Strain-dependence of the structure and ferroic properties of epitaxial

$\text{Ni}_{1-x}\text{Ti}_{1-y}\text{O}_3$ thin films grown on sapphire substrates

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Abstract

Polarization-induced weak ferromagnetism has been predicted a few years back in compounds MTiO_3 ($M = \text{Fe, Mn, Ni}$) [Fennie, Phys. Rev. Lett. 100 (2008) 167203]. We set out to stabilize this metastable, distorted perovskite structure by growing NiTiO_3 epitaxially on sapphire Al_2O_3 (001) substrate, and to control the polar and magnetic properties via strain. Epitaxial $\text{Ni}_{1-x}\text{Ti}_{1-y}\text{O}_3$ films of different Ni/Ti ratios and thicknesses were deposited on Al_2O_3 substrates by pulsed laser deposition at different temperatures, and characterized using several techniques. The effect of film thickness, deposition temperature, and film stoichiometry on lattice strain, film structure, and physical properties was investigated. Our structural data from x-ray diffraction, electron microscopy, and x-ray absorption spectroscopy shows that substrate-induced strain has a marked effect on the structure and crystalline quality of the films. Physical property measurements reveal a dependence of the Néel transition and lattice polarization on strain, and highlight our ability to control the ferroic properties in NiTiO_3 thin films by film stoichiometry and thickness.

INTRODUCTION

The one-atmosphere, equilibrium structure of NiTiO_3 is the ilmenite structure with space group $R\bar{3}$ [1]. Ilmenite NiTiO_3 undergoes a phase transition to a disordered $R\bar{3}c$ structure at 1565 K [2]. Under high pressure, the acentric $R3c$ structure (also known as the LiNbO_3 -type or LNO structure) is expected to form [3], although its synthesis in the bulk has not been reported. The ilmenite phase is antiferromagnetic with a Néel temperature of 23.2 K and an effective magnetic moment of $4.01 \mu_B$ (from single crystal neutron diffraction, $3.16 \mu_B$ from powder) [4].

There has been a recent surge of interest in the MTiO_3 ($M = \text{Fe}, \text{Mn}, \text{Ni}$) compounds as a result of a theoretical prediction that their $R3c$ phase exhibits multiferroic properties and may enable switching of the direction of magnetization by the application of an electric field [5,6]. Future demonstration of coupling between the ferromagnetic and ferroelectric order parameters required for such switching will demand either bulk single crystals or epitaxial films. Thin film deposition by molecular beam epitaxy or pulsed laser deposition (PLD) are often the methods of choice to prepare high-quality epitaxial films because they allow for the stabilization of otherwise metastable structures and tuning material properties by the introduction of lattice strain. Thin film deposition also eliminates the need for specialized high-pressure apparatus needed for growing crystals of the above MTiO_3 compounds in the LNO-type structure [7-10].

Recently, we have demonstrated that epitaxial NiTiO_3 films can be grown on sapphire substrate by PLD [11], and that such films exhibit both lattice polarization and weak ferromagnetism [12]. The latter report confirmed that our epitaxial NiTiO_3 films were indeed of the LNO-type structure. In the present work, film thickness and film stoichiometry are employed to influence the strain experienced by the films. Based on high-resolution x-ray diffraction (HRXRD), transmission electron microscopy (TEM), and K-edge x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS), we describe the

effect of strain from lattice mismatch on the structure of the films. Our complimentary physical property characterization by AC magnetic susceptibility and second harmonic generation (SHG) suggests that both film stoichiometry and thickness can be employed to control the ferroic properties of these potentially multiferroic films grown on this common and inexpensive substrate.

I. EXPERIMENT

Epitaxial NiTiO_3 films were grown on sapphire Al_2O_3 (001) substrates by off-axis PLD. The Al_2O_3 (001) substrates (MTI Corporation, Richmond, CA) were ultrasonically cleaned in acetone and isopropanol for 10 minutes each prior to loading in the PLD chamber. Multiple NiTiO_3 films were synthesized using identical deposition conditions with different deposition times to achieve different thicknesses. Film growth was also attempted at different temperatures to investigate the effect of substrate temperature on the growth. Sample composition was also varied with the goal of observing the possible effect of off-stoichiometry on the formation of NiTiO_3 with the LiNbO_3 -type structure and the physical properties. The commercially purchased NiTiO_3 (Plasmaterials, Inc., Livermore, CA), NiO , and Fe_2O_3 targets (Kurt J. Lesker, Co., Livermore, CA) were all 2-inch diameter and used as received. The NiO target was used to adjust the Ni/Ti ratio in the films. This ratio varied from ~ 0.6 to 1.3 (from Ni-deficiency to excess Ni). 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. These “layer sequences” were repeated as many times as necessary to achieve NiTiO_3 films of typically ~ 30 - 50 nm thickness. A repetition rate of 2 Hz was used for the KrF laser ($\lambda = 248$ nm). The laser energy as measured at the laser was 315 mJ. The laser spot (nominally of 1×10 mm² area)

across the rotating target while the substrate was also being rotated to ensure uniform film thickness across the substrate. Prior to growth, the targets were ablated for 15 minutes at a laser repetition rate of 10 Hz in 1.33 Pa O₂ in order to eliminate carbonaceous surface contamination. The substrate temperature was held constant during growth at 600, 650 or 700 °C and the O₂ partial pressure in the chamber was 1.33 Pa during deposition. Substrates were cooled to room temperature in 1.33 Pa O₂ following growth, with no post-growth annealing. The combination of the off-axis geometry and a relatively high oxygen pressure to reduce molten droplet incorporation in the films has been shown to result in high-quality oxide films [13-15].

