher charge state of Cr due to species of CrN (red) near 575.8eV and an additional higher BE peak possibly Cr2N. As an additional example, Figure 16 is a spectrum taken of a single crystal, Cr\(_2\)O\(_3\) (0001) surface. As expected, a dominant element to the line shape is a symmetric peak attributable to the Cr 3+ charge state (Violet). As an example of chemical shifts, due to incomplete oxidation of the metal substrate, there remains a Cr metal peak (Brown) at slightly lower BE and much reduced area. In the simplest of cases stated above, we declared that the BE of the ejected core electron is found by (3.2.1) however as stated above, if a core electron is removed, a core hole is left behind, and the screen provided by the ejected electron is gone thereby shifting final state energy (BE) levels higher. This can be alternately stated in a number of ways 1) The true BE of an electron cannot be measured, only the relaxed final state, 2) one can begin to approximate the BEs of the final state through not an atom with N electrons but N-1 electrons 3) The BE measured is then the difference in the total energy of the final state and the total energy of the initial state or \( E_B = E_f(N - 1) - E_i(N) \). Further final state effects can be seen in Figure 16 in the additional peaks found above the mail line peak of Cr3+. While first observed in oxygen, nitrogen dimers and NO, these multiplet splitting effects are also
evident in the transition metal oxides like Cr$_2$O$_3$. Unpaired d orbital electrons couple with unfilled valence orbitals via combinations of orbital and spin angular momentum producing multiple BE lines in the process.

3.4. Ultra-Violet Photo-electron Spectroscopy: UPS.

Providing an alternate light source in the configuration of XPS, namely an excited plasma of He 2, $hv = 21.22eV$, in the case of UPS allows for analysis of valence band states. Utilization of the emissions from H, He, Ne or Ar provides for light source in the energy range of 10-30eV although the usable energies due to the discretization of the emission lines force only the use of a handful of wavelengths. Where XPS probes through excitation of core electron levels, UPS has sensitivities in the VB to $E_f$ and as a probe for work function $E_f$ to $r \to \infty$. Where for main stream instrumentation, XPS touts resolution in the ~0.1eV range, at the lower BE scale and close to $E_f$, UPS can easily provide ~0.01eV. An order of magnitude better resolution is possible for both techniques given specialized equipment and procedures.

As is the case with all PES, sample sensitivity is governed by the inelastic mean free path. As a first approximation, the empirical expression from Seah and Dench$^{12}$ is utilized to predict the sampling depth of the solid surface which can range from a few atomic layers to a several nm in the case of hard x-rays.

Figure 17 Log-Log graph of the empirical IMFP vs. Electron energy function. The minimum resides at approximately 1.5 Angstroms.
UPS is utilized, as reported in the results section, to determine the occupation of VB d – orbits of the VTiO$_3$ thin film. This knowledge helps in qualifying the nature of the corundum structure.

### 3.5. X-Ray Photo-electron Diffraction: XPD.

Experimentally, XPD employs the same equipment as XPS with the additional ability to reliably position the sample to control the electron emission angle through useful polar and azimuthal angles and the improved functionality of a variable wavelength light source. Doing so exploits the localized scattering of electrons and the interference effects of electrons. The output then is a two-dimensional mapping ($\theta, \phi$) of diffraction modified photoemission intensities that can be correlated to an atomic structure model.

XPD is useful in determination of the local surface crystal structure as well as its chemical nature.

Referencing Figure 17, photon energies can be selected to augment the surface sensitivity of the technique. The scattering process begins by an excitation of a core electron (Figure 11) that can radiate uniformly away from the ion center. Nearby (see Figure 18) bound electrons can then be scattered through electron – electron interactions. After emission from the surface of the sample,
electrons interfere to produce the diffraction pattern via difference in path length. The scattering events are coupled through interaction on the local scale and naturally have equivalent kinetic energies and constant phase angle. Scattering amplitude as a function of scattering angle is predominantly a function of electron KE with high energy electrons favoring a forward scattering configuration. Low energies, while forward orienting, also demonstrate lateral and back scattering angles. The simple single electron scattering event then is used to consider multiple scattering in all directions. In concert, all of the above form to yield a surface sensitive (structural) technique that can be used say to determine the nature of epitaxial ad layers or the relaxation of the few atomic layers in front of forward scatted electron centers. Further complications exist when attempting to segregate a single surface layer with a slight shifted chemical signature and incoherent matching of the surface with respect to strongly forward scattered bulk signals. A small shift, as mentioned above, of surface layers due to the local environment can be difficult to segregate when the differencing BE between surface and bulk is only a few eV. Additionally, when strongly coupled, emitted electrons from lower well-ordered layers loose coherence with the surface layers then the diffraction pattern in no longer a simple superposition of scattering events.

Computer modeling for comparison to the diffraction patterns created by XPD in this work has been performed by EDAC simulations software and the author’s set of C language programs designed to average multiple domain terminations and mirror twins. The EDAC software is a multiple scattering and diffraction recursion process with approximations of the muffin-tin potential model applied to a parabolic atomic cluster typically of 600-1000 atoms. Multiple models are created simultaneously parameterizing inter layer spacing sequentially along the depth in an attempt to find the relaxation position of surface and near surface layers. Each
lattice spacing value generates an R-factor defined by: 

\[ R = \frac{\sum (\chi_{exp} - \chi_{sim})^2}{\sum [\chi_{exp}^2 + \chi_{sim}^2]} \]

that quantifies the difference between the experimental and simulated data from which, a the parameter corresponding to the minimum R value is chosen.

3.6. Atomic Force Microscopy

Atomic force microscopy is, at room temperature, an effective topographical mapping technique on the mesoscopic scale. The mechanisms of AFM exploit atomic force interactions between tip and sample. The van der Waals force describes the weak atomic force between nonbonding atoms and is given by the Lennard-Jones potential pictured in Figure 19. The sample/tip interaction is exploited during the approach of the silicon scanning tip as well as during imaging. As the tip approaches the sample surface, a deflection of the tip is felt as the tip nears the surface and this deflection is measured by a simple position sensitive photo-diode. In this work, measurements were made in what is commonly referred to as non-contact mode. In this state, the tip is resonated near its natural frequency and, once coupled to the sample, the driving force is maintained by adjusting the height (z) of the tip while scanning. The coupling of the tip and sample results in a feedback response in reaction to both the repulsive and attractive nature of the L-J potential during the tip oscillations. Height (z position) is correlated to the applied voltage for the cantilever deflection and an error signal associated with the applied voltage is also recorded for later analysis. In addition to height as a function of x/y position, the phase angle between the driving (control) and resonant (response) frequency is recorded. Combined, the z position, phase and error produce a topological map. Care must be taken when interpreting this topography as the tip/sample system is not only sensitive to surface structure but also contaminants that are plentiful since the measurement is made in ambient conditions.
Vibrations contribute to the source of error and if these restrictions can be overcome through the use of cleanroom conditions and vibration isolation methods then the limit to resolution falls on the tip profile and thermal contributions. In the case of the former, one considers that the imaging process is as much of a tip imaging as it is a sample imaging process. In the case of the latter, the thermal contribution practically limits the resolution to a few hundred nm at ambient conditions.

**Figure 19** The L-J potential predicts weakly attractive force at distances beyond the scale of atomic radii and strong repulsion at close proximity.

