Epitaxial single-crystal thin films of $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ grown on (rutile) TiO_2 substrates with pulsed laser deposition: Experiment and theory

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Abstract

Epitaxial rutile-structured single-crystal $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films were synthesized on rutile- (110) and -(001) substrates using pulsed laser deposition. The films were characterized by reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and aberration-corrected transmission electron microscopy (ACTEM). Under the present conditions, 400°C and $P\text{O}_2 = 20$ mTorr, single crystal epitaxial thin films were grown for $x = 0.13$, where x is the nominal average mole fraction of Mn. In fact, arbitrarily thick films could be grown with near invariant Mn/Ti concentration profiles from the substrate/film interface to the film surface. In contrast, at $x = 0.25$, Mn became enriched towards the surface and a secondary nano-scale phase formed which appeared to maintain the basic rutile structure but with enhanced z -contrast in the tunnels, or interstitial sites. *Ab initio* thermodynamic calculations provided quantitative estimates for the destabilizing effect of expanding the β - MnO_2 lattice parameters to those of TiO_2 -rutile, the stabilizing effect of diluting Mn with increasing Ti concentration, and competing reaction pathways for surface oxide formation.

Key words: thin films; pulsed laser deposition; ab initio thermodynamics; rutile; manganese.

1.0 Introduction

The titanium dioxide rutile phase is a wide-band gap semiconductor (~ 3.0 eV [1]) that has found use in a broad range of applications that include but is not limited to photocatalysis, solar cells, and water purification. Nonetheless, the pure phase can only harness the UV portion of solar radiation. This limitation has spurred intensive research to find low cost dopants that can significantly decrease the band gap. Promising candidates include N[2-8], B[9-11], and Mn[12-

17]. Recent first principles theoretical work[14] has demonstrated that doping TiO_2 (rutile) with Mn induces a strong red shift, consistent with experiment [15, 16], along with intermediate bands having desirable properties that can efficiently shuttle electrons into the conduction band. Consequently, variable Mn doping is a leading candidate for tuning the band gap of rutile and broadening its application.

The interest here is in vacuum-based thin film synthetic methods and the possibility of making oriented epitaxial single-crystals of rutile structured $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$. The endmember TiO_2 (rutile) and $\beta\text{-MnO}_2$ (pyrolusite) phases are isostructural and are composed of single chains of edge sharing MO_6 octahedra linked to each other by corner-shared oxygens to form so called 1×1 channels[18]. However, the $a=b$ and c lattice constants of pyrolusite are smaller than those of rutile by about -4 and -3%, respectively [19]. There are several reasons why such films would be desirable: 1.) reduction of the interfacial area between grain boundaries focuses the work on intrinsic structure-property relationships, 2.) the ability to express a particular surface, while varying the volume independently, with minimum grain boundaries for fundamental catalysis/reactivity studies, 3.) the potential for studying the effect of strain on properties of interest due to lattice pinning by the substrate, and 4.) rutile and some manganese oxides exhibit tunnel structures that facilitate studies of coupled ion/electron transport. Matsumoto et al.[20] used laser molecular beam epitaxy (MBE) to grow Mn-doped TiO_2 (rutile)(100) on a $\alpha\text{-Al}_2\text{O}_3$ (0001) substrate. However, this was a broad combinatorial doping study that considered a range of transition metal dopants with little detailed information given concerning the Mn-doped film. Chambers and Liang[19] attempted to grow pure $\beta\text{-MnO}_2$ on TiO_2 (rutile)(110) by oxygen plasma-assisted MBE, but could not get ordered films beyond a few bi-layers. The difficulty in obtaining the film was attributed to the marginal lattice match with the substrate, as discussed

above. An attempt to grow pure β - $\text{MnO}_2(110)$ by starting with Ti-rich films and systematically increasing the Mn concentration every 10 nm was deemed not successful and details were not provided. Radio frequency (RF) magnetron sputtering has also been used to make oriented fibrous, i.e., polycrystalline, rutile films on oxidized silicon and fused quartz surfaces with up to $\sim 40\%$ Mn[15, 16]. Interestingly, the preferred orientation changed from predominantly (110) at low Mn % to predominantly (100) at higher Mn%. Despite this expanding and significant body of work on Mn-doped $\text{TiO}_2(\text{rutile})$, there have been no systematic studies on growing single-crystal epitaxial $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films.

In this contribution, we used pulsed laser deposition (PLD) to synthesize epitaxial rutile structured single-crystal $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films on rutile- (110) and -(001) substrates. The (110) and (001) surfaces are the most and least stable, respectively. However, the tunnels are only directly accessible via the (001) surface which makes the expression of this orientation desirable for studying coupled ion/electron transport. The films were synthesized using the slowest available deposition rate over a range of temperature at $P\text{O}_2 = 20$ m Torr and for $x = 0.13 - 0.5$. One objective was to determine a solubility/thickness limit, albeit in a coarse grain manner at $P\text{O}_2 = 20$ m Torr over a limited range of T for Mn in epitaxial single-crystal $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films coherently strained to (110) and (001) rutile substrates. The experimental results were then compared to a limited set of *ab initio* thermodynamic calculations that were performed to provide a conceptual framework to better understand the results of this study as well as to demonstrate a potential tool for efficiently exploring composition, temperature, and $P\text{O}_2$ space as a guide for future experimental work. These preliminary calculations included Mn/Ti mixing and straining the film to the $\text{TiO}_2(\text{rutile})$ bulk lattice, but did not treat coherent strain, film thickness, surface energy, oxygen vacancies or amorphous structures. The films were characterized by

reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and aberration-corrected transmission electron microscopy (TEM).