Film composition and thickness were determined by Rutherford backscattering spectrometry (RBS) measurements carried out using 2 MeV He⁺ ions. Backscattered helium ions were collected at the scattering angle of 150° using a surface barrier detector. The SIMNRA [16] simulation program was used to model experimental RBS spectra, yielding the stoichiometries and thicknesses of the films. In these simulations, the sample is divided into several thin layers of variable thickness and composition. This code utilizes the known Rutherford backscattering cross-section and all other experimental parameters such as incident ion energy, atomic number of the ion, incident and scattering angles, energy calibration values for the detectors, solid angle of detection and the total charge deposited by the incident beam together with the proposed structure to calculate the theoretical spectrum. The composition profiles and film areal densities (in units of atoms/cm²) are then systematically varied until the best fit to experiment is obtained. The areal densities were then converted to actual film thickness (in nm) by using the bulk density of NiTiO₃ (5.1 g/cm³).

Lattice parameters, crystal quality, and lattice strain were investigated using HRXRD with a Philips X'Pert Materials Research Diffractometer 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. Grazing-incidence diffraction measurements to verify epitaxial character of the films before the HRXRD and x-ray reflectivity for film thickness and roughness determination were carried out on a Philips X'Pert Multipurpose Diffractometer also equipped with a fixed Cu anode operating at 45 kV and 40 mA. The analysis of diffraction data was carried out using JADE 9.1.5 (Materials Data Inc., Livermore, CA) with the PDF4+ database from ICDD (Newtown Square, PA). The lattice parameters for the NiTiO₃ films were determined by simultaneously fitting the (006) and (0012) out-of-plane peaks (for parameter c), and the (104), (116), and (1010) in-plane peaks (a and b) using the software TOPAS 4.2 (Bruker AXS GmbH, Karlsruhe, Germany).

TEM and high angle annular dark field scanning TEM (HAADF-STEM) images were collected on a probe-corrected Titan 80-300 TEM operated at 300 kV. HAADF-STEM images were acquired with an annular inner angle greater than 50 mrad. Cross-sections were prepared using a focused ion beam (FIB)-based lift-out approach on an FEI Helios FIB/SEM, with final cleaning at 2 kV.

High-resolution x-ray photoelectron spectroscopy (XPS) measurements using a Phi 5000 VersaProbe were used to verify the film composition as well as for the determination of the oxidation state from the lineshape and chemical shift. This system consists of a monochromatic focused Al-K α x-ray (1486.68 eV) source and a hemispherical analyzer. The x-ray beam was incident normal to the sample and the emitted photoelectrons were collected at an emission angle of 45° relative to the sample normal. Wide scan data were collected using a pass energy of 117.4 eV. High-resolution scans were obtained using a pass energy of 23.5 eV. The XPS spectra

were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at 932.67 ± 0.05 eV and Au $4f$ at 84.0 ± 0.05 eV. Low energy electrons at ~ 1 eV, 40 μ A and low energy Ar^+ ions were used to minimize the surface charging. XPS depth-profile data were collected using 2 kV Ar^+ sputtering over a $3 \text{ mm} \times 3 \text{ mm}$ area of the specimen. The sputter rate for 2 kV Ar^+ over a $3 \text{ mm} \times 3 \text{ mm}$ raster area is determined to be ~ 6.5 nm/minute using SiO_2/Si reference material with known thickness from x-ray reflectivity and ellipsometry. The Ti $2p$, Ni $2p$, O $1s$ XPS peaks were charge corrected to the adventitious C $1s$ peak taken to be 284.8 eV.

The chemical state and local structure of NiTiO_3 was studied by Ni and Ti K -edge XANES and EXAFS. Data were collected in fluorescence mode on beamline 9-BM-B at the Advanced Photon Source, Argonne National Laboratory.

AC magnetic susceptibility and temperature- and field-dependent magnetization of the films was measured on a Quantum Design Physical Property Measurement System. Optical SHG mapping was performed with a fundamental wave generated from a coherent Chameleon tunable Ti-sapphire laser with 100 fs pulses of wavelength 872 nm incident normal to the sample surface. Two-dimensional mapping of the signal was done using a Zeiss LSM 710 multiphoton microscope with a 40X NA0.75 air objective. A none-descanned detector was used to maximize the detection efficiency. An emission band pass filter at 436 nm was used to collect SHG signal and reject any fluorescence signal.

II. THEORY

Lattice parameters and metal-oxygen bonding distances were predicted for the for the $R\bar{3}$ and $R3c$ phases of both FeTiO_3 and NiTiO_3 by density functional theory (DFT) calculations. Spin-polarized periodic DFT calculations have been performed in the generalized gradient

approximation [17] using the Vienna ab initio Simulation Package [18-20]. The core electrons are described by the projector augmented wave method [21], and the Kohn-Sham valence states (3p, 3d, and 4s for Fe, Ni and Ti and 2s, 2p for O) are expanded in plane wave basis sets up to a kinetic energy of 400 eV. The Brillouin zone is sampled with 8x8x8 Monkhorst-Pack k-point meshes, which are found to be sufficient for DFT total energies to converge to within 0.05 eV. The known structures of bulk $R\bar{3}$ NiTiO₃ [22] and FeTiO₃ [23] were used as starting points for bulk parameter calculations. Thin film lattice parameters were calculated for each film using the measured lattice parameters as starting values.