**Figure 20** The micro-spot laser reflects from and position is affected by the silicon tip that is allowed to defect in response to the sample surface. The change in position is recorded by the quadrupole photo-diode. GregorioW (CC-SA 3.0)
4. RESULTS

4.1. Epitaxial Corundum-\(\text{VTiO}_3\) Thin Films Grown on c-cut Sapphire

4.1.1. Introduction

Controlled synthesis of multicomponent transition metal oxides is a prerequisite for unlocking their many potential applications in energy production and storage. Growth of epitaxial films is one approach of utilizing a suitable substrate for stabilizing specific crystal structures. Sapphire (corundum \(\text{Al}_2\text{O}_3\)) substrates, because of their stability and availability in high surface quality and purity, is a common substrate for the growth of oxides with corundum-crystal structure. The corundum structure can be found for many oxides that have their cations in a \(3^+\) charge state. This includes \(\text{Fe}_2\text{O}_3\) (hematite), \(\text{Cr}_2\text{O}_3\), \(\text{Rh}_2\text{O}_3\), \(\text{Ga}_2\text{O}_3\), \(\text{V}_2\text{O}_3\) and \(\text{Ti}_2\text{O}_3\). Many of these transition metals, however, also exhibit multi-valences that allow them to form stable oxides with various other stoichiometries and structures. For example, for the afore mentioned oxides, titania prefers a \(4^+\) oxidation state and thus is commonly observed as \(\text{TiO}_2\) in either rutile, anatase, or brookite-structure. Vanadia, on the other hand exists with vanadium charge states between \(2^+\) and \(5^+\) with corresponding various crystal structures. The \(\text{VO}_2\) structure is isostructural to rutile and thus titania and vanadia share the same crystal structure for both their \(4^+\) and \(3^+\) charge states.

C-cut sapphire, i.e \((0001)\) orientation of \(\alpha\)-aluminia, has been used for growing several epitaxial corundum films [
with various physical vapor deposition techniques, indicating that the lattice-mismatch between the sapphire substrate and the film can be accommodated by formation of interface misfit dislocations. On the other hand, rutile-structured transition metal dioxides, e.g. TiO$_2$ [61, 62, 63, 64] and SnO$_2$ [65], can be grown on r-cut sapphire as epitaxial films with (011) orientation, because of similarities in the crystal lattices for these orientations. The stabilizing effect of the substrate is particularly important for oxides that can occur in different oxidation states and structures. For instance, V$_2$O$_3$ is grown successfully on c-cut sapphire if the growth conditions, in particular oxygen background pressure and temperature, during growth are chosen appropriately [66, 67, 68, 69, 70, 71, 72]. On the other hand, to our knowledge, corundum Ti$_2$O$_3$ has not been successfully grown in a good quality epitaxial film on sapphire, likely because of its preference to form Ti$^{4+}$. The only report for growth of epitaxial Ti$_2$O$_3$ is on Mo(110) [73].

In addition to single cation oxides, solid solutions [74, 75, 76] or structures closely related to the corundum structure, as for example the ilmenite structure, can be formed between oxides that condense in the corundum phase. For instance, the Fe$_2$O$_3$-Ti$_2$O$_3$ system forms the ilmenite-structure for a cation ratio of Fe:Ti=1:1. Ilmenite can be considered a corundum structure with an ordered cation sub-lattice. In addition, while both Fe and Ti are 3+ in their pure corundum phases, in ilmenite Fe reduces to 2+ and Ti oxidizes to 4+, which illustrates the preference of Ti to exist as 4+, while Fe exists in both 2+ and 3+ charge states, as for instance in magnetite-Fe$_3$O$_4$. Furthermore, Fe$_2$O$_3$ can form a solid solution with ilmenite, i.e. for a cation ratio of Fe:Ti > 1, which causes replacement of Ti-cation sites with Fe and thus re-introduction of Fe$^{3+}$. This has been investigated in epitaxial films on sapphire in view of its ferromagnetic properties [77, 78, 79]. Here we investigate if V$_2$O$_3$ and Ti$_2$O$_3$ also forms a solid solution corundum structures if grown on c-
cut sapphire with a 1:1 cation ratio. The goal of this study is predominantly to investigate if VTiO$_3$ film with corundum structure can be stabilized by epitaxial growth on a sapphire substrate.

Solid solutions of V$_2$O$_3$:Ti$_2$O$_3$ with corundum structure and without cation ordering have been reported by vacuum melting of oxides in the correct composition and oxygen concentration \[^{80, 81, 82, 83, 84}\]. For a V:Ti ratio of 1:1 a corundum unit cell of a=5.0174 Å, c=13.993 Å was determined. However, the V-Ti-O phase diagram is complex with many other possible structures \[^{26}\]. Mineral data indicate that other crystal structures are preferred, i.e. to our knowledge corundum VTiO$_3$ does not exist as a naturally occurring mineral. For the V-Ti-O system known mineral structures include berdsinskiite with a composition of V$_2$TiO$_5$ and schreyerite with a composition of V$_2$Ti$_3$O$_9$. In these minerals V adopts a 3+ valence-state, while Ti is 4+. Phase equilibria in the V$_2$O$_3$-TiO$_2$ system at 1200 °C was investigated by Brach et al. \[^{84}\]. In addition to berdsinskiite (V$_2$Ti$_3$O$_9$) they also found V$_2$Ti$_2$O$_7$, V$_2$Ti$_4$O$_{11}$, and V$_2$Ti$_6$O$_{15}$, which can be described as V(III)$_2$Ti(IV)$_n$O$_{2n+1}$. The schreyerite structure (n=5), with intermediate composition, was also found but was metastable under the experimental conditions. It has been shown that the crystal structures of all these different compositions are related. The non-berdsinskiite structures can be constructed from two basic ‘building blocks’—a berdsinskiite-type layer with V$_2$Ti$_3$O$_5$ and Ti$_2$O$_4$-layers with a structure related to the high pressure phase of TiO$_2$ with a α-PbO$_2$ structure. Periodic intergrowth of these layers thus then give rise to the different observed structures \[^{85}\]. These slabs can be expressed as $pV_2TiO_5 \square qTi_2O_4$. This allows one to derive the different phases; e.g. schreyerite may be expressed by $p$=1 and $q$=1 and as an alternating stacking of these layers. A composition of V$_2$Ti$_2$O$_7$ is obtained for $p$=2 and $q$=1, i.e. periodic stacking of two berdsinskiite-type V$_2$TiO$_5$ slabs and one Ti$_2$O$_4$ slab. Similar to the V-Ti-O system the (Cr,Fe)-Ti-O system shows the same structures of stacked slabs, i.e. (Cr,Fe)$_2$TiO$_5$ (berdesinskiite-type), (Cr,Fe)$_2$Ti$_2$O$_7$, \[^{ }\]
(Cr,Fe)$_6$Ti$_7$O$_{23}$, (Cr,Fe)$_4$Ti$_5$O$_{16}$, (Cr,Fe)$_2$Ti$_3$O$_9$ [86,87]. From the mineral data it is apparent that in these mineral compounds Ti exhibits a 4+ and V a 3+ charge state. To stabilize a corundum phase one of the two cations need to be in a lower oxidation state, which may be less favorable.

Growth of thin films can be very different from minerals or synthesis of bulk-structures close to thermodynamic equilibrium with a controlled amount of oxygen. While the oxygen background pressure enables some control over the oxygen concentration during film growth, it does not directly control its stoichiometry. Furthermore, in epitaxial grown films, lattice-matching conditions at the interface can result in crystal structures that are not necessarily known as equilibrium structures and thus provide a route for designing materials with desirable properties [88]. For instance for V-Ti-O on sapphire (0001) the monoclinic unit cell of the berdsinskiite-type slab does not give an obvious lattice matching condition with the hexagonal (0001) surface. The a-vector of sapphire of 4.75 Å may be reasonable close to the b-vector of schreyerite, but the diagonal of the hexagonal unit cell of sapphire is 8.22 Å, which is quite significantly different from the a-vector in schreyerite. Also because of the different symmetries (hexagonal vs. rectangular) of the substrate and the base-plane of the monoclinic structure, formation of rotational domains should occur in the grown film. Thus the lack of clear epitaxial relationships between known mineral structures of the V-Ti-O system and the substrate may favor the formation of a corundum phase mixed VTiO$_3$ structure.