2.0 Material and methods

2.1 PLD. Targets (MnO_2 and TiO_2) were 2" in diameter and purchased commercially from the Kurt J. Lesker Company. Prior to growth, all targets were ablated for 15 minutes at a laser repetition rate of 10 Hz in 10 mTorr O_2 to eliminate carbonaceous surface contamination. Single-side epi-polished $10 \times 10 \times 1 \text{ mm}^3$ or $10 \times 10 \times 0.5 \text{ mm}^3$ TiO_2 (001 or 110) substrates purchased from Crystec were used to grow all films. After substrate introduction and prior to growth, the substrates were heated to 400°C in 20 mTorr O_2 to eliminate adventitious carbon from the growth surface. A KrF laser (248 nm) was used with a fluence of 2.4 J/cm^2 and a repetition rate of 1 Hz. The laser spot ($\sim 1 \times 10 \text{ mm}^2$) was rastered across a rotating target while the substrate was also rotating, allowing for uniform thickness across the substrate. A computer-controlled combination of laser pulses at the two different targets was calibrated and used when a stoichiometry other than that of the end-members was desired. In a typical two-target growth procedure, each target was irradiated with a few laser pulses, followed by closing the shutter and moving the second target into the ablation position. The sequence would be repeated as many times as necessary to achieve the desired film thickness. The oxygen partial pressure in the deposition chamber during film growth was 20 mTorr and the substrate temperature for all successful growths was maintained at $\sim 400^\circ\text{C}$.

2.2 XRD. Epitaxial relationship, crystalline quality, and lattice parameters were investigated using high-resolution x-ray diffraction (HRXRD) with a Philips X'Pert Materials Research

Diffraction (MRD) equipped with a fixed Cu anode operating at 45 kV and 40 mA. A hybrid monochromator, consisting of four-bounce double crystal Ge (220) and a Cu x-ray mirror, was placed in the incident beam path to generate monochromatic Cu K_{α} x-rays ($\lambda = 1.54056 \text{ \AA}$) with a beam divergence of 12 arc seconds. Crystal quality was further examined by means of triple-axis rocking curve measurements in which an additional three-bounce Ge (220) channel-cut analyzer was placed in front of a proportional counter to obtain the same divergence as the incident beam. As a result, the diffractometer exhibited an angular precision and reproducibility of 0.0001° and 0.0003° , respectively.

2.3 XPS. The Physical Electronics Quantum 2000 Scanning ESCA Microprobe uses a focused monochromatic Al K_{α} X-rays (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16 element multichannel detection system. A 105 W X-ray beam focused to 100 μm diameter was rastered over a 1.4 mm x 0.3 mm rectangle on the sample. The X-ray beam is incident normal to the sample and the X-ray photoelectron detector is at 45° off-normal. The high energy resolution data was collected using a pass-energy of 46.95 eV with a step size of 0.125 eV. For the Ag $3d_{5/2}$ line, these conditions produced a full width at half maximum (FWHM) of 0.98 eV. Binding energies were referenced to C 1s at 285.0 eV. A combination of electron flood gun and a low energy Ar $^{+}$ ion beam provided charge neutralization. Shirley backgrounds were subtracted from the Mn $2p_{3/2}$ and Ti $2p$ lines and instrument specific sensitivity factors used for quantification. An empirical method was adapted from Beisinger et al.[21] to extract oxidation state information for Mn by fitting the Mn $2p_{3/2}$ line with sets of Gaussian/Lorentzian peaks calibrated to the end member manganese oxides MnO, Mn₂O₃, and MnO₂. For each oxidation state, the FWHM, height, and energies of the peaks are fixed relative to each other but can change as a packet relative to the other oxidation states. The

methodology should be considered a provisional empirical approach: It does not include information above the $2p_{3/2}$ spin-orbit split peak and does not take into account potential bonding environment effects due to mixing of Mn with Ti and having multiple Mn oxidation states in the films. Nonetheless, it does attempt to take into account the distinct multiplet structures associated with Mn(II), Mn(III), and Mn(IV).