III. RESULTS AND DISCUSSION

A. Structural and morphological properties of the films

Several series of films were prepared; films of different thicknesses with the same composition, films of similar thicknesses with different stoichiometry, and films of similar thicknesses and composition deposited at different temperatures. A full list of the films prepared with synthesis temperature, composition, thickness, and lattice parameters is provided in Table A1 of Appendix 1. Following a general characterization of film structure in this section, the effect of lattice mismatch, film thickness, and deposition temperature on film structure and physical properties will be discussed in detail in sections B-E.

All of the films discussed here were epitaxial, and consisted of a single phase, Ni_{1-x}Ti_{1-y}O₃ as suggested by XRD and microscopy. (This chemical formula represents the varied stoichiometry discussed later. We assume for this study that no O-vacancies are present.) Fig. 1(a) shows a representative 2θ - θ HRXRD pattern of a NiTiO₃ film grown on Al₂O₃ (001) (50-nm thick film sample NTO-25, see Table A1). The out-of-plane scans for all films exhibit the expected (001)-

oriented rhombohedral structure (only the (006) and (0012) film peaks detected) with no evidence for secondary phase formation. The inset in Fig. 1(a) shows a rocking curve around the (006) reflection of the same NiTiO₃ sample. A single peak is observed with a full width at half maximum (FWHM) of $\sim 1^\circ$. This value is representative for most of our NiTiO₃/Al₂O₃ samples except those with smaller thicknesses (further discussion including rocking curves in section C). An XRD ϕ scan in the (116) film plane is shown in Fig. 1(b). In the (116) plane one sees six peaks from the (001) sapphire substrate in the 0-360° range due to six-fold symmetry (only three would be expected in some other in-plane directions such as the (104) due to threefold symmetry). The equal number and the overlap of the Bragg peaks for the film and the substrate confirm the expected hexagonal-on-hexagonal structure with the epitaxial relationship NiTiO₃ (001) [001] // Al₂O₃ (001) [001]. The reciprocal space map collected around the (1010) reflections in the same sample (Fig. 1c) indicates a film in-plane parameter very different from that of the substrate suggesting that the film is relaxed (mostly free of epitaxial strain). Film lattice parameters measured for different samples fall between 4.995-5.048 Å for in-plane parameter a , and 13.767-13.920 Å for out-of-plane parameter c , depending on the degree of strain/relaxation (above a certain thickness, strain may just be stoichiometry-induced).

The TEM micrograph for NiTiO₃/Al₂O₃(001) sample NTO-3 in Fig. 2(a) reveals a film comprised of columnar grains. The columnar growth presumably results from the -5.7 % lattice mismatch between NiTiO₃ (001) and Al₂O₃ (001). These images were found to be representative for our NiTiO₃/Al₂O₃ films. STEM analysis confirms that the films are crystalline and have a high degree of epitaxy, in agreement with XRD (Fig. 2b). Atomic resolution images of the interface reveal that there is often a structurally distinct ~2-nm thick layer between the substrate and the well-oriented film. This intermediate layer appears to be Ni- and Ti-rich when probed

using energy-dispersive x-ray spectroscopy. STEM images evidence a number of defects along the interface, consistent with the sizeable lattice mismatch and the apparent columnar growth. Fourier transformations of local areas (not shown here) indicate that the diffraction spots of the interface layer are broader than in the film, which can be explained by buckled lattice plains and small regions with small deviations from the epitaxial relationship. Buckling of layers at the film-substrate interface has been inferred earlier in $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ based on XRD data [11]. No evidence of Ni/Ti segregation was found. Some of the flawed regions near the interface may be due to the formation of strained islands to release strain energy as observed in other large or moderate mismatch systems [24]. The columnar growth is consistent with the peak broadening observed by XRD and the large rocking curve FWHM values (see section C). The typical lateral crystallite size is ~ 5 nm as estimated from FWHM of in-plane XRD peaks by peak profile fitting in TOPAS 4.2. Our high-resolution HAADF-STEM imaging reported earlier [12] suggests that NiTiO_3 exhibits a rhombohedral arrangement consistent with the $R3c$ structure. The structure and physical properties of these films in relation to the biaxial strain are discussed in the next sections.

B. Influence of strain from lattice mismatch on structure

It has been previously demonstrated that the structure and physical properties of electric and magnetic materials in thin film form can be modified or controlled by substrate-induced strain [25-31]. Biaxial strain was used to increase the transition temperature in high- T_C superconductors [25,26], and ferroelectric materials [27-29]. The saturation magnetization in ferromagnets [30], and the spontaneous polarization in ferroelectrics were also shown to be affected by strain [28,31]. Our goal was to employ substrate-exerted strain to stabilize the desired

