



# Epitaxial corundum-VTiO<sub>3</sub> thin films grown on c-cut sapphire



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## ABSTRACT

Corundum structured VTiO<sub>3</sub> 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 TiO<sub>2</sub>, also exhibits a pronounced Ti<sup>4+</sup> component. Similarly TEM-electron energy loss spectroscopy indicates a mixture of Ti<sup>3+</sup> and Ti<sup>4+</sup>. 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 Ti<sub>2</sub>O<sub>3</sub> than for V<sub>2</sub>O<sub>3</sub>, suggesting that mostly the a<sub>1g</sub> molecular states are occupied.

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## 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<sub>2</sub>O<sub>3</sub>) substrates, because of their stability and availability in high surface quality and purity, are 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<sub>2</sub>O<sub>3</sub> (hematite), Cr<sub>2</sub>O<sub>3</sub>, Rh<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub> and Ti<sub>2</sub>O<sub>3</sub>. 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 aforementioned oxides, titania prefers a 4+ oxidation state and thus is commonly observed as TiO<sub>2</sub> 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<sub>2</sub> 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  $\alpha$ -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<sub>2</sub> [5,6,7,8] and SnO<sub>2</sub> [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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> has not been successfully grown in a good quality epitaxial film on sapphire, likely because of its preference to form Ti<sup>4+</sup>. The only report for growth of epitaxial Ti<sub>2</sub>O<sub>3</sub> is on 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<sub>2</sub>O<sub>3</sub>-Ti<sub>2</sub>O<sub>3</sub> system forms the ilmenite-structure for a cation ratio of [Fe]/[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<sub>3</sub>O<sub>4</sub>. Furthermore, Fe<sub>2</sub>O<sub>3</sub> 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<sup>3+</sup>. This has been investigated in epitaxial films

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on sapphire in view of its ferromagnetic properties [21,22,23]. Here we investigate if  $V_2O_3$  and  $Ti_2O_3$  also form a solid solution corundum structure if grown on c-cut sapphire with  $[V]:[Ti] = 1$ . 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  $[V]:[Ti]$  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  $V_2Ti_5O_{15}$  and schreyerite with a composition of  $V_2Ti_3O_9$ . In these minerals V adopts a 3+ valence-state, while Ti is 4+. Phase equilibria in the  $V_2O_3$ - $Ti_2O_3$  system at 1200 °C was investigated by Brach et al. [28]. In addition to berdsinskiite ( $V_2Ti_3O_9$ ) they also found  $V_2Ti_2O_7$ ,  $V_2Ti_4O_{11}$ , and  $V_2Ti_6O_{15}$ , which is described as  $V(III)_2Ti(IV)_n - 2O_{2n-1}$ . 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  $\alpha$ - $PbO_2$  structure. Periodic intergrowth of these layers thus then give rise to the different observed structures [29]. These slabs can be expressed as  $pV_2TiO_5 \cdot qTi_2O_4$ . 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  $V_2Ti_3O_5$  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 needs 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 355 nm and 5 Hz repetition frequency) for ablation of a mixed  $TiO_2:V_2O_3$  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 h. 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/h, 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 h 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  $2.0 \times 10^{-6}$  Torr  $O_2$  for 1 h. The substrate growth temperature and oxygen background were maintained during growth at 750 °C and  $2.0 \times 10^{-6}$  Torr  $O_2$ , respectively. Analysis of the peak intensities in XPS using tabulated atomic sensitivity factors yielded a  $[Ti]/[V]$  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-1 s binding energy allowed some comparison of the relative binding energies, however, analysis clearly suffered from the assumption that the O-1 s binding energy is the same for all oxides. In all the data analysis the O-1 s 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  $\theta$ - $2\theta$  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.

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