2.4 TEM. Sample preparation for TEM analysis consisted of preparing a thin section using a focused ion beam-scanning electron microscope (FEI Helios). Prior to cutting the sample, a 200–400 nm Pt layer followed by a 2 μ m C layer were deposited on the sample surface to protect it from ion beam damage. Once the thin section was prepared and placed into a TEM grid, a Ga beam followed by an Ar ion beam was used to thin Pt/C surface encapsulation to less than 50 nm. High angle annular dark field (HAADF) transmission electron microscopy TEM imaging was performed with a FEI Titan 80-300 operated at 300 kV. The instrument is equipped with a CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows imaging with 0.1 nm resolution in scanning transmission electron microscopy (STEM) mode. The images were acquired in STEM mode using a HAADF detector with an inner collection angle of 52 mrad.

2.5 Theory. Structures were optimized and total energies were obtained from first principles spin-polarized density-functional theory (DFT) calculations using the generalized gradient approximation of Perdew, Burke, and Ernzerhof[22] as implemented within the DMol³ program.[23, 24] An atom-centered numerical basis set of double-zeta plus polarization quality was used with a real space cutoff of 4.3 Å. Using a Monkhorst-Pack grid the lattice energies were converged at a Brillouin Zone sampling of $4 \times 4 \times 7$ for the rutile oxides, $3 \times 3 \times 3$ for the 9.4 Å Mn₂O₃ lattice, and $5 \times 5 \times 4$ for the body-centered tetragonal Mn₃O₄ lattice. Energies

were converged with respect to the lattice constants and ion coordinates to 10^{-5} Hartrees. For the β -MnO₂ calculations the lowest energy antiferromagnetic electronic configuration was utilized. For Mn₂O₃ and Mn₃O₄ with complicated antiferromagnetic structures, a ferromagnetic state was used, as the total energy differences between ferro and antiferromagnetic states are negligible from a thermodynamic perspective at elevated temperatures.[25]

The DFT-GGA functional is known to underestimate the band gap of transition metal oxides such as β -MnO₂ due to the DFT self-interaction error. Pyrolusite is calculated to be metallic, whereas the experimental band gap had been determined to be 1.0 eV.[26] Methods that have been demonstrated to correct the underestimated band gap, such as hybrid functionals and DFT+U [27], however, have yielded inconsistent results for the thermodynamics of nonstoichiometric oxides by destabilizing anions and favoring oxygen-poor compounds.[28] This has resulted in incorrect trends in heats of formation for manganese oxides.[29] PBE has been shown to have errors that are systematic and yield correct trends in formation energies for Mn oxides in different oxidation states.[28] For systems as diverse as the oxidation of the (0001) surface of Fe₂O₃,[30, 31] reduction of the (110) surface of SnO₂ [32], and bulk UO_{2+x} [33-35] where the thermodynamics of nonstoichiometric oxides and surfaces have been studied, GGA has provided results consistent with experimental redox conditions whereas other methods have had challenges. Hence since we are focused on the thermodynamics of nonstoichiometric oxides and surfaces and not on band gaps, we have utilized the PBE GGA functional in this work.

To incorporate the experimental conditions of temperature and pressure, the DFT calculations were linked with macroscopic thermodynamics using the technique of *ab initio* thermodynamics.[36, 37] The methodology has been successfully applied to the bulk structures and surfaces of manganese oxides pyrolusite and manganite (γ -MnOOH) by Oxford and

Chaka.[38] Comparing thermal stability across mixed manganese and titanium oxides with incommensurate lattice templates that result in strained structures is, however, considerably more complicated and summarized below.

To determine which phase of Mn oxide will be stable under experimental conditions, and how the addition of Ti affects phase stability, we calculated the chemical potential of Mn, μ_{Mn} in the various oxide phases under different conditions. The phase with the lowest μ_{Mn} will be the most stable thermodynamic phase. In general, the chemical potential μ of a mixed Mn-Ti oxide can be expressed as follows:

$$\mu_{\text{Mn}_x\text{Ti}_y\text{O}_z} = x\mu_{\text{Mn}} + y\mu_{\text{Ti}} + z\mu_{\text{O}} \quad [1]$$

Solving for μ_{Mn} yields:

$$\mu_{\text{Mn}} = \frac{1}{x}(\mu_{\text{Mn}_x\text{Ti}_y\text{O}_z} - y\mu_{\text{Ti}} - z\mu_{\text{O}}) \quad [2]$$

If titanium in the mixed oxide is considered to be in equilibrium with the bulk TiO_2 substrate, then

$$\mu_{\text{TiO}_2} = \mu_{\text{Ti}} + 2\mu_{\text{O}} \quad [3]$$

and

$$\mu_{\text{Ti}} = \mu_{\text{TiO}_2} - 2\mu_{\text{O}} \quad [4]$$

Therefore Eq. 2 becomes:

$$\mu_{\text{Mn}} = \frac{1}{x}(\mu_{\text{Mn}_x\text{Ti}_y\text{O}_z} - y\mu_{\text{TiO}_2} + (2 - z)\mu_{\text{O}}) \quad [5]$$

At a specific temperature T and pressure p , $\mu_i(T,p) = \mu_i(0K) + \Delta\mu_i(T,p)$. In *ab initio* thermodynamics, $\mu_i(0K)$ is obtained from the total energy calculations of the solid or O_2 molecule, and $\Delta\mu_i(T,p)$ is obtained from experimental data such as the JANAF tables if available, or the DFT calculated vibrational partition function. To convert to pressures other than the

reference of 1 bar, the ideal gas law was used. Where the calculated $\Delta_f H^\circ$ for the metal oxides from the elements differ significantly from the experimental values, corrections are used. The bond dissociation energy for the O₂ molecule, which is known to be off by 0.5 eV in GGA DFT calculations, was corrected. For mixed oxides for which no experimental data are available, linear interpolations for corrections were used. These approximations introduce some uncertainty, but within the class of structures, such as rutile or spinel, the relative change in μ_{Mn} due to the addition of titanium is reliable and systematic and shows clear trends that lead to greater understanding.