multiferroic phase in the films, and manipulate the physical properties by applied strain, where strain was varied by either film thickness, or film stoichiometry. While the bulk ilmenite-type phase ($R\bar{3}$) and the acentric LNO-type ($R3c$) phase of NiTiO_3 are expected to be structurally similar, there is a subtle change from $R\bar{3}$ to $R3c$ that is accompanied by an increased distortion of the coordination octahedra and a reduction of the unit cell size [8,9]. This change can be brought about by compression. In bulk FeTiO_3 it results in a volume reduction of 1.1 % (the unit cell volume of the ilmenite phase is $V = 315.93 \text{ \AA}^3$ [23], while for the high-pressure LNO phase $V = 312.53 \text{ \AA}^3$) [9]. Due to the lack of nonmagnetic and/or non-polar substrates with lattice parameters that match NiTiO_3 more closely, sapphire Al_2O_3 (c -cut, (0001)) substrate with a large (5.7 %) lattice mismatch to bulk NiTiO_3 was chosen as the best commercially available, and low-priced option. Sapphire substrates have been used previously to grow epitaxial FeTiO_3 films [32], and more recently, epitaxial NiTiO_3 films [11,12]. One potential benefit to using sapphire substrates is the inherent biaxial compression resulting from the considerable lattice mismatch between bulk ilmenite NiTiO_3 ($a = 5.030 \text{ \AA}$) [22], and sapphire Al_2O_3 ($a = 4.759 \text{ \AA}$) [33], which may mimic a high-pressure compression employed in the growth of bulk FeTiO_3 [9]. Using the formula $\epsilon_{\text{ALO}} = (a_{\text{film}} - a_{\text{substrate}})/a_{\text{substrate}}$, the compressive strain (in-plane direction) is estimated to be $\epsilon_{\text{ALO}} = -5.7\%$.

The strain from lattice mismatch for each film in the out-of-plane (c -axis) direction was measured from out-of-plane XRD scans, specifically from simultaneously fitting the (006) peaks of the film and the substrate, and deriving the strain from the splitting of film and substrate peaks using dynamical simulation by the program Bede RADS (Jordan Valley Semiconductors Ltd, Austin, TX) [34]. A representative fit is depicted in Fig. 3a. The resulting strain is plotted versus the experimentally measured lattice parameters (calculated from fitting out-of-plane and in-plane

peaks simultaneously) in Fig. 3b. There is one less in-plane (a) parameter than out-of plane (c) parameter, because the a parameter for the 5-nm thick sample NTO-7 could not be determined from the XRD due to low signal from the very thin film. Strain was varied by the thickness of the deposited films. Thickness as a variable and its effect will be discussed in detail in the next section. The measured lattice parameters were expected to reflect that a greater compressive strain results in smaller cell parameters, which is true for the in-plane parameters, where the measured strain decreases with a . However, the out-of-plane parameter shows an opposite trend; greater strain from mismatch in the c direction is accompanied by a larger out-of-plane parameter indicating that lattice compression in the a direction causes the lattice to relax in the other. This is understood as the way the lattice tries to accommodate the compression brought about by the substrate, and it highlights the limitations to what may be achieved by biaxial strain when the lattice mismatch is as large as 5.7 %.

C. Influence of film thickness on strain and film properties

The effect of film thickness on strain and film properties was investigated in the NiTiO₃/Al₂O₃ samples grown in the 5-200 nm thickness range. The stability/instability of strained epitaxial layers is determined by the strain energy present in the growing film. Starting from the substrate/film interface, the strain energy increases as more and more layers are deposited. This energy can be released by e.g. the formation of misfit dislocations (as found to be present in our films) beyond the critical thickness. We estimated the critical thickness in our NiTiO₃/Al₂O₃ films using the Matthews-Blakeslee formula [35]:

$$h_c = \frac{b}{4\pi f \cos \lambda} \frac{(1 - \nu \cos^2 \beta)}{(1 + \nu)} \ln \left(\alpha \frac{h_c}{b} \right) \quad (1)$$

where h_c is the critical thickness, b is the magnitude of the Burgers vector (the rhombohedral lattice parameter $a = 5.030 \text{ \AA}$ was used here [36]), f is the lattice mismatch (0.057), ν is the Poisson ratio (0.3 was estimated [37]), β is the angle between the dislocation line and its Burgers vector (the misfit dislocations are believed to be mostly (110) or (100) based on microscopy images, where $\beta = 90^\circ$), λ is the angle between the slip direction and the direction perpendicular to the line of intersection of the slip plane and the interface (assumed to be 0° here), and α is the dislocation core cutoff parameter (estimated to be ~ 4 [38]). The critical thickness is estimated to be about 1.2 nm using the Matthews-Blakeslee model, corresponding to roughly 3 monolayers. This is considerably smaller than that expected based on the variation of lattice parameters with film thickness (Fig. 4). The strain from mismatch estimated from the XRD data shows that the compressive strain, and the lattice parameters, track with film thickness up to about 20-25 nm. The strain quickly drops with increasing film thickness up to ~ 20 nm film thickness before it essentially levels off as the film fully relaxes (Fig. 4a). Consistently, the in-plane lattice parameter a increases up to about 20 nm thickness (Fig. 4b), which is also in line with that observed for the dependence of a on compressive strain in Fig. 3b for the same samples. There appears to be a drop in the magnitude of the a parameter in the 20-50 nm thickness range before it returns to bulk-like values. As the anomaly also appears for the same thickness samples in the form of a strain increase in the strain vs thickness data (plot Fig. 4a), it is possible that those samples exhibit some sort of a “spring-back” when strain from the substrate is no longer in effect. The c parameter displays an essentially linear decrease with film thickness up to 30 nm (see inset of Fig. 4c), then a small increase followed by settling around the bulk NiTiO_3 parameter. This is consistent with the observed increase of the out-of-plane parameters with strain shown in Fig. 3b. In summary, the in-plane parameters increase, while the out-of-plane