In this study we show that corundum VTiO$_3$ can be indeed grown on sapphire (0001) while the charge state of V can be assigned a nominal charge of 3+ the x-ray photoemission (XPS) and electron energy loss spectroscopy (EELS) both indicate a mixture of 3+ and 4+, which may suggest excess oxygen within the film compared to stoichiometric VTiO$_3$. 

3
4.1.2. Experimental methods

The thin films are grown by laser-MBE using a solid state Nd:YAG laser (430 mJ power at wavelength of 355nm and 5 Hz repetition frequency) for ablation of a mixed TiO₂:V₂O₃ target. The target was made with a 1:1 cation ratio, pressed and then sintered in air at 650 °C for 10 hr. In addition a pure vanadium oxide target was used for growing V₂O₃ reference samples. The deposition rate was measured with a quartz microbalance and its accuracy was confirmed from film thicknesses of the grown films measured by transmission electron microscopy (TEM). Typical growth rates in our set-up were very slow at about ~6.0 nm/hour. The laser MBE chamber has a base pressure of 10⁻⁹ Torr, the oxygen background pressure was varied by leaking O₂ into the growth chamber. The pressure was measured with a nude ion gauge prior to deposition and kept constant during growth. C-cut sapphire substrates were annealed in air in a tube furnace to 1400 °C for 3 hours prior to mounting them on Ta-sample plate by spot-welding of Ta-strips at the corners of the substrate. Prior to film growth the substrate was annealed in the growth chamber at 750 °C in 2.0 x 10⁻⁶ Torr O₂ for 1 hr. The substrate growth temperature and oxygen background was maintain during growth at 750 °C and 2.0 x 10⁻⁶ Torr O₂, respectively. The growth chamber is also equipped with a reflection high-energy electron diffraction (RHEED) system. The RHEED characterization was only performed after the chamber was evacuated and the sample cooled down. For characterization of the film by XPS the sample could be transferred from the growth chamber to an XPS analysis chamber without breaking vacuum. This analysis chamber was equipped with a dual anode (Al, Mg) x-ray source and hemispherical analyzer. A somewhat better resolution XPS system with a 7-channel Omicron Sphera EA 2000 Analyzer was available in another UHV system. The sample could be transferred to this chamber via a vacuum suitcase that maintained a vacuum of ~ 10⁻⁸ Torr during transfer. In addition to XPS, the other chamber was
also equipped with ultra violet photoemission utilizing a VUV He-lamp. Generally, thin films grown on sapphire suffered from charging effects in photoemission studies. Referencing the core-level positions to the O-1s binding energy allowed some comparison of the relative binding energies, however, analysis clearly suffered from the assumption that the O-1s binding energy is the same for all oxides. In all the data analysis the O-1s binding energy has been set to 530 eV.

In addition to in vacuum characterization, the samples were also characterized ex-situ with x-ray diffraction using a θ - 2θ geometry and by atomic force microscopy in tapping mode. Moreover, samples were characterized by transmission electron microscopy (TEM) at the Center for Functional Nanomaterials at Brookhaven National Lab using a FEI Titan 80-300 Cs-corrected TEM. TEM images and electron diffraction patterns were measured on thin cross-sectional TEM samples prepared by lift-off and thinned by FIB. Electron energy loss spectroscopy was performed in a Hitachi HD2700C dedicated Scanning TEM (STEM) at a collection angle of 15 mrad.

4.1.3. Results

We have previously grown rutile and anatase TiO$_2$ epitaxial films on r-cut sapphire and LaAlO$_3$(100) substrates, respectively [61,62]. These samples provide reference spectra for Ti$^{4+}$ measured with the same instrument. Although several reports for the growth of corundum V$_2$O$_3$ on sapphire(0001) already existed, we first examined the growth of vanadia in order to determine the growth conditions for corundum V$_2$O$_3$ in our experimental set-up and to obtain reference XPS and RHEED pattern. Subsequently, we grew VTiO$_3$ under the same conditions.
Figure 22 shows a comparison of the RHEED pattern for the sapphire substrate, V_2O_3 and VTiO_3 films along the (1-210) and (10-10) directions of the sapphire substrate. The V_2O_3 and VTiO_3 was grown with an oxygen background pressure of 2.0 x 10^{-6} Torr and a substrate temperature of 750 °C. For both V_2O_3 and VTiO_3 a similar streaky RHEED pattern is obtained, indicative of an epitaxial growth. However, a comparison of the RHEED patterns clearly shows that the V_2O_3 has a sharper diffraction pattern compared to VTiO_3 indicating a better-ordered surface for V_2O_3. Cross-section of the streaks and comparison to the Al_2O_3 substrate allows an estimate of the lattice constants parallel to the surface as summarized in Figure 22.

Figure 21 shows an AFM image of the VTiO_3 confirming that the films are very flat with rms-roughness of ~0.2 nm, in agreement with the streaky RHEED pattern. The AFM image also shows
small terraces with irregular step edges. This surface morphology makes it impossible to measure any reliable step height in AFM and the small terraces may contribute to the less defined RHEED pattern compared to V$_2$O$_3$.

Confirmation of the c-axis oriented corundum structure for our VTiO$_3$ films also comes from XRD of a 20 nm thick film Figure 23 shows a large angle scan of the clean alumina substrate and after film growth. The only additional diffraction peaks present after film growth are at 2$\theta$ = 39.88° and 79.76° and can be assigned to the (000 6) and (000 12) peak of the corundum structure with R-3c symmetry. Thus XRD shows that VTiO$_3$ has the corundum structure with a c-axis of 13.88 Å. This is only less than 1% smaller than the reported bulk value for corundum VTiO$_3$ or 13.99 Å. A similar decrease in the lattice constant for thin films grown on sapphire was reported for V$_2$O$_3$. Yamaguchi [89] et al. report a c-lattice constant of 13.87 Å for V$_2$O$_3$ compared to the bulk value for V$_2$O$_3$ of 14.01 Å. [90,91]

Final evidence for the corundum structure of the film is provided by TEM images and diffraction patterns. Cross-sectional (XTEM) images of the film shown in Figure 24(b) reveal a mostly single crystalline VTiO$_3$ film. Small regions, indicated towards the top of Figure 24(b), containing inclusions of a different structure or rotated grains are, however, observed. In order to
obtain detailed information of the alignment of the film with respect to the substrate and also to gain additional measurements of the lattice spacing, we compare the diffraction pattern of the Al₂O₃ substrate alone (Figure 24(c)) with that of the substrate plus film (Figure 24(d)). The diffraction patterns differ only in the lattice constants confirming that the Al₂O₃ substrate and the VTiO₃ film are aligned along the [001] and [210] directions. The alignment of the unit cells of the substrate with those of the film indicates that the film grows as an epitaxial film. Using the diffraction spots of the Al₂O₃ substrate as a scale-bar ($c_{\text{Al}_2\text{O}_3} = 12.99 \, \text{Å}$ [Ref 35]) enables us to determine the c spacing for the VTiO₃ as 13.92Å, which compares well to the value derived from XRD.