3.0 Results and Discussion

Results are presented for growth conditions at $T = 400^\circ\text{C}$ and $PO_2 = 20$ mTorr. The films were amorphous at $T < 375^\circ\text{C}$ but crystalline at 400°C . Given the known instability of Mn(IV)O₂ at relatively high T and low PO_2 [39] we chose to focus on the lowest possible T that still yielded crystalline rutile-structured $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$. In fact, attempts to grow pure $\beta\text{-MnO}_2$ on (110) substrates at $T \geq 400^\circ\text{C}$ yielded Mn_2O_3 . Reflection high energy electron diffraction (RHEED), X-ray diffraction (XRD), and aberration-corrected transmission electron microscopy (ACTEM) results for (110) and (001) films are presented and discussed separately. XRD is only reported for films thicker than about 20 nm that indicated high-quality RHEED patterns. This is followed by a discussion of oxygen vacancy and inclusion formation in the context of X-ray photoelectron spectroscopy (XPS) results. The last subsection focuses on insights gained from *ab initio* thermodynamic calculations of film stability.

3.1 (110) substrates. RHEED for (110) oriented $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films are given in Figures 1a and b. The surface structure is highly crystalline, smooth, and consistent with the rutile structure

for nominal $x = 0.125$ (15-24 nm thick) (Figure 1a); note the presence of Kakuchi lines and third order spots. XRD of the ~ 24 nm thick film indicates that the film is epitaxial, crystalline, and coherently strained to the substrate (Figure 2, top panels). Given $a = 4.594$ Å for rutile(TiO_2)[40], the film is compressed by 0.35% in the $[110]$ direction where $a = 4.577$ Å. XRD and RHEED imply growth of high-crystallinity films; however, this does not exclude possible lateral disorder in the bulk of the film. In order to more fully characterize the material, aberration corrected TEM was performed on cross sections of selected films. Figures 3 and 4 are views down the $[001]$ (~ 15 nm thick) and $[110]$ (~ 24 nm thick) directions, respectively, where light blotches are remnant gallium from the milling process. The bright spots are Mn/Ti atoms, but the oxygen sub-lattice is not visible. In Figure 3 the tunnels run perpendicular to the plane of the image whereas in Figure 4 they extend parallel to the plane of the image. In both cases, it appears that the rutile structure extends right up to the surface termination and that the boundaries between the films and substrates are continuous with no obvious demarcation (i.e., no dislocations) except for the Mn/Ti ratio. As clearly demonstrated in Figure 4, energy dispersive spectroscopy (EDS) analyses indicate that the Mn/Ti ratio is mainly invariant from the substrate-film interface to the film surface. Except for possible antiphase boundaries (Figure 4), the film would be classified as single-crystal (certainly by bulk XRD criteria) and compositionally homogeneous, with a continuous tunnel structure.

At higher Mn concentrations, nominal $x = 0.25$ (~ 12 nm thick), the surface appears rougher, the Kakuchi lines are diminished, the third order diffraction spots disappear, and the background is relatively brighter (Figure 1b). Consequently, although the surface structure maintains a rutile-like aspect, disorder is apparent. Oriented nano-scale features (hence forth called “inclusions”) extend from the surface to about the middle of the film (Figure 5). Further, there appears to be a

secondary phase at the surface. Nonetheless, RHEED indicates that either this surface phase cannot be continuous or it bears some structural similarity to rutile (Figure 1b). Unfortunately, neither the inclusions nor the surface phase have been definitively identified yet, although they are likely related. Under visual inspection the surface structure appears similar to rutile except for some increased z-contrast in the interstitial sites (or tunnels). Likewise, the interstitial sites bordering the inclusions also manifest increased z-contrast. Further, one can seemingly trace the octahedral sites from the bulk phase, across the precipitates, and back into the bulk; however, the octahedral positions (bright spots in the bulk material) appear to diminish in intensity in the inclusions whereas the interstitial sites appear to gain intensity. Nonetheless, this is simply a descriptive device and the identity of these inclusions remains elusive. The inclusions widen toward the surface and merge with the surface structure. These secondary features will be discussed later in the context of the XPS analyses and oxygen vacancy formation. An EELS profile indicates that the Mn/Ti ratio steadily increases from the film-substrate interface to ~5 nm below the surface, dips from ~5 to 2.5 nm, then spikes just before sharply decreasing within about 1 nm of the surface (Figure 6). The Ti L-edge fine structure shows that the ligand field splitting typical of the rutile structure disappears near the top of the film, coincident with the appearance of the inclusions and surface phase. Further, sub-vertical to flat lamellae of low density Ti and O are visible which may represent incipient delamination.