parameters decrease with film thickness up to ~20 nm, where the substrate-induced compressive strain disappears. The lattice parameters become similar to those of bulk NiTiO_3 for thicknesses above 50 nm. In the intermediate, 20-50 nm thickness range, the strain and the lattice parameters vary anomalously, perhaps as the film structure adjusts to the lack of strain. The observed decrease in the a and increase in the c lattice parameter (even above the bulk ILM NiTiO_3 c parameter value) may also be a consequence of a buckling of a few ilmenite-like monolayers at the film/substrate interface. The large difference between the calculated critical thickness of 1.2 nm and the practically observed strain cutoff thickness of ~20 nm can be explained as follows: strain relaxation begins above the critical thickness and gradually continues up to 20 nm. The film can be considered fully relaxed by the thickness of 20 nm (this is supported by reciprocal space maps collected on 20- and 25-nm films, not shown here). The critical thickness for a system where the lattice mismatch is so large (-5.7%) is expected to be quite small; critical thicknesses of about 2 nm were reported for LAO/STO (001) films, where the lattice mismatch was -2.91% [39].

Out-of-plane (006) and in-plane (116) rocking curve measurements were performed to examine epitaxial film quality, and the results are summarized in Fig. 5(a-b). In general, the width and shape of the rocking curve peaks contain information on the extent of mosaic spread in the film. Generally, relatively larger and well-aligned crystallites should result in a sharper in-plane rocking curve peak, while relatively smaller and poorly aligned crystallites result in broader peaks. Both the out-of-plane and in-plane rocking curves reveal a clear dependence of film crystalline quality on film thickness. The out-of-plane (006) rocking curves show a broadening with film thickness with the FWHM reaching a plateau around a 100 nm (Fig. 5a). The films show a greater mosaic spread, a reduction in crystalline quality with increasing

thickness. Similarly, the in-plane rocking curves show an increasing FWHM with thickness, giving a close-to-linear trend in the measured range (Fig. 5b). Both these trends indicate that, under our growth conditions, crystallite orientation becomes more random as the layers are deposited farther and farther from the substrate-film interface. The quite large widths of these curves suggest that the structural quality of the films is most likely not limited by the structural quality of the substrate.

We have studied the effect of strain on the Ni and Ti local environments in the NiTiO_3 films by x-ray absorption spectroscopy (XAS; both XANES and EXAFS). The samples investigated by Ni and Ti K-edges XAS included NiTiO_3 films of different (50-115 nm) thicknesses, grown on Al_2O_3 , and as reference, a bulk NiTiO_3 powder sample. No significant difference is seen in the Ni K-edge XANES spectra of two different thickness film and the bulk samples (Fig. 6a) indicating an essentially identical Ni coordination environment in all of them. The Ni has the expected octahedral coordination with a Ni coordination environment as observed before in an epitaxial NiTiO_3 film.[11] Similar spectral features were observed before for octahedral Ni in nickel monoxide by Li *et al.* [40], and in $\text{K}_{0.8}\text{Ni}_{0.4}\text{Ti}_{1.6}\text{O}_4$, a Ni-containing hydronium intercalate, and NiO by Paek *et al.* [41]. Fig. 6b compares the Ti K-edge XANES spectra for several film and bulk samples and suggests a similar Ti coordination environment for all. There seems to be a visible effect of film stoichiometry on the Ti coordination environment in the XANES. The 50-nm film was stoichiometric (Ni/Ti=1), while the 64- and 115-nm films were Ni-deficient with Ni/Ti= 0.65. The Ti K-edge XANES of the stoichiometric film and bulk NiTiO_3 are very similar to one another. Both the pre-edge and the main edge appear to be somewhat suppressed in the Ni-deficient samples (64- and 115-nm samples). It is difficult to be certain due to the general noisiness of the XAS of the film samples but the Ti coordination environment may be closer to

that of rutile TiO_2 in these samples as a result of the Ni deficiency. A comparison of the XANES of these samples with that of rutile powder (Fig. 6c) shows an edge shape resembling the TiO_2 phase with small differences (Note: the 115-nm sample has considerable noise in the pre-edge region). In general, the Ti K-edge XANES suggests a somewhat distorted octahedral Ti coordination, similar to rutile.

The formal valence state of the Ni, Ti, and Fe cations can be determined by comparing the energy of the inflection point (first derivative) of their XANES spectra to literature reports. This is most likely a better test of their valence state in the film than XPS as XANES probes the entire film as opposed to the film surface. In addition, sputter reduction effects that may occur in XPS measurements are excluded in XANES. The inflection point from the Ni K-edge XANES is 8344.3 ± 0.1 eV for all NiTiO_3 films and the NiTiO_3 powder used as reference, in agreement with the reported 8343.8 eV for Ni^{2+} [42], and the trend reported by Sánchez *et al.* for a Ni^{3+} to Ni^{2+} shift [43]. Ni^{2+} in the films was also verified by XPS (not shown here); the Ni $2p_{3/2}$ XPS at 855.3 eV is characteristic of Ni^{2+} . Ti^{4+} was confirmed by both Ti K-edge XANES showing the inflection point for Ti between 4982-4983 eV for all films and our reference NiTiO_3 powder, consistent with the ~ 4982 eV value reported for TiO_2 [44], and by XPS where the Ti $2p_{3/2}$ XPS shows a peak at 458.3 eV characteristic of Ti^{4+} as in BaTiO_3 and PbTiO_3 [45].