The structural analysis of the films indicate that we succeeded in growing c-axis oriented corundum VTiO₃. The main question that remains is the respective charge state of the cations in

![Figure 24 TEM analysis of VTiO₃ film on c-cut sapphire. (a) Interface between sapphire and VTiO₃ film. The scale bar is 2 nm. (b) Higher resolution image of the VTiO₃ film. In the upper region an inclusion of a rotated grain or secondary phase is visible. The scale bar is 1nm. (c) and (d) Diffraction pattern of just the sapphire substrate and sapphire substrate plus VTiO₃ film, respectively. In (d) the comparison between the substrate and film diffraction spots enables to estimate the lattice parameters for the film.](image)
this compound. To this end we performed STEM- electron energy loss spectroscopy (EELS) of the Ti-L_{2,3}-edges and XPS analysis. Figure 25(a) shows our experimental spectrum in comparison of two reference data for Ti^{4+} in SrTiO\textsubscript{3} and Ti^{3+} in LaTiO\textsubscript{3}[\textsuperscript{92}]. Neither of the two reference spectra fit our experimental result well. In order to provide a reasonable match a weighted sum of the reference spectra are calculated and a best match with the experimental data are obtained for a 1:1 (Ti^{3+}:Ti^{4+}) ratio as shown in Figure 25(b). Thus EELS measurement indicate that both Ti^{3+} and Ti^{4+} cations are present in the film.

![Figure 25](image.png)

Figure 25 TEM-EELS Ti-L\textsubscript{2,3} edge analysis of V\textsubscript{3}O\textsubscript{3} film. (a) the experimental data (black circles) is compared to reference spectra for typical Ti^{3+} and Ti^{4+} compounds, i.e. from LaTiO\textsubscript{3} (red), SrTiO\textsubscript{3} (blue)[\textsuperscript{36}]. The experimental spectrum is best reproduced by a weighted sum is shown as a black solid line. TEM-EELS Ti-L\textsubscript{2,3} edge analysis of V\textsubscript{3}O\textsubscript{3} film. (a) the experimental data (black circles) is compared to reference spectra for typical Ti^{3+} and Ti^{4+} compounds, i.e. from LaTiO\textsubscript{3} (red), SrTiO\textsubscript{3} (blue)[\textsuperscript{92}]. The experimental spectrum is best reproduced by a weighted sum of these two reference spectra with a 1:1 ratio. This weighted sum is shown as black solid line. The ratio that best represents our data has been evaluated by calculating the mean square error, \( \text{MSE} = \frac{1}{n} \sum_{i=1}^{n} (x_e - x_o)^2 \), between experimental data and the spectra composed of different weighted sums of the reference spectra. The minimum in the MSE is found for 1:1 ratio as shown in (b).

XPS measurements for V-2p are shown in Figure 26(b) for V\textsubscript{2}O\textsubscript{3} and V\textsubscript{3}O\textsubscript{3} for the as grown samples. The peak shape and position agrees well with literature reference data for V\textsuperscript{3+} [\textsuperscript{93} 94 95 96 97 98 99 100 101]. All the peaks are referenced to the O-1s peak. The many oxidation states of vanadium and the existence of vanadium oxides with mixed valence states complicate the interpretation of the vanadium core levels. However, both the pure vanadia and the V\textsubscript{3}O\textsubscript{3} films exhibit identical line shapes and this line shape has the best match with V\textsubscript{2}O\textsubscript{3}, i.e. 3+. Thus, as
previously shown, corundum vanadia can be grown on c-cut sapphire and the VTiO$_3$ also exhibits a 3+ charge state. Both V$_2$O$_3$ and VTiO$_3$ behave similar and for annealing temperatures higher than 850 °C in UHV a lower binding energy shoulder develops (not shown) that indicates a reduction of the film and formation of V$^{2+}$ and/or metallic V.

The Ti-2p peak for the VTiO$_3$ film is shown in Figure 26(a). In addition, we also show the Ti-2p for an anatase film grown and characterized in the same instrument. Again the peaks are aligned so that the O-1s peak overlap. The Ti-2p peak of the VTiO$_3$ sample is clearly broader than that of TiO$_2$ with significant additional spectral weight on the low binding energy side. In order to fit this peak we assume two components, one component was chosen to be identical to the Ti$^{4+}$ measured in our TiO$_2$ references samples, i.e. a peak with binding energy at 458.7 eV, FWHM of 1.2 eV and a spin orbit splitting of 5.7 eV, and a second component to account for the broadening of the Ti-2p peak towards low energy binding energy. This second component could be fit with a binding energy of 457.7 eV and a FWHM of 1.6 eV, as shown in Figure 26(a). The area ratio of the two components is obtained to 1.16. Standard reference spectra of Ti$^{3+}$, for instance in Ti$_2$O$_3$ [102], are even broader and the low energy components are in between 546.8 and 457.8 eV.
A recent study on LaTiO$_3$, which exhibits Ti in a 3+ charge state, showed that in such a clear 3+ compound the Ti-2p spectrum shows a strong ‘4+’ component [106]. This has been explained by final state effects in XPS measurements and consequently it was concluded that the presence of the ‘Ti$^{4+}$’ component may not necessarily indicate presence of 4+ cations in the material. Instead a ‘4+’-component in XPS may be (partially) attributed to final state effect for a compound with Ti in a 3+ state. Regardless of the origin of the lower binding energy component, the low binding energy component of Ti-2p is at a relatively high binding energy for a Ti$^{3+}$ cation, suggesting that it may be in an intermediate charge state compared to nominal 3+ and 4+. Further evidence for some Ti$^{3+}$ species in the film, can be found by inspection of the valance band spectra from UPS measurements shown in Figure 27. This measurement indicates that the 3d states are indeed occupied, suggesting a Ti$^{3+}$ state. Figure 27 compares the UPS spectrum for our VTiO$_3$ film with those of vacuum-cleaved V$_2$O$_3$ [ ] and Ti$_2$O$_3$ [ , ]. Because of charging effects, the Fermi-level in our spectrum could not be experimentally determined and thus the Fermi-level was set to the lowest binding energy at which photoemission intensity was measured. For all three spectra shown in Figure 27, the valence band spectrum can be nominally divided into occupied transition
metal 3d-bands close to the Fermi-level and O-2p derived valence band below 2 eV binding energy. Interestingly the VTI\(_3\) O-2p band appears at significantly (~1eV) lower binding energy than both Ti\(_2\)O\(_3\) and V\(_2\)O\(_3\) reference spectra.