3.2 (001) substrates. The surface structures of a (001) oriented films with nominal $x = 0.125$ (up to ~60 nm thick) appear rough but highly crystalline and consistent with rutile (Figure 1c). Likewise, XRD of the 60 nm thick film indicates that it is highly crystalline and coherently strained to the substrate with $c = 2.948 \text{ \AA}$ compared to $2.953 \text{ \AA}$ [40] for rutile-TiO₂ (Figure 2, bottom two panels). ACTEM of films up to 60 nm thick indicate no marked trend in Mn/Ti ratios

from the interface to the surface (Figure 7). Further, despite extensive chevroning of the surface, the tunnel structures extend to the very top surface. This is important for future planned experimental work involving coupled ion/electron transport (i.e., the tunnels are readily accessible). We note that chevroning is not unexpected given that the (001) surface is the least stable.

At higher Mn concentration (nominal $x = 0.25$) the surface of a 10 nm thick film is highly crystalline (Figure 1c). However, whereas ACTEM confirms that the film is structurally single-crystal from the film-substrate interface up to the surface (Figure 8), the Mn/Ti ratio increases exponentially from the interface towards the surface. RHEED of thicker films of this nominal composition indicate less surface crystallinity (not shown), which might be due to increasing Mn/Ti ratios towards the surface. ACTEM of a ~40 nm thick film with nominal $x = 0.38$ shows that the top 2/3 of the film is largely amorphous (not shown). For nominal $x = 0.5$, the highest Mn concentration attempted, even a film only 10 nm thick showed a significant decrease in surface crystallinity (Figure 1d).

3.3 Oxygen vacancies. The $\text{Mn}2p_{3/2}$ spin-orbit peak was used to estimate the oxidation state of Mn at the near-surface (top ~3 nm) of selected films. The method takes advantage of the inherent and distinct multiplet structure for the different oxidation states of Mn (See Experimental) with less reliance on absolute binding energies (BE's). As shown in Beisinger et al. [21], there can be considerable overlap between the dominant $\text{Mn}2p$ multiplet peaks for Mn_2O_3 and MnO_2 which makes BE's less reliable for oxidation state determinations. Further, fitting a $\text{Mn}2p$ spectrum with single peaks representing each oxidation state runs the likely risk of mistaking a multiplet peak of one Mn oxidation state for another oxidation state. However, using the peak shapes for endmember Mn oxides introduces uncertainty as well, due to possible

bonding environment effects on the multiplet structures. With this caveat, fitting the Mn2p_{3/2} peak indicates that the dominant oxidation state is Mn(III) for all the samples examined (Table 1). The fitting procedure is illustrated in Figure 9; note that there are fewer degrees of freedom than the number of peaks would indicate (see Experimental). The average oxidation state of Mn decreases with increasing Mn concentration and angle resolved XPS also indicates that Mn is more reduced nearer the surface; suggesting that Mn might be more oxidized in the bulk of the film than XPS indicates. If so, this is consistent with *ab initio* calculations of β -MnO₂ indicating that surface Mn is more easily reduced than bulk Mn.[41] Because Mn(III) has a larger ionic radius than Mn(IV), reduction of Mn(IV) in the film might be a mechanism for relieving accumulated coherent strain to the larger TiO₂(rutile) lattice; however, it is not clear what role oxygen vacancies play. Nonetheless, given that there is no detectable reduction of Ti (i.e., narrow single, symmetrical peaks with Ti2p_{3/2} at 458.5 eV) and that the rutile structure was documented to extend all the way to the surface of films with nominal x = 0.125 (Figures 4 and 7), it is likely that any oxygen loss required for charge balance is associated with Mn octahedra. This too is consistent with theory that predicts larger oxygen-vacancy formation energies for TiO₂(rutile) surfaces compared to β -MnO₂. [41-43]

Therefore, it is plausible that the surface phase and inclusions, discussed above (Figure 5), are related to an accumulation of Mn and associated oxygen vacancies towards the surface that was induced, in part, by coherent strain of the film to the substrate. Further, given the appearance of z-contrast in the interstitial sites associated with the inclusions and surface phase (Figure 5), a working hypothesis is that Mn/Ti atoms have migrated into the tunnels. Further speculation is not warranted and resolving these issues will likely require the close interplay between *ab initio* structure modeling and microscopy.