In order to learn about the effect of lattice strain on the metal coordination environment in the films, first-shell metal-oxygen distances were extracted from the Ni and Ti K-edge EXAFS fitting performed using crystal structure data for ilmenite NiTiO_3 as starting model. The derived interatomic distances for the films were compared with those reported for ilmenite- NiTiO_3 and calculated for LNO- NiTiO_3 (see Table I). In general, based on our simulated nearest-neighbor metal-oxygen distances, the average nearest Ni-O distances were expected to be shorter (by

~0.04 Å) in the film with the LNO-type structure than in the bulk ilmenite phase, while the nearest Ti-O distances were expected to be more similar to reported bulk values, maybe slightly longer (by ~0.01 Å). This expectation would be consistent with a greater distortion of the NiO₆ octahedra due to substrate-exerted strain, and a Ti-O bonding environment more similar to that reported in bulk ilmenite-NiTiO₃. Our EXAFS-derived bonding distances reveal that the Ni-O distance is indeed reduced from 2.088 Å (reported for bulk ilmenite-NiTiO₃ [22]) to when the film is strained: 2.052 Å for NTO-3, the thinnest of the films examined (17 nm). The measured Ni-O distance in the 17-nm NiTiO₃/Al₂O₃ film is in good agreement to that calculated for the desired LNO structure. However, the Ni-O distances relax and get longer (~2.1 Å for NTO-20 and NTO-25, 115 and 50 nm thick, resp.) as the strain is removed as a result of growing the film thicker and/or changing the stoichiometry. In these thicker NiTiO₃/Al₂O₃ films, the Ni-O distances are closer to that reported for bulk NiTiO₃. The Fourier-transformed *R*-space spectra at the Ni K-edge are consistent with this picture (Fig. 7a): the Ni-O, Ni-Ni, and Ni-Ti peaks for the thin (~17 nm) NiTiO₃ film is shifted to shorter distances, while those of the thicker (115 nm) film center at similar distances as the bulk. In fact, part of the Ni-O distances in the 17-nm NiTiO₃ film are greater than in the bulk (Ni-O peak grew a shoulder), and the Ni-Ni, Ni-Ti distances are shifted to greater *R*. The average Ti-O distances also appear reduced in the strained NiTiO₃/Al₂O₃ film relative to the bulk (NTO-3: from 1.985 to 1.945 Å). As the substrate-exerted strain is reduced, the Ti-O bonding distances get longer, and they approach that calculated for bulk LNO-type NiTiO₃. This trend is also reflected in the Fourier-transformed spectra (Fig. 7b); the Ti-O and Ti-Ni, Ti-Ti peaks appear at smaller distances for the 17-nm film, while those for the 115-nm film are very much like the bulk sample. Also notable is the narrower Ti-O peak for the 17-nm thick sample, indicating a narrower distribution of Ti-O distances in the film. The

increase in the metal-oxygen distances with lattice relaxation is consistent with the XRD results suggesting an ~ 30 nm “cut-off” thickness for strain from Al_2O_3 (see section C), and show the limitations of sapphire substrate to achieve a homogeneously strained film. Our EXAFS results are also consistent with a slight reduction of the unit cell in the more strained (thinner) films relative to the ilmenite phase, and perhaps more pronounced distortion of the TiO_6 octahedra. The value of $1.945 \text{ \AA}$ for the average Ti – O distance in the thinnest film (16.6 nm) is smaller than that predicted for the LNO-type phase, and similar to the Ti – O distance calculated for anatase [46], one of the TiO_2 polymorphs with a more distorted Ti coordination environment.

D. Influence of growth temperature

NiTiO_3 films were deposited at 600, 650, and 700 °C substrate temperatures by PLD. The 600-700 °C temperature range was chosen based on previous experience [11] and reports [32]. Given that we were attempting to stabilize a metastable phase of NiTiO_3 , we considered the effect of increased thermal motion on the deposited structure. When comparing films of similar thicknesses grown at 600, 650, and 700 °C substrate temperatures, we observed a slight degradation in crystalline quality with increased temperature resulting in broadening of the film XRD peaks perhaps due to formation of binary oxides. This is contrary to the observations of Popova *et al.* for FeTiO_3 films where film crystallinity improved up to about 735 °C [32]. We believe that due to its expected lower enthalpic stability relative to the binary oxides, the NiTiO_3 system has a lower thermodynamic equilibrium temperature at the substrate surface than FeTiO_3 [3]. As a consequence, NiTiO_3 may begin decomposing to NiO (or Ni_2O_3) and TiO_2 at higher substrate surface temperatures causing a greater variation of lattice parameters in the film. The limited available lattice parameter vs temperature data suggests that the in-plane lattice parameter

value decreases and approaches that of bulk NiTiO_3 as the substrate temperature increases. On the contrary, the out-of-plane parameter value increases and moves away from the bulk reference at higher temperatures. The dependence of crystalline quality on substrate temperature during deposition, as reflected in the FWHM vs temperature plots in Fig. 8, suggests that crystalline quality suffers when higher (650 or 700 °C) deposition temperature is employed. The 600 °C substrate temperature appears to be a good compromise both between the in-plane and out-of-plane lattice deformations to achieve a slightly compressed structure, as well as to avoid the decomposition of NiTiO_3 entities to binary oxides in the plume. Post-deposition annealing has not been attempted on these films but is considered as part of a later study.

