Epitaxial Corundum-VTiO₃ Thin Films Grown on c-cut Sapphire

Alan Kramer,¹ Eli Sutter,² Dong Su,³ Matthias Batzill^{1,*}

¹ Department of Physics, University of South Florida, Tampa, FL 33620, USA

² Department of Mechanical and Materials Engineering, University of Nebraska
Lincoln, Lincoln, NE 68588, USA

³ Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY
11973, USA

Abstract:

Corundum structured VTiO₃ has been grown as epitaxial films on c-cut sapphire by laser molecular beam epitaxy. The properties of the film were characterized by reflection high energy electron diffraction, x-ray diffraction, transmission electron microscopy (TEM), and photoemission spectroscopy. All the structural probes clearly indicate the corundum structure of the film. X-ray photoemission spectroscopy (XPS) indicates that V is in a 3+ charge state implying that Ti also should adopt a 3+ charge state in order for the corundum structure to form. However, the Ti-2p XPS, while clearly broadened to the lower binding energy side compared to TiO₂, also exhibits a pronounced Ti⁴⁺ component. Similarly TEM-electron energy loss spectroscopy indicates a mixture of Ti³⁺ and Ti⁴⁺. This is tentatively assigned to a combination of final state effects in XPS measurements and existence of excess (interstitial) oxygen. The valence band spectra show occupation of 3d metal states that resemble more closely those of Ti₂O₃ than for V₂O₃, suggesting that mostly the a_{1g} molecular states are occupied.

Key words: *epitaxial oxide films; mixed oxides; corundum; vanadia; titania; x-ray photoemission spectroscopy; molecular beam epitaxy.*

* *corresponding author:* email: mbatzill@usf.edu

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 Al_2O_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 Fe_2O_3 (hematite), Cr_2O_3 , Rh_2O_3 , Ga_2O_3 , V_2O_3 and Ti_2O_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 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 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 α -alumina, has been used for growing several epitaxial corundum films [1,2,3,4] 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 [5,6,7,8] and SnO_2 [9], 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_2O_3 is grown successfully on c-cut sapphire if the growth conditions, in particular oxygen background pressure and temperature, during growth are chosen appropriately [10, 11, 12, 13, 14, 15, 16]. On the other hand, to our knowledge, corundum Ti_2O_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_2O_3 is on $\text{Mo}(110)$ [17].

In addition to single cation oxides, solid solutions [18,19,20] 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_2O_3 - Ti_2O_3 system forms the ilmenite-structure for a cation ratio of $[\text{Fe}]/[\text{Ti}]=1$. 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_3O_4 . Furthermore, Fe_2O_3 can form a solid solution with ilmenite, i.e. for a cation ratio of $[\text{Fe}]/[\text{Ti}] > 1$, 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 [21,22,23]. Here we investigate if V_2O_3 and Ti_2O_3 also forms a solid solution corundum structure if grown on c-cut sapphire with $[\text{V}]:[\text{Ti}]=1$. 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_2O_3 : Ti_2O_3 with corundum structure and without cation ordering have been reported by vacuum melting of oxides in the correct composition and oxygen concentration [24, 25, 26, 27, 28]. For a $[\text{V}]:[\text{Ti}]$ ratio of 1 a corundum unit cell of $a=5.0174 \text{ \AA}$, $c=13.993 \text{ \AA}$ 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_2TiO_5 and schreyerite with a composition of $\text{V}_2\text{Ti}_3\text{O}_9$. In these minerals V adopts a 3+ valence-state, while Ti is 4+. Phase equilibria in the V_2O_3 - TiO_2 system at 1200 °C was investigated by Brach et al. [28]. In addition to berdsinskiite ($\text{V}_2\text{Ti}_3\text{O}_9$) they also found $\text{V}_2\text{Ti}_2\text{O}_7$, $\text{V}_2\text{Ti}_4\text{O}_{11}$, and $\text{V}_2\text{Ti}_6\text{O}_{15}$, which is described as $\text{V(III)}_2\text{Ti(IV)}_{n-2}\text{O}_{2n-1}$. 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 $V_2Ti_3O_5$ and Ti_2O_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 [29]. These slabs can be expressed as $pV_2TiO_5 \bullet qTi_2O_4$. 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 $V_2Ti_2O_7$ is obtained for $p=2$ and $q=1$, i.e. periodic stacking of two berdsinskiite-type V_2TiO_5 slabs and one Ti_2O_4 slab. Similar to the V-Ti-O system the (Cr,Fe)-Ti-O system shows the same structures of stacked slabs, i.e. $(Cr,Fe)_2TiO_5$ (berdesinskiite-type), $(Cr,Fe)_2Ti_2O_7$, $(Cr,Fe)_6Ti_7O_{23}$, $(Cr,Fe)_4Ti_5O_{16}$, $(Cr,Fe)_2Ti_3O_9$ [30,31]. 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 thermodynamical 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 [32]. 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