3.4 Ab initio thermodynamics and limits to Mn doping. Under the present experimental conditions and using both (110) and (001) rutile substrates, a clear limit to Mn concentration in epitaxial single-crystal $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films was determined. In fact, attempts to grow pure β - MnO_2 on rutile TiO_2 (110) and (001) substrates with $P\text{O}_2 = 20$ mTorr yielded amorphous material at $T \leq \sim 375^\circ\text{C}$ and non-epitaxial bixbyite (Mn_2O_3) at $T \geq 400^\circ\text{C}$ (T between 375° and 400°C were not explored). Without *a priori* knowledge there is a large matrix of possible directions to explore, including: Increasing $P\text{O}_2$ for a given laser sputtering rate, which would also slow deposition rates, and experimenting with combinations of $P\text{O}_2$, target ablation rates, and T . In some sense, a large portion of T - $P\text{O}_2$ space has already been explored by the PLD study of Yang[44] that resulted in Mn_2O_3 and Mn_3O_4 , but not crystalline β - MnO_2 , although their substrate would not be expected to grow epitaxial β - MnO_2 . Likewise the oxygen plasma-assisted (OPA) MBE study of Chambers and Lang [19] did not yield well-ordered β - MnO_2 on $\text{R}(110)\text{TiO}_2$ thicker than a ~ 6 bilayers. An exception appears to be the OPA-MBE study of Xing et al. [45], which claimed to make 60 nm thick films of epitaxial β - MnO_2 on $\text{MgO}(001)$ and $\text{LaAlO}_3(001)$, despite large lattice mismatches. We tried but failed to duplicate their results using $\text{MgO}(001)$ and OPA-MBE; instead the synthesis yielded Mn_2O_3 despite close adherence to the conditions in Xing et al..

Nonetheless, it would be beneficial to have theoretical guidance to optimize synthesis conditions to grow films of a desired composition and orientation, as well as to place results into a conceptual framework. In particular, we are interested in the feasibility of synthesizing higher Mn% single-crystal epitaxial films by varying temperature and $P\text{O}_2$ for a given substrate. Although thin film synthesis is considered to be a non-equilibrium process [46], with deposition rate and diffusion important factors, thermodynamics provides a framework for understanding

the physical limits of the deposition process. For example, a phase which is too unfavorable thermodynamically may not form no matter how experimental conditions are adjusted. In this regard, Figure 10 and Table 2 summarize the results of *ab initio* thermodynamic calculations for the MnO_x and $\text{Mn}_x\text{Ti}_{1-x}\text{O}_2$ systems at $P\text{O}_2 = 20 \text{ mTorr}$; DFT determined lattice constants are compared to experimental values [47-50] in Table 3. Calculations are given for MnO_x and $\text{Mn}_x\text{Ti}_{1-x}\text{O}_2$ bulk phases either constrained to the pure rutile TiO_2 lattice (“ TiO_2 lat” in Figure 10) or allowed to relax to an optimum lattice (“opt lat” in Figure 10). Although XPS clearly indicates that Mn exists in multiple oxidation states (Figure 9), at least at the near-surface of the films, consideration of oxygen vacancies, surface energies, film thickness, and coherent strain to the substrate is beyond the present scope and will be incorporated into a future publication. Note that allowing the solid solution to relax in the direction perpendicular to the substrate, or coherently strain to the substrate, would stabilize the film at intermediate energies relative to both complete relaxation (i.e., opt lat) and conformation to the TiO_2 lattice (i.e., TiO_2 lat).

With these simplifications noted, Mn_2O_3 is the most stable phase at experimental conditions (Figure 10), which is in accord with failed attempts to synthesize pure $\beta\text{-MnO}_2$. Expanding $\beta\text{-MnO}_2$ to the bulk rutile TiO_2 lattice, labeled $\text{MnO}_2(\text{TiO}_2 \text{ lat})$, further destabilizes MnO_2 . Addition of 50% Ti to $\text{MnO}_2(\text{TiO}_2 \text{ lat})$ significantly increases the stability of the rutile structured phase, with an even larger gain if the lattice is allowed to optimize. Coherently straining the film to the substrate (i.e., partial relaxation in the out of plane direction; not treated) should also appreciably increase the stability of the film, but to a lesser extent than full bulk relaxation. Such an effect is expected as increasing Ti will decrease the strain energy due to better lattice matching with the substrate. *Ab initio* thermodynamics calculations also indicate that Ti can be expected to suppress the formation of competitive reaction products such as Mn_2O_3 and Mn_3O_4 ,

potentially broadening the stability field of $\text{Mn}_x\text{Ti}_{1-x}\text{O}_2(\text{TiO}_2 \text{ lat})$ further. Although theory clearly predicts that at $\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_2$ can be stable relative to Mn_2O_3 in a Ti-rich system under present conditions, experiment indicates that structures or phases other than bixbyite become more stable at $x \geq 0.25$. This suggests that other factors need to be considered such as surface energy and oxygen vacancies. Indeed, alternative structures/pathways, such as those that could lead to inclusion formation (Figure 5) or a amorphous material were not considered. Despite the uncertainty, this exercise shows that it is possible to treat thin films using *ab initio* thermodynamics and that accurate quantitative predictions are close at hand.