**4.1.4. Discussion**

All the structural probes, i.e. RHEED, XRD, and TEM, demonstrate that the VTI\(_3\) films condense in a primarily c-axis oriented corundum structure under the low oxygen growth conditions on Al\(_2\)O\(_3\)(0001). This suggests that the film should have a VTI\(_3\) composition. The main challenge is in describing the charge state of the cations. XPS of V can be satisfactorily described as a 3+ charge state. However both EELS of the Ti- L\(_{2,3}\) edges and Ti-2p XPS do not show a clear 3+ charge state for Ti compared to reference spectra. While the EELS spectra may be explained by a fractionalization of the Ti-ions in 3+ and 4+ cations and thus obtaining a spectrum that is a super positioning of the individual spectra, this approach is not possible for Ti-2p XPS. Although the XPS spectrum of Ti\(^{3+}\) is somewhat controversial, it has been shown for LaTiO\(_3\)\(^{[106]}\) and also for Ti\(_2\)O\(_3\)\(^{[107]}\) that it should consist of two components with a low binding energy peak attributable to d\(^1\) at 456.9 eV and a second peak (d\(^{9}\)) at higher binding energy of 458.4 eV. The latter is close to that of Ti\(^{4+}\) and may be consequence of final state effects in XPS. The Ti-2p XPS for VTI\(_3\) is also best fit with two components, where the high energy component (458.7eV) is very close to that reported above but the low energy component at 457.7 eV is somewhat higher in energy than the reports for other Ti\(^{3+}\)-compounds. Consequently, because of the lack of a clear Ti\(^{3+}\) low binding energy component, the spectrum may not be explained by a mixture of Ti\(^{3+}\) and Ti\(^{4+}\) cations. Instead we propose that the Ti-cations must exist in an intermediate charge state, which implies some electron transfer from Ti to V compared to the pure corundum Ti\(_2\)O\(_3\) and V\(_2\)O\(_3\) compounds. Such an intermediate charge state of Ti may also explain the EELS data. An alternative explanation
to an intermediate charge state may be that the film can accommodate excess oxygen at for example interstitial sites. Such excess oxygen can lead to oxidation of Ti$^{3+}$ in a stoichiometric VTiO$_3$ film to Ti$^{4+}$. Such a mechanism of interstitial oxygen has been recently demonstrated in the perovskite NdTiO$_3$ [108].

The valence band of VTiO$_3$ exhibits a few interesting variations compared to the electronic structure of the two pure mother compounds, i.e. corundum V$_2$O$_3$ and Ti$_2$O$_3$. Generally the valence band for octahedrally coordinated V or Ti oxides consists of an O-2p derived band at binding energies higher than ~ 2eV and partially occupied transition metal 3d $t_{2g}$ states close to the Fermi-level. Comparison of the UPS spectra for VTiO$_3$ with those previously reported for Ti$_2$O$_3$ and V$_2$O$_3$ shows a clear difference in the binding energy of the predominantly O-2p states. In VTiO$_3$ the O-2p states are significantly shifted to lower binding energy with a band onset at ~ 2.5 eV, as shown in Fig.7 (a). This is a significant band bowing compared to the O-2p band onsets of 3.5eV and 4.0eV in V$_2$O$_3$ and Ti$_2$O$_3$, respectively. Since we only measure the occupied states, this shift may not necessarily indicate a band gap narrowing, but may be related to a shift of the Fermi-level with respect to the 3d $t_{2g}$ states.

The electronic structure of both V$_2$O$_3$ and Ti$_2$O$_3$ has been intensively studied because of the prototypical role V$_2$O$_3$ plays as the Mott-Hubbard system and its metal-insulator transition at 168 K. In contrast to V$_2$O$_3$, Ti$_2$O$_3$ shows a gradual metal-insulator transition between 400 and 600 K. The differences between these isostructural compounds may be partially explained by the bonding between cations across the octahedral faces of the metal 3d states [109]. The standard energy level diagram for V$_2$O$_3$, shown in Figure 27(b), was proposed by Castellani et al. [110]. The octahedral coordination of the metal site causes a splitting of the 3d states into lower $t_{2g}$ and higher $e_g^\sigma$ levels, which split further due to trigonal symmetry into $a_{1g}$ and $e_g^\sigma$ states. Thus the distinct two
states observed for the occupied states in UPS measurements of V$_2$O$_3$ may be assigned to the $a_{1g}$ and $e_g$ (see Figure 27(a)). In contrast, UPS for Ti$_2$O$_3$ [102] only exhibits one peak that is consequently assigned as the $a_{1g}$ state, consistent with the energy level diagram proposed by Van Zandt et al. [111]. As in V$_2$O$_3$ the $a_{1g}$ facilitate bonding between Ti-Ti pairs in the face sharing octahedral, however, unlike V$_2$O$_3$ an energy gap is proposed between $a_{1g}$ and $e_g$ with the Fermi-level in between. This causes the insulating phase of Ti$_2$O$_3$ and only at higher temperature an overlap of these states occur giving rise to the gradual transition to a metallic phase. Eyert et al. [109] speculated that this gap is a consequence of the stronger cation-cation bonding in Ti$_2$O$_3$ than in V$_2$O$_3$. In their computational study they showed that a similar gap between $a_{1g}$ and $e_g$ can be induced in V$_2$O$_3$ by reducing the V-V separation by 10% and thus increasing the V-V interactions.

In experiments the cation bonding may not that easily changed as in a computational study, but in the new VTiO$_3$ compound we may have two effects that increase the cation interaction through the shared octahedral face. Firstly, XRD and reference data show that the c-axis of VTiO$_3$ is minutely smaller than that for V$_2$O$_3$ and thus we have a slightly reduced cation-cation separation, and secondly, the purely V-V pairs are replaced by V-Ti pairs (or if we assume a random distribution of V and Ti in the cation sub-lattice we should observe random pairs of V-Ti, V-V and Ti-Ti) with potentially stronger cation-cation bonding. UPS spectra of VTiO$_3$ shows a single component which we assign to $a_{1g}$ state and thus an electronic structure more similar to Ti$_2$O$_3$ than to V$_2$O$_3$. However, comparison with Ti$_2$O$_3$ spectra also shows that the peak for VTiO$_3$ is broader which may be a consequence of randomness of the cation pairs. Another similarity to Ti$_2$O$_3$ is the onset of the spectrum close to the Fermi-level. As discussed above, Ti$_2$O$_3$ possesses a small band gap at RT between the occupied $a_{1g}$ and the empty $e_g$, while V$_2$O$_3$ is metallic at RT. This is represented in the reference UPS spectra by the fairly sharp onset of density of states at the Fermi-

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level for V₂O₃ while the spectral intensity for Ti₂O₃ is suppressed close to the Fermi-level. The spectrum for VTiO₃ shows the same suppression as Ti₂O₃, thus suggesting that VTiO₃ may have the same splitting and gap between $a_{1g}$ and $e_g^x$ states. Thus one may expect that VTiO₃ behaves more similar to Ti₂O₃ than V₂O₃ and we speculate that it may also show a gradual metal-insulator transition at higher temperatures. Above we concluded that the Ti-oxidation state is in between 3+ and 4+, which in turn suggests that the 3d states of Ti are not occupied to the same level as they are in Ti₂O₃. The cation-cation interaction through the $a_{1g}$ states may facilitate the charge transfer in V-Ti pairs and thus implying that the observed $a_{1g}$ is predominantly V-derived.

### 4.1.5. Conclusions

We successfully grew c-axis oriented VTiO₃ epitaxial films on c-cut sapphire by laser MBE. Although bulk corundum VTiO₃ samples were previously grown as bulk samples under controlled oxygen fugacity, this is the first report that this material can be grown as thin films. The epitaxial relationship to the c-cut alumina substrate is believed to play an important role in stabilizing the growth VTiO₃ and avoiding of formation of other VTi-oxide compounds known to exist as minerals.
4.2. Comparison of surface structures of corundum Cr$_2$O$_3$(0001) and V$_2$O$_3$(0001) ultrathin films by x-ray photoelectron diffraction.