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 $\text{TiO}_2\text{:V}_2\text{O}_3$ target. The target was made with a 1:1 cation ratio, pressed in a linear die with a total force of 25 kN and then sintered in air at 650 °C for 10 hr. In addition, a pure vanadium oxide target, prepared by similar methods, was used for growing V_2O_3 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, because the PLD system has a long target-to-substrate distance, optimized for monolayer epitaxial film growth. The laser MBE chamber has a base pressure of 10^{-9} Torr, the oxygen background pressure was varied by leaking O_2 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 2.0×10^{-6} Torr O_2 for 1 hr. The substrate growth temperature and oxygen background were maintained during growth at 750 °C and 2.0×10^{-6} Torr O_2 , respectively. Analysis of the peak intensities in XPS using tabulated atomic sensitivity factors yielded a $[\text{Ti}]/[\text{V}]$ ratio to 0.98. Given, the uncertainty in this method of around 10% we conclude that we have a close to

stoichiometric transfer from the prepared target to the film. 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 $\sim 10^{-8}$ 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 focused ion beam (FIB) lift-off technique using a using FEI-Helios FIB system. The final thinning was performed with a low Ga-ion beam energy of 2 kV, in order to remove the protective surface layer and expose the interior of the sample for the TEM investigations. Electron energy loss spectroscopy in scanning TEM mode (STEM-EELS) was performed in an aberration-corrected Hitachi HD2700C dedicated STEM, equipped with a high-resolution parallel EELS detector (Gatan Enfina-ER) at a collection angle of 15 mrad, with an energy resolution of about 0.35 eV, by measuring the full width at half maximum (FWHM). For the EELS measurements low beam currents were used (5 pA) and spectra were

recorded with relatively short acquisition times on adjacent pristine areas across the cross-sectional sample.

Many samples were grown under the same conditions that all showed the same characteristics. Confirmation of the surface structure was performed in situ immediately after growth by RHEED and chemical analysis by XPS. One sample was employed in measurements of the reported RHEED, EELS, HR-TEM, Diffraction, XRD and AFM. All but the reported RHEED and XPS measurements were made ex-situ. XPS data was recorded for all samples grown. The reported XPS and UPS data were taken on a separate sample that was transferred to a UHV system with the help of a vacuum suitcase without exposure to air.

3. Results

We have previously grown rutile and anatase TiO_2 epitaxial films on r-cut sapphire and $\text{LaAlO}_3(100)$ substrates, respectively [5,6]. These samples provide reference spectra for Ti^{4+} measured with the same instrument. Although several reports for the growth of corundum V_2O_3 on sapphire(0001) already existed, we first examined the growth of vanadia in order to determine the growth conditions for corundum V_2O_3 in our experimental set-up and to obtain reference XPS and RHEED pattern. Subsequently, we grew VTiO_3 under the same conditions.

Figure 1 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 2.0×10^{-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 1. Figure 2 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_2O_3 .