E. Magnetism and lattice polarization

For a potential multiferroic material with predicted coexisting ferroelectric and ferromagnetic orders, one needs to achieve, and possibly control, both the magnetism and polarization. We have shown before from field-dependent DC magnetization measurements that $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films exhibit ferromagnetic behavior [12]. Fig. 9 shows isothermal magnetization measured in the 50-nm $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ film in the $(-1) - 1$ T field range at room temperature (300 K) and at 10 K, well below T_N (120 K for that sample). A clear S-shape magnetization curve is observed in the low-temperature data, indicative of residual magnetization from weak ferromagnetism. Due to the weak ferromagnetic moments, the large diamagnetic background from the substrate, and the general noisiness of the data, attempts to study the dependence of ferromagnetism on strain in these films were unsuccessful. However, we have studied the dependence of the Néel temperature (T_N) on NiTiO_3 film stoichiometry by performing temperature-dependent magnetization measurements on $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films with varying Ni/Ti ratio. We have found

earlier that the NiTiO_3 structure was able to tolerate a significant amount of off-stoichiometry (Ni/Ti ratio down to 2/3) [11]. The appearance of ferromagnetism should be tied to the onset of the antiferromagnetic (AFM) state (occurring at T_N) according to the theory, where the Dzyaloshinskii-Moriya interaction results in the canting of the collinear antiferromagnetic spins [5]. In order to manufacture a technologically viable multiferroic material, one would need to achieve ferromagnetism at, or close to, room temperature. The samples measured and included in Fig. 10 range from a Ni/Ti ratio of 0.6 ($\sim\text{Ni}_{0.7}\text{Ti}_{1.2}\text{O}_{3-x}$) to 1.3 ($\sim\text{Ni}_{1.1}\text{Ti}_{0.8}\text{O}_{3-x}$). The measured T_N increases linearly with the increasing amount of Ni, the magnetic ion, in the structure. This suggests that the more Ni is inserted into the structure, the stronger the AFM ordering becomes, as it takes higher temperature (more thermal energy) to destroy the AFM ordering of the spins/domains. We note that we observed a hysteretic behavior in our sample with the highest Ni/Ti ratios (1.3); a different T_N was measured in the field-cooled (FC) than in the zero-field-cooled (ZFC) experiment: ~ 120 K *vs* ~ 160 K, respectively (see Fig. A1 in the Appendix). This hysteretic behavior provides insight into the anisotropy of the domain state; in a sample composed of FM and AFM domains, cooling in a magnetic field (FC experiment) may “lock” in the magnetic domains in a metastable state relative to the ground state (ZFC experiment). This may result in a different energy barrier to overcome in the two experiments. As the temperature is increased after field-cooling, the system will encounter a smaller energy barrier (due to the “locked-in” energy) to overcome the metastable configuration and break down the AFM order. However, in the ZFC experiment, where the system is already in its most stable domain configuration, one has to overcome a greater barrier to dissolve the magnetic ordering marked by a higher T_N . Alternatively, the difference between the FC and ZFC experimental results may be due to the simultaneous presence of both stoichiometric regions and those that contain excess Ni.

Assuming that greater strain from the substrate would result in a more homogeneous domain state and improved magnetic ordering, one can also make the connection between these magnetic data and the strain state of the samples with different Ni/Ti ratios. It is plausible that sample stoichiometry affects the biaxial strain due to, for instance, formation of islands of different stoichiometry when there is a deficiency of Ni. These islands may alleviate the substrate-exerted strain and result in a weaker AFM domain ordering and a corresponding lower T_N . In the more stoichiometric samples, the AFM ordering is stronger, therefore T_N is higher. In all, these stoichiometry-dependent magnetization results suggest that the magnetic properties may be manipulated by stoichiometry and strain. We have achieved a 70-degree increase in T_N by going from Ni/Ti ratio of 0.6 to 1.3. Our ability to control the magnetic properties by strain engineering suggests that pushing T_N closer to room temperature in MTiO_3 phases may be possible.

We have explored the polar properties of the NiTiO_3 films using optical SHG. Optical SHG involves the conversion of light at a given frequency into an optical signal at double the frequency by a nonlinear medium (the sample) through the creation of a nonlinear polarization. SHG occurs only in the absence of inversion symmetry (in this case for the acentric $R3c$ structure), which is also a necessary condition for a polar medium such as a ferroelectric. It should not occur for a non-polar substance such as the sapphire substrate or ilmenite-type NiTiO_3 . First, as a reference, we demonstrated that the non-polar sapphire substrate shows no signal, i.e. any observed SHG contrast will come from the film, and showed the strong signal obtained from a ferroelectric LNO crystal substrate (see bottom images in Fig. 11). Next, we performed optical SHG on a three $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ samples of different thicknesses: 38, 60, and 150 nm, respectively. By comparing the three images in Fig. 11, we find that as the film thickness increases, the optical SHG signal gets weaker and weaker, and eventually the film

becomes non-polar at thicknesses around 150 nm. This supports what is expected, that is, the thinner films are more strained, and thus more polarized than the thicker films. At thicknesses greater than 150 nm, the film becomes bulk ilmenite-like. The random brighter spots seen in two of the images (38-nm and 150-nm samples) are suspected to occur due to dust particles, but they need further investigation by an appropriate surface analysis method to exclude that they are special growth/crystallization spots.