4.2.1. Introduction

Many sesquioxides condense in the corundum structure\textsuperscript{15, 16, 17, 18, 19, 20}, of which chromia and vanadia are two examples. While these oxides have the same bulk structure they differ in their surface structure. Moreover the surface composition has been shown to depend on the oxygen chemical potential of the system\textsuperscript{21-26} and thus may vary with temperature and oxygen pressure. For oxide growth and characterization of single crystal surfaces low oxygen pressures in ultra-high vacuum systems are common and thus the relevant surface structures under these conditions are those under low oxygen chemical potential, which should result in a stoichiometric or transition metal-rich surface composition, rather than oxygen-rich surface terminations. Different surface structures have been proposed based on experimental studies and/or density functional theory (DFT) simulations. Figure 1 shows models of the most commonly discussed surface structures. Fig 1(a) and (b) show bulk truncations with oxygen or metal termination, i.e. an oxygen or metal rich surface. In addition to the bulk truncations, models for which non-bulk sites are occupied have been discussed, e.g. metal atoms can occupy ‘interstitial’ sites in the near surface layer and it has been suggested that sub-surface metal atoms may ‘rise’ from the bulk into these interstitial sub-surface sites as illustrated in Fig. 1(c).
Similarly, in this paper we propose a structure with all subsurface sites occupied including ‘interstitial’ sites near the surface with excess metal, as shown in as shown in Fig. 1(d). Finally, a common surface structure that has been discussed extensively in the literature, particularly for the V$_2$O$_3$(0001) surface, is a surface terminated by double bonded oxygens coordinated to a single metal atom, so called chromyl or vanadyl groups. Such a surface structure is illustrated schematically in Fig. 1(f). The vanadyl terminated V$_2$O$_3$ has been proposed in many experimental studies\textsuperscript{27 28 29 30 31} but recently this was questioned by Window et al.\textsuperscript{32 33} and Kroeger et al.\textsuperscript{34} based on scanned-energy mode photoelectron diffraction\textsuperscript{35} and instead a model similar to that shown in Fig. 1(e) was suggested. For Cr$_2$O$_3$(0001) surfaces, fewer studies have been reported. A quantitative LEED I-V analysis\textsuperscript{25, 26} of Cr$_2$O$_3$ single crystal surface suggested the most stable surface is the half metal termination. On the other hand, surface x-ray diffraction by Bikondoa\textsuperscript{22 23} et al. suggested a structural model related to the one shown in Fig 1(b) under UHV conditions. Only at higher oxygen pressures of 1 x 10\textsuperscript{2}-mbar were partial occupancy chromyl terminated surfaces found.

In this communication we are investigating the surface structures of

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Figure 28 Models of (0001) corundum-oxide surfaces in top- and side-view. a) bulk oxygen terminated; b) bulk metal terminated; c) extra interstitial metal in first layer compensated by metal vacancies in second metal layer (indicated by open circles); d) same as c) but without subsurface vacancies; e) partial metal termination; and f) surface with double bonded oxygen (chromyl/vanadyl groups).
Cr$_2$O$_3$(0001) surfaces that are formed by oxidation of a Cr(110) single crystal under low oxygen pressures inside a UHV chamber. The formation of such surfaces has been previously discussed by several groups$^{36,37,38,39}$ using similar preparation conditions as those discussed below. After characterizing the Cr$_2$O$_3$ surface, we use it as a substrate to grow epitaxially the isostructural V$_2$O$_3$ ultrathin film. Previous experimental$^{40}$ and DFT$^{41}$ calculations show that vanadia has a lower surface energy than chromia and thus no surface segregation of chromia is expected. This allows us to characterize the surface structure of these few monolayer thick vanadia films and compare the surface structures of both chromia and vanadia ultrathin films in the same experiment. Here we employ angle-scanned x-ray photoelectron diffraction (XPD) using synchrotron soft-x-rays for the structural probe. Angular scans$^{21,42}$ and 2D mapping$^{43}$ of XPD intensity studies of these surfaces are rare and have mainly employed lab x-ray sources with less surface sensitivity and thus they could not reach meaningful conclusions about the surface structure. The results from our study confirm the vanadyl termination for the V$_2$O$_3$(0001) ultrathin films, while the experimental data for the Cr$_2$O$_3$(0001) surface are best reproduced with an oxygen terminated surface. Such an oxygen rich surface may be, however, unrealistic under UHV conditions and thus a stoichiometric model with interstitial metal sites occupied in the second layer is proposed, which gives similar good agreement with the experiment.

4.2.2. Experimental procedures

All the sample preparations and characterizations were conducted at the SuperESCA beamline at the Elettra synchrotron in Trieste, Italy. Throughout the experiments the Cr(110) single crystal was inside the UHV end-station of the beamline with a base pressure of 1 x 10^{-10} mbar.
4.2.3. Sample preparation

The Cr(110) crystal was cleaned by cycles of 2.0 keV Ar⁺ hot sputtering at 1000 K. Sputtering is halted and annealing is allowed to continue to recrystallize the surface. Periods of hot sputtering and annealing last 20 minutes each. After a final annealing, the sample is allowed to cool and a final flash anneal occurs to 1100K. Chromium is notoriously difficult to clean because of nitrogen and carbon impurities in the bulk. Because of these impurities even after 20 cycles nitrogen could still be detected in XPS. These nitrogen impurities also give rise to superstructure spots and streaky LEED patterns that are well documented in the literature because of the formation of surface nitrides. This LEED pattern is shown in Fig. 2(a). Procedures for the formation of a Cr₂O₃(0001) thin layer on Cr(110) have been previously discussed in the literature. Our procedure follows these accounts. Briefly, the chromium crystal is flash annealed to 1100K and then oxidized in stages. Oxygen is backfilled to 1 x 10⁻⁶ mbar with sample held at 550K for 1 minute, then heated to 800K for 2 minutes. The sample is allowed to cool under UHV and then flash annealed to 1000K. After oxidation, nitrogen could not be detected in soft-XPS and LEED exhibited a hexagonal pattern, shown in Fig. 2(b) as expected for a Cr₂O₃(0001) surface. The absence of nitrogen indicates that any surface nitride is replaced with a pure oxide layer.
The Cr₂O₃ thin film on Cr(110) was used as a substrate to grow thin vanadia films. Both oxides condense in the corundum structure and are closely lattice matched as their lattice constants shown in table 1 indicates and therefore a formation of an epitaxial vanadia film on chromia is expected.

![Figure 29 LEED characterization with 120eV electron energy of (a) Cr(110) surface after cycles of hot sputtering and annealing and (b) after oxidation described in text. The sputtered and annealed surface is not clean and exhibits complex superstructure spots due to nitride formation. After oxidation a hexagonal LEED pattern is observed consistent with the formation of an epitaxial Cr2O3(0001) surface.](image)

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<td>4.9717 Å⁵⁰</td>
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Table 1 comparison of lattice constants of chromia and vanadia.

Vanadia films are grown by vapor deposition of vanadium from a water cooled e-beam evaporator in a 1.0 x 10⁻⁷ mbar O₂ background pressure. After deposition of vanadia, the film is annealed in 1.0 x 10⁻⁷ mbar O₂ background pressure to 730 K.
4.2.4. X-ray photoelectron spectroscopy and photoelectron diffraction

Core level spectra, both high resolution (HR-XPS) and fast-XPS were measured at normal and grazing angle emission typically at photon energies of $h\nu = KE + 110\text{eV}$ in order to exploit surface sensitive measurements by minimizing the inelastic mean free path. Spectra were acquired at the SuperESCA beamline at the Elletra Synchrotron\textsuperscript{51}. The UHV chamber is equipped with a hemispherical analyzer and fitted with an in house made designed delay-line detector. The incident beam and analyzer positions are fixed while the sample is adjust on a 5-axis mount in order to adjust emission angle. HR-XPS spectra are fitted with a Shirley background and one or more Gauss-Lorentz (30) symmetric peaks. Binding energy calibrations were performed by comparison to the clean Chromium metal Fermi Level and by the binding energy of the bulk chromia O 1s main line.