Confirmation of the c-axis oriented corundum structure for our $VTiO_3$ films also comes from XRD of a 20 nm thick film. Fig. 3 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 $2\Theta = 39.88^\circ$ 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 $VTiO_3$ of 13.99 Å. A similar decrease in the lattice constant for thin films grown on sapphire was reported for V_2O_3 . Yamaguchi [33] et al. report a c-lattice constant of 13.87 Å for V_2O_3 compared to the bulk value for V_2O_3 of 14.01 Å. [34,35]

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 Fig. 4 (b) reveal a mostly single crystalline $VTiO_3$ film. Small regions, indicated towards the top of Fig. 4 (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 Al_2O_3 substrate alone (Fig. 4 (c)) with that of the substrate plus film (Fig. 4 (d)). The diffraction patterns differ only in the lattice constants confirming that the Al_2O_3 substrate and the $VTiO_3$ 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 Al_2O_3 substrate as a scale-bar ($c_{Al_2O_3} = 12.99$ Å [Ref 35]) enables us to determine the c spacing for the $VTiO_3$ as 13.92 Å, 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 $VTiO_3$. The main question that remains is the respective charge state of the cations in this compound. To this end we performed STEM-electron energy loss spectroscopy (EELS) of the Ti-L_{2,3}-edges and XPS analysis. Fig. 5

(a) shows our experimental spectrum in comparison of two reference data for Ti^{4+} in SrTiO_3 and Ti^{3+} in LaTiO_3 [36]. 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 ($\text{Ti}^{3+}:\text{Ti}^{4+}$) ratio as shown in Fig. 5 (b). Thus EELS measurement indicate that both Ti^{3+} and Ti^{4+} cations are present in the film.

XPS measurements for V-2p are shown in Fig. 6 (b) for V_2O_3 and VTiO_3 for the as grown samples. The peak shape and position agrees well with literature reference data for V^{3+} [37,38,39,40,41,42,43,44,45]. 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 VTiO_3 films exhibit identical line shapes and this line shape has the best match with V_2O_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_2O_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 Fig. 6(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 Fig. 6 (a). The area ratio of the two components that represent Ti^{4+} and Ti^{3+} is 1.16. Standard reference spectra of Ti^{3+} , for instance in Ti_2O_3 [46], are even broader and the low energy components are in between 546.8 and 457.8 eV

[47,48,49]. 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 [50]. This has been explained by final state effects in XPS measurements and consequently it was concluded that the presence of the 'Ti⁴⁺' 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 Ti³⁺ 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 valence band spectra from UPS measurements shown in Fig. 7. This measurement indicates that the 3d states are indeed occupied, suggesting a Ti³⁺ state. Figure 7 compares the UPS spectrum for our VTiO_3 film with those of vacuum-cleaved V_2O_3 [51] and Ti_2O_3 [52,53]. 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 Fig. 7, 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 TiVO_3 O-2p band appears at significantly ($\sim 1\text{eV}$) lower binding energy than both Ti_2O_3 and V_2O_3 reference spectra. In fact the O-2p binding energy onset is more similar to that of n-type TiO_2 , whose spectrum⁵⁴ is also shown for comparison in Fig. 7. An additional note of caution is that UPS probes the very surface region and therefore potential compositional variations in the surface, due to for example thermodynamically driven segregation, can affect the measured electronic structure from that of the bulk material.

4. Discussion

All the structural probes, i.e. RHEED, XRD, and TEM, demonstrate that the VTiO_3 films condense in a primarily c-axis oriented corundum structure under the low

oxygen growth conditions on $\text{Al}_2\text{O}_3(0001)$. This suggests that the film should have a VTiO_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 [50] and also for Ti_2O_3 [55] 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^0) 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 VTiO_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_2O_3 and V_2O_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 [56].