In contrast, Mn doped $\text{R}(\text{TiO}_2)$ films grown by RF magnetron sputtering of Mn and Ti targets onto silicon substrates at $T = 550^\circ\text{C}$ and high rates of Ar/O_2 flow, yielded oriented but fibrous films (i.e., not single crystal) containing up to 42% Mn without obvious evidence for exsolution [15, 16]. XPS indicated that Mn was highly reduced, in qualitative agreement with the results shown here. The authors suggest that this high concentration of Mn may represent a metastable state, perhaps due to the very high rate of deposition. This supposition could be constrained using *ab initio* thermodynamics given new calculations at appropriate $P\text{O}_2$ values.

4.0 Conclusions

High quality epitaxial compositionally-homogeneous single-crystal films of $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ were grown on $\text{R}(110)\text{TiO}_2$ and $\text{R}(001)\text{TiO}_2$ substrates at 400°C and 20 mTorr, whereas films were RHEED amorphous at $T \leq 375^\circ\text{C}$. The apparent effective concentration limit of Mn in TiO_2 for (110) and (001) orientations was $\sim 0.13 \leq x < \sim 0.25$ given film thicknesses (the highest tested thus far) of $\sim 24 \text{ nm}$ (110) and 60 nm (001). There are two likely factors limiting the concentration of Mn in $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$; the first is the marginal lattice match between $\beta\text{-MnO}_2$ and

rutile-TiO₂ (~ -4 and -3% in $a=b$ and c , respectively). The effect of this structural mismatch on the stability of the epitaxial films was quantified using *ab initio* thermodynamics. Theory was also used to quantify the increase in film stability with increasing Ti. An unexpected insight gained from *ab initio* thermodynamics was the effect of Ti on competitive reaction pathways. For example, increasing Ti not only stabilized epitaxial rutile-structured Mn_xTi_{1-x}O₂ films, but destabilized the competitive reaction products Mn₂O₃ and Mn₃O₄.

However, both XPS and TEM indicated that other reaction pathways leading to film instability need to be considered. For example, atomic resolution TEM of a ~12 nm thick (110) film with nominal $x = \sim 0.25$ showed formation of a nano-scale secondary surface phase and inclusions, possibly involving the migration of cations into the interstitial sites or tunnels. XPS demonstrated that the primary oxidation state of near-surface Mn was trivalent which implied that inclusion formation could be associated with oxygen vacancies.

This study highlights the inherent tension between requiring a sufficiently high temperature to make a crystalline film and the tendency for Mn(IV) to reduce with the attendant formation of oxygen vacancies. The issue is exacerbated by the use of a template/substrate (needed to make an epitaxial single-crystal) that induces strain in the film. Unfortunately, it appears that lowering T is not an option (i.e., $T < \sim 375^\circ\text{C}$ yields amorphous films) and (rutile)TiO₂ is the closest lattice match to β -MnO₂. Barring the discovery of an excellent accidental lattice match, the one thermodynamic parameter, as opposed to kinetic parameters, left to explore is $P\text{O}_2$. This is not a straightforward option with our present system because the distance between the ablation targets and the substrate is large such that substantial increases in $P\text{O}_2$ will markedly lower film growth rates. Consequently, prior to performing expensive trial and error experiments, an option is to use *ab initio* thermodynamics to explore the effect of increasing $P\text{O}_2$. Future calculations,

however, will have to go beyond the present contribution by incorporating the effect of film thickness, surface energies, coherent strain to the substrate, and oxygen vacancy formation. Nonetheless, this study has demonstrated the potential power of theory towards the rational design of thin films.

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Table 1. Mn 2p_{3/2} XPS analyses

^a substrate	Mn/(Mn + Ti)	thickness (nm)	Mn(IV)%	Mn(III)%	Mn(II)%	average Mn valence
(110) 90°	0.125	15	12.4	73.5	14.1	<2.983>
(110) 90°	0.25	12	7.2	77.0	15.7	<2.915>
(110) 12°	0.25	12	5.2	75.1	19.7	<2.855>
(001) 90°	0.25	10	6.5	75.1	18.4	<2.881>
(001) 12°	0.25	10	n.d.	83.2	16.8	<2.832>
(001) 90°	0.5	10	3.3	68.2	28.5	<2.747>
(001) 12°	0.5	10	3.9	69.5	26.6	<2.773>

^a Film orientation and emission angle during XPS analysis.

Table 2. DFT total energies of unit cells. Z is the number of formula units per unit cell

Phase	Z	Energies(eV)
<i>Rutile structures</i>		
β -MnO ₂ (pyrolusite)	2	-70818.37
β -MnO ₂ (TiO ₂ lattice)	2	-70818.00
TiO ₂	2	-54414.93
MnTiO ₄	1	-62616.62
<i>Bixbyite structures</i>		
α -Mn ₂ O ₃	16	-1100362.69
Mn ₂₈ Ti ₄ O ₄₈ ^a	1	-1067553.982
Mn ₂₈ Ti ₄ O ₄₈ ^b	1	-1067553.981
TiO ₂	16	-837864.960
<i>Spinel structures</i>		
Mn ₃ O ₄	8	-817090.83
Mn ₁₆ Ti ₈ O ₃₂ ^c	1	-751467.34
Ti ₃ O ₄	8	-620208.54