The structure of the films and their surfaces is assessed by XPD. For XPD we acquired core-level intensities over polar angles varied from normal emission to 70 degrees. Azimuthal segments of 160 degrees were measured for the Cr 2p\textsuperscript{3/2} core level and 90 degrees for the remaining oxygen and vanadium spectra. These are then plotted as a function of intensity in a 2D polar plot.

For the XPD measurements we subtract a linear background and keep the separation and FWHM of the peak components fixed. The total peak area of the two components is plotted as a stereographic projection as a function of emission by implementing the modulation function

$$\chi = \frac{I(\theta, \phi) - I_0(\theta)}{I_0(\theta)}$$

(1)

to obtain the XPD plot where $I_0$ is in the average intensity along the full azimuthal line scan at a fixed polar angle.
4.2.5. EDAC simulations

In order to relate the XPD patterns to surface structures we performed systematic electron multiple scattering simulations implemented in the EDAC code\textsuperscript{14}. We considered models displayed in Fig. 1 and systematically varied atomic-layer separations normal to the surface to optimize the agreement between measured and simulated XPD patterns. Since the sample exhibits two equivalent rotational domains with respect to the substrate rotated by 60°, the simulated XPD pattern was averaged over two 60° rotated patterns. In addition, the triple layer repetition normal to the surface is taken into account by calculating each possible termination and averaging weighted equally among the six possible contributions. The agreement between experiment and simulations was adjudged from the $R$-factor defined by:

$$R = \frac{\sum (\chi_{exp} - \chi_{sim})^2}{\sum [\chi_{exp}^2 + \chi_{sim}^2]} \quad (2)$$

4.2.6. Results and Discussion

The XPS analysis and XPD patterns for Cr$_2$O$_3$(0001) and ultrathin V$_2$O$_3$(0001) films are discussed separately. In both cases we only show the results for the models that give the best match with the experiments. In the supplementary information we show EDAC simulations for other commonly discussed models with their optimized atom separations and corresponding $R$ factors.
4.2.6.1. **Cr$_2$O$_3$(0001)**

For the Cr$_2$O$_3$ film we monitored the O 1s and the Cr 2p$_{3/2}$ core levels. Normal emission spectra of these core levels are shown in Fig. 3 (a) and (b), respectively. The peak shape of Cr 2p is complex but has been previously discussed in detail$^{52, 53, 54, 21}$. The chromium oxide peak can be fitted by 4 components with the main photoemission line of Cr 2p$_{3/2}$ at BE= 576.3eV and three shake-up peaks at 577.5, 578.5 and 579.3 eV. At normal emission, a weak metallic component is observed due to emission from the substrate. This shoulder may be due to some islanding of the Cr$_2$O$_3$ layer as previously observed in STM$^{39}$ and thus may originate from the Cr-substrate between the islands. For XPD only the two main components at BE= 576.3 and 577.35eV are taken into account that comprise 98% of the peak intensity. As we discuss below, interpretation of the XPD pattern for Cr$_2$O$_3$ requires that the chromia film is at least 0.8 nm thick. To fit the O oxygen as it increases at grazing emission angles. A small peak at high binding

![Figure 30 XPS and XPD characterization of Cr$_2$O$_3$ sample. (a) The O 1s peak measured with hν= 645 eV in normal emission. (b) high resolution Cr 2p/2 peak, fitted with a Cr$^{3+}$ main peak and three additional shake-up satellites. At low binding energies a small shoulder is assigned to metallic Cr from the substrate. (c) XPD pattern for O 1s of the Cr$_2$O$_3$ sample. Experimental data for a 90° azimuthal section and polar angle from 0 to 70° is shown in ‘gold’ overlaid on the multiple scattering simulations for the model described in Fig. 4 (a). (d) XPD pattern for the Cr 2p$_{3/2}$ experimental data for a 160° azimuthal section and polar angle from 0 to 70° overlaid in ‘gold’ on the multiple scattering simulations for the model described in Fig. 4 (a). (e) O1s experimental data overlaid on simulated data shown is for the stoichiometric surface model of Fig. 4 (b). (f) Cr 2p$_{3/2}$ experimental data overlaid on simulated data shown in (b) is for the stoichiometric surface model of Fig. 4 (b). Corresponding R-factors are indicated in the sub-figures.](image)
energy (532 eV) is assigned to a surface contaminant, likely hydroxyls. 1s peak in Fig. 3(a) at least two components are needed, i.e. in addition to the main O 1s peak a smaller component at lower binding energy is observed. This component is assigned to surface

The O-1s XPD superimposed on the corresponding EDAC simulation is shown in Fig. 3(c). Figure 3 (d) shows the experimental XPD pattern for Cr 2p on the corresponding EDAC simulations for the optimized model, shown in Fig. 4 (a). The atomic model that gives the best match with the experiment is that of a bulk truncated crystal with an oxygen surface, i.e. the structure shown in Fig. 1(a). To minimize the R factor the atoms in the surface layer are relaxed normal to the surface and the atom relaxations compared to bulk Cr$_2$O$_3$ are indicated in Fig. 4(a). The R factors for the simulations of this model are 0.27 and 0.22, for the Cr 2p and O 1s models respectively. While this model gives the lowest R factor, the oxygen terminated surface would suggest an oxygen rich surface layer. This seems rather unlikely considering the preparation under very low oxygen pressures in UHV, which usually leads to a stoichiometric or even metal-rich surface. Therefore, we consider other models that exhibit similar atom configurations but are stoichiometric in the surface. Structures with chromium in the very surface layer, such as those illustrated in Fig. 1 (b) or (e), or chromyl terminated surfaces (Fig. 1(f)) give no good agreement with the experiments (see supplement). The model in Fig. 1(c) was previously considered$^{55}$ and has occupied interstitial sites in the first chromium layer, however, these chromium atoms have been pulled up from the second chromium layer of the bulk, so that the overall surface composition has not been changed, but remains oxygen rich. Instead we propose a model where the bulk composition of the second Cr-layer is not changed but the ‘interstitial’ sites in the first
layer are occupied. This is the model illustrated in Fig. 1(d). This model gives a stoichiometric surface. EDAC simulations of this structure for O 1s and Cr 2p are shown in Fig. 3 (e) and 3 (f), respectively, with our experimental data superimposed.

The R factor for the model in Fig. 4(b) is only slightly worse than the R of the model in Fig 4 (a), i.e. for the Cr 2p 3/2, 0.28 compared to 0.27. The O 1s, on the other hand is noticeably improved from 0.22 to 0.16. The possibility of surface oxygen coordinated to more Cr-atoms than in a bulk truncation may also be supported by the O 1s core-level. As pointed out above, the O 1s of the Cr$_2$O$_3$ surface requires two components to be fit and is markedly broader than that for instance for the V$_2$O$_3$ film, which we discuss below. The ratio of the two O 1s components varies from 1/2 for normal emission to 5/2 for an polar emission angle of 70°, i.e. the low binding energy component becomes more pronounced at grazing.
emission angle, which suggests that this low binding energy component is due to a surface species. We speculate that the occupation of the interstitial sites in the first surface layer could explain the presence of a different charge state for the surface oxygen, further supporting the structural model.