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_2O_3 and Ti_2O_3 . Generally the valence band for octahedrally coordinated V or Ti oxides consists of an O-2p derived band at binding energies higher than $\sim 2\text{eV}$ 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_2O_3 and V_2O_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_2O_3 and Ti_2O_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_2O_3 and Ti_2O_3 has been intensively studied because of the prototypical role V_2O_3 plays as the Mott-Hubbard system and its metal-insulator transition at 168 K. In contrast to V_2O_3 , Ti_2O_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 [57]. The standard energy level diagram for V_2O_3 , shown in Fig. 7(b), was proposed by Castellani et al. [58]. The octahedral coordination of the metal site causes a splitting of the 3d states into lower t_{2g} and higher e_g^σ levels, which split further due to trigonal symmetry into a_{1g} and e_g^π states. Thus the distinct two states observed for the occupied states in UPS measurements of V_2O_3 [51] may be assigned to the a_{1g} and e_g^π (see Fig. 7(a)). In contrast, UPS for Ti_2O_3 [46] 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. [59]. As in V_2O_3 the a_{1g} facilitate bonding between Ti-Ti pairs in the face sharing octahedral, however, unlike V_2O_3 an energy gap is proposed between a_{1g} and e_g^π with the Fermi-level in between. This causes the insulating phase of Ti_2O_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. [57] speculated that this gap is a consequence of the stronger cation-cation bonding in Ti_2O_3 than in V_2O_3 . In their computational study they showed that a similar gap between a_{1g} and e_g^π can be induced in V_2O_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_2O_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 VTiO₃ shows a single component which we assign to a_{1g} state and thus an electronic structure more similar to Ti₂O₃ than to V₂O₃. However, comparison with Ti₂O₃ spectra also shows that the peak for VTiO₃ is broader which may be a consequence of randomness of the cation pairs. Another similarity to Ti₂O₃ is the onset of the spectrum close to the Fermi-level. As discussed above, Ti₂O₃ possesses a small band gap at RT between the occupied a_{1g} and the empty e_g^π , while V₂O₃ is metallic at RT. This is represented in the reference UPS spectra by the fairly sharp onset of density of states at the Fermi-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^π 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.

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.

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Figure Captions:

Figure 1: Comparison of RHEED of c-cut sapphire substrate, V_2O_3 -epitaxial films, and $VTiO_3$ films. RHEED along the $\langle 1-210 \rangle$ and $\langle 10-10 \rangle$ direction are shown in addition to intensity profiles along the indicated lines. The intensity peaks have been used to estimate the lattice constants. Also notable is the less well-defined diffraction pattern for the $VTiO_3$ film compared to V_2O_3 indicating more disorder in $VTiO_3$.

Figure 2: Ambient tapping mode AFM image of a $VTiO_3$ film. Terraces and atomic steps are visible. A line scan along the indicated direction shows the overall surface roughness is of the order of atomic-step heights.

Figure 3: XRD scan with 2θ from 15° to 95° of c-cut sapphire substrate (red) and a $VTiO_3$ film (blue) the singular peaks corresponding to the (0006) and (00012) planes of $VTiO_3$ are evident near 38° and 83° . The $d_{(0006)}$ plane spacing for $VTiO_3$ is $13.88\text{\AA}$.

Figure 4: TEM analysis of $VTiO_3$ film on c-cut sapphire. (a) Interface between sapphire and $VTiO_3$ film. The scale bar is 2 nm. (b) Higher resolution image of the $VTiO_3$ 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 $VTiO_3$ film, respectively. In (d) the comparison between the substrate and film diffraction spots enables to estimate the lattice parameters for the film.

Figure 5: TEM-EELS Ti- $L_{2,3}$ edge analysis of $VTiO_3$ film. (a) the experimental data (black circles) is compared to reference spectra for typical Ti^{3+} and Ti^{4+} compounds, i.e. from $LaTiO_3$ (red), $SrTiO_3$ (blue)[³⁶]. 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, $MSE = \frac{1}{n} \sum_{i=1}^n (x_e - x_o)^2$, 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).

Figure 6: XPS data for Ti 2p (a), and V 2p and O 1s (b). (a) A reference spectrum for TiO_2 is shown in addition to $VTiO_3$ film. The Ti-2p peak of $VTiO_3$ is fitted with two components. One component has the peak shape and position of the reference data for TiO_2 (blue) and the second component represents the lower binding energy contribution (red). (b) Comparison of O 1s and V 2p peaks for a V_2O_3 (blue) and $VTiO_3$ (red) films. Both films have V 2p peak shapes and positions consistent with V^{3+} .

Figure 7: Valence band spectra (a) and molecular orbital model for corundum V_2O_3 oxides (b). (a) The UPS spectrum measured for $VTiO_3$ film (black) is compared to reference spectra for Ti_2O_3 and V_2O_3 taken from ref [⁴⁶] and [⁵¹]. (b) Energy level diagram for molecular orbitals in V_2O_3 , adapted from Castellani et al. [⁵⁸].

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