^aTi in 4 octahedral sites

^bTi in 4 tetrahedral sites

^cTi in tetrahedral sites

Table 3. Calculated (PBE) lattice constants compared to experimental values

	a (Å)	b (Å)	c (Å)
<u>β-MnO₂ (pyrolusite)</u>			
experiment (ref 47)	4.398	4.398	2.873
PBE	4.465	4.465	2.959
<u>TiO₂ (rutile)</u>			
experiment (ref 48)	4.594	4.594	2.959
PBE	4.650	4.650	2.989
<u>MnTiO₄ (rutile structure)</u>			
PBE	4.554	4.554	2.950
<u>α-Mn₂O₃ (bixbyite)</u>			
experiment (ref 49)	9.41	9.41	9.41
PBE	9.52	9.52	9.52
<u>Mn₃O₄ (hausmanite)</u>			
experiment (ref 50)	5.71	5.71	9.35
PBE	5.70	5.70	9.15

Figures

Figure 1: RHEED micrographs of $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films: (a) ~15 nm thick (110) orientation with $x = 0.13$, (b) ~12 nm thick (110) orientation with $x = 0.25$, (c) ~60 nm thick (001) orientation with $x = 0.125$, and (d) ~10 nm thick (001) orientation with $x = 0.5$

Figure 2: (a) High-resolution out-of plane 2θ - θ XRD pattern of an $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}/\text{TiO}_2(110)$ film showing a (110)-oriented epitaxial film. Insets: magnifications of the (220) and (330) substrate + film peaks to show the two components; (b) In-plane reciprocal space map of the same $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}/\text{TiO}_2(110)$ film around the (321) reflection suggesting a strained film; (c) High-resolution out-of plane 2θ - θ XRD pattern of an $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}/\text{TiO}_2(001)$ film showing the (002) substrate and film reflections, the only pair of peaks observed; (d) In-plane reciprocal space map of the $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}/\text{TiO}_2(001)$ film around the (112) reflection indicating a strained film. Data collected using Cu K α (1.54056 Å) radiation.

Figure 3: ACTEM micrograph of ~15 nm thick $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ film with nominal $x = 0.13$ on (110) TiO_2 substrate. The bright spots are columns of Mn and Ti atoms, whereas the oxygen sub-lattice is not visible. The tunnels, or [001] direction, are perpendicular to the page.

Figure 4: ACTEM micrograph of ~24 nm thick $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ film with nominal $x = 0.13$ on (110) TiO_2 substrate. The bright spots are columns of Mn and Ti atoms. The tunnels, or [001] direction extend from right to left. EDS analyses record nearly invariant Mn/Ti ratios from substrate/film interface to surface of film.

Figure 5: ACTEM micrograph of ~ 12 nm thick $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ film with nominal $x = 0.25$ on (110) TiO_2 substrate. The bright spots are columns of Mn and Ti atoms, whereas the oxygen sublattice is not visible. The tunnels, or [001] direction, are perpendicular to the page. Oriented inclusions and a secondary surface phase are visible (see discussion in text).

Figure 6: Low resolution TEM micrograph of ~ 12 nm thick $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ film with nominal $x = 0.25$ on (110) TiO_2 substrate. The tunnels, or [001] direction, are perpendicular to the page. Accompanying EELS analyses showing lamellae with low Ti and O intensity as well as increasing Mn/Ti ratios from substrate/film interface to film surface (see text for discussion).

Figure 7: ACTEM micrograph of ~ 60 nm thick $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ film with nominal $x = 0.13$ on (001) TiO_2 substrate. The bright spots are columns of Mn and Ti atoms. The tunnels, or [001] direction extend vertically. Note that despite the instability of the (001) surface that the tunnel structures extend to the very surface of the film (see top panel).

Figure 8: ACTEM micrograph of ~ 10 nm thick $\text{Mn}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ film with nominal $x = 0.13$ on (001) TiO_2 substrate. The bright spots are columns of Mn and Ti atoms. The tunnels, or [001] direction extend vertically. Note that despite the instability of the (001) surface that the tunnel structures extend to the very surface of the film. EDS analyses indicate exponential increase in Mn/Ti ratios from substrate/film interface to surface of film.

Figure 9: Mn2p_{3/2} XPS for ~12 nm thick Mn_xTi_{1-x}O_{2-δ} (001) film with nominal x = 0.25. Each oxidation state is given by an empirical set of multiplet peaks derived from end-member MnO_x standards (see Methods).

Figure 10: Stability fields, calculated by *ab initio* thermodynamics (see text), for various (rutile)Mn_xTi_{1-x}O₂ and MnO_x phases as function of temperature at $P_{O_2} = 20$ mTorr. The vertical blue line marks the temperature of reported experiments. The designations (TiO₂ lat) and (opt lat) refers to Mn_xTi_{1-x}O₂ either expanded to the bulk (rutile)TiO₂ lattice or the relaxed optimum lattice, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10