4.2.6.2. \( \text{V}_2\text{O}_3(0001) \)

During vanadia deposition the sample was at room temperature. Utilizing the fast XPS capabilities of the SuperESCA beamline we monitored the Cr 3s and V 3s core level intensities with \( h\nu = 160 \text{ eV} \). These core-levels have been chosen because of their close proximity in energy and thus could be measured in a single energy sweep. Fig. 5 (a) shows the evolution of the peaks (for selected deposition times). Using the suppression of the Cr-3s at the end of the deposition to about half its value at the beginning and an estimate of the mean free path lengths at a kinetic energy of 80 eV of ~1 nm we obtain a film thickness of about 0.7 nm or roughly three atomic layers.
Figure 32 Monitoring of Cr- and V- core levels during reactive vanadium deposition on Cr$_2$O$_3$(0001) surface with 160 eV photon energy. The variation of Cr 3s and V 3s core level region as a function of deposition time of vanadium is shown in (a). The same core-levels before during and after annealing of the sample is shown in (b), with the spectra vertically offset for clarity. The Cr 3s/V 3s intensity ratio during the annealing cycle is also plotted in (c) as a function of sample temperature. No change in the ratio suggest that the vanadia film does not intermix with the chromia. The LEED pattern shown in (d) after annealing shows the same hexagonal pattern as for the chromia substrate before vanadia deposition, indicating formation of an epitaxial vanadia film. The electron energy for LEED was 120 eV.

Figure 5 (b) shows the fast XPS of the Cr-3s/V-3s region before, during, and after annealing. Also the peak intensities was monitored as a function of temperature during this annealing procedure. Only very little change in the peak intensities are observed and plotting the ratio of the Cr-3s/V-3s peak intensities shows almost no change, as shown in Fig. 5 (c). This indicates that at these annealing temperatures, there is no detectable intermixing between the vanadia and chromia layers and vanadia remains at the surface as an ultrathin adlayer. LEED of
the vanadia layer also shows a 1x1 structure, which, because of the same lattice constant to Cr$_2$O$_3$, is qualitatively indistinguishable from the LEED pattern of Cr$_2$O$_3$. The LEED pattern of vanadia is shown in Fig. 5 (d).

For the V$_2$O$_3$ film we monitored the O 1s and V 2p $^{3/2}$ level, with their normal emission spectra shown in Fig. 6 (a) and (b) respectively. The V-2p peak is best fit with 2 components as shown in Fig. 6(b) with one component shifted by 1.6 eV to higher binding energy. This component has been previously attributed to vanadyl species at the surface$^{30,31}$. For XPD we plotted the intensity of both components summed.

![Figure 33 XPS and XPD characterization of V$_2$O$_3$ samples.](image)

(a) The O 1s peak measured with $h\nu= 650$ eV in normal emission. Note that the O 1s peak is much narrower than that of the Cr$_2$O$_3$ sample shown in Fig. 3. The V 2p$^{3/2}$ is shown in (b). The V 2p$^{3/2}$ is fit with two components, where the high binding energy component is assigned to vanadyl surface species. (c) Experimental XPD pattern for O 1s of the V$_2$O$_3$ sample for a 90° azimuthal section and polar angle from 0 to 70° overlaid on the multiple scattering simulations for the model described in Fig. 7. (d) Experimental XPD pattern for the V 2p$^{3/2}$ peak of V$_2$O$_3$ sample for a 90° azimuthal section and polar angle from 0 to 70° overlaid on the multiple scattering simulation of the model described in Fig. 7. The corresponding R-factors are indicated.

The experimental XPD patterns superimposed on their corresponding EDAC simulations for O-1s and V-2p are shown in Fig 6(c) and 6(d) respectively. These XPD patterns can only be satisfactorily simulated with the vanadyl terminated surface, illustrated in Fig. 1 (f). For the optimized structures we find
the lowest R values of 0.22 and 0.24 for V-2p and O-1s, respectively. The relaxations and atom separations of the optimized model are illustrated in Fig. 7 and can be compared to those reported from DFT simulations\textsuperscript{56}, also shown in Fig. 7 for comparison. Using the reported DFT values for the vanadyl structure for calculating the XPD pattern with the EDAC code the R values are slightly worse (R = 0.31 and 0.16 for V and O, respectively), than those of our optimized structure, as shown in the supplement. Other models, suggested in Fig. 1, give much worse R factors and are not further considered here. Thus our results indicates that the vanadyl termination is the preferred surface structure also for ultrathin vanadia films heteroepitaxily grown on another corundum oxide substrate.

![Figure 34 Surface model of V2O3 with vanadyl termination. The atom separations are optimized for minimizing R values. The percentage relaxations of atom positions compared to bulk values is given. In addition, a comparison of the optimized structure to reported DFT simulations also given.](image-url)
4.2.7. Conclusions

Corundum structured oxides are common for many sesquioxides and combinations of them may form solid solutions\textsuperscript{18}. However, even for bulk solid solutions, surface segregation will result in a preferential surface termination. It has been shown that vanadia has a lower surface energy than chromia and thus vanadia termination is expected in such a mixed oxides. Here we simulated such a surface termination by growing a vanadia film on chromia. We find that even for very thin vanadia films, epitaxially grown on an isostructural chromia substrate that the surface exhibits a vanadyl termination. This suggests that even in mixed corundum oxides the surfaces are well represented by the surface structures of the individual oxides. For the pure chromia surface, on the other hand, we propose based on the XPD results a new stoichiometric surface structure that is oxygen terminated but has excess chromium atoms in the first chromium layer by occupation of chromium interstitial sites.
5. SUMMARY AND FUTURE WORK

The production of a new corundum structure VTiO$_3$ presents an intriguing pathway forward towards. Controlling the V:Ti ion ratio in the realm of 1:2 through 2:1 would help to identify the mechanism that dominates the epitaxial growth of the corundum structure. Along with various other substrates that introduce a range of lattice mismatch, the two parameters could identify whether the growth correlated more strongly towards V:Ti ratio or substrate. In concert, the role that oxygen plays are as critical a data point. Specifically, what is the threshold of the ion ratio that will support the corundum structure? How does the charge state of Ti transition from +3 to +4 and what are the resultant stoichiometries? Preliminary (unpublished) investigations reveal VTiO$_3$ has exhibited room temperature magnetic properties. Understanding the magnetic response involves determining whether the source is due to unpaired d-orbitals, i.e. Ti$^{3+}$ vs. Ti$^{4+}$ (d$^4$) complex in a strong $\Delta \sigma>P$ splitting crystal field or though oxygen deficiency that for TM oxides, are strongly correlated systems of local d – electrons. Considering the research of the surface terminations of chromia and vanadia, XPD analysis of the refined VTiO$_3$ film would aid in understanding the surface energy and potential applications in the fields of gas sensors through surface chemistry or as ferroelectric materials.

Correlation to the DFT data presented in the reference by Jonoyata et al. provide an opportunity to lend experimental refinement of the models utilized there. Specifically, although DFT with a Hubbard on site potential term ($U$) is used to correct for delocalization error inherent in DFT calculations for strongly correlated systems, these studies did not agree with experimental studies on how the surface (structure) layers of Cr$_2$O$_3$ terminate. Surface energy calculations did predict surface segregation of vanadia and chromia observed in experiment. This
would involve further XPD and HR-XPS data collection on Fe, Cr, V and other TMO on a variety of corundum substrates. With respect to the presented research, further work is needed to fully understand the surface interaction of V or other TMs. To do so requires partial ML deposition of V on Cr$_2$O$_3$ and Cr on V$_2$O$_3$ characterized by the same techniques reported here.
6. REFERENCES


83. C. E. Rice, W. R. Robinson, Structural changes in the solid solution (Ti1−xVx)2O3 as x varies from zero to one. J. Sol. State Chem. 21 (1977) 145.


7. APPENDIX I

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