Conclusions

We have grown a series of epitaxial NiTiO_3 thin films on $\text{Al}_2\text{O}_3(001)$ substrate with controlled thickness and stoichiometry by pulsed laser deposition. Our results indicate that the metastable perovskite structure (acentric space group $R3c$) was stabilized in $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films of up to at least 30 nm thickness. Strain was employed to control the polar and magnetic properties of the films. X-ray diffraction, electron microscopy, and x-ray absorption spectroscopy shows that substrate-exerted strain has a marked effect on the structure and crystalline quality of the samples. Physical property measurements reveal a dependence of the Néel transition and lattice polarization on strain, and further highlight our ability to control the ferroic properties in NiTiO_3 thin films by film stoichiometry and thickness. From $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films and the conditions examined here, a 20-30 nm film with up to 30 % excess Ni would be the most promising multiferroic material. Our ability to control the magnetic properties by strain engineering suggests that pushing T_N closer to room temperature in MTiO_3 phases may be possible, especially if one considers doped structures as well in future work. Experiments aimed at probing the coupling of the polar and magnetic orders in NiTiO_3 thin films, as well as growth

on different substrates covering a wider strain range, are being pursued and will be reported when succeeded.

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Appendix

Table A1: Summary of the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ films grown including sample IDs, synthesis conditions, stoichiometry, thickness, and lattice parameters. Sapphire (0001) substrates were used for all depositions. Bulk NiTiO_3 ($R\bar{3}$) lattice parameters: 5.030; 13.790 Å [22].

Sample ID	Growth method/ Temperature	Ni/Ti ratio (stoichiometry)	Thickness (nm)	Lattice parameter a and c , resp. (Å)
NTO-1	PLD, 600 °C	0.67	32.5	5.025, 13.773
NTO-2	PLD, 600 °C	0.69	10	4.995, 13.87
NTO-3	PLD, 600 °C	1.17	17	5.042, 13.851
NTO-5	PLD, 600 °C	0.60	155	5.013, 13.860
NTO-6	PLD, 600 °C	0.72	23	5.043, 13.792
NTO-7	PLD, 600 °C	0.56	5	(unknown), 13.92
NTO-9	PLD, 650 °C	0.61	5	5.03, 13.918
NTO-13	PLD, 650 °C	0.67	33.5	5.014, 13.834
NTO-16	PLD, 600 °C	-	200	5.041, 13.799
NTO-18	PLD, 600 °C	0.65	52	5.047, 13.779
NTO-20	PLD, 700 °C	0.61	115	5.048, 13.767
NTO-21	PLD, 700 °C	-	25	5.031, 13.804
NTO-23	PLD, 600 °C	1.33	60	-
NTO-24	PLD, 600 °C	0.91	38	5.040, 13.868
NTO-25	PLD, 600 °C	1.10	50	5.021, 13.840
NTO-28	PLD, 600 °C	1.10	50	5.021, 13.840

Table A2. Details of the EXAFS fitting at the Ni- and Ti K-edges. The structural models that were used along with the resulting quality of fit indicator (R -factor), Debye-Waller factor (σ^2) and change in half-path length (Δr) are presented. Fits were carried out in both R space and q space. Values of S_0 and E_0 obtained for ilmenite-type NiTiO_3 were used for the rest of the models/fits; for Ni K-edge S_0 : 0.87 (R -space), 1.02 (q -space), E_0 : -2.50 eV (R -space), -0.67 eV (q -space); for Ti K-edge S_0 : 0.41 (R -space), 0.49 (q -space); E_0 : -2.43 eV (R -space), -4.80 eV (q -space). For all the fits a k -range of 2 – 10 $\text{\AA}^{-1}$ and an R -range of 1-4 $\text{\AA}$ were employed. Values in the shaded cells were used to calculate the average M – O bond lengths discussed in section C of the manuscript.

Absorption edge	Sample	M-O path lengths ($\text{\AA}$)*	R space fit	q space fit
			6-coordinate metal	6-coordinate metal
Ni K-edge	NiTiO ₃ Powder	2.046(18) x3 2.103(18) x3 $\sigma^2 = 0.005$	R : 0.028 S_0 : 0.69(5) E_0 : -1.17 $\pm$ 1.52 Δr : -0.014(18)	R : 0.037 S_0 : .69(8) E_0 : .27 $\pm$ 2.09 Δr : -0.002(25)
	NTO-20	2.069(22) x3 2.127(22) x3	R : 0.114 σ^2 : 0.005 Δr : 0.010(22)	R : 0.082 σ^2 : 0.005 Δr : 0.009(30)
	NTO-25	2.121(20) x3 2.178(20) x3	R : 0.133 σ^2 : 0.005 Δr : 0.061(20)	R : 0.130 σ^2 : 0.005 Δr : 0.065(23)
Ti K-edge	NiTiO ₃ Powder	1.826(37) x3 2.046(37) x3 $\sigma^2 = 0.0009$	R : 0.091 S_0 : 0.535(37) E_0 : -3.831 $\pm$ 2.161 Δr : -0.032(37)	R : 0.130 S_0 : 0.525(10) E_0 : -4.810 $\pm$ 2.781 Δr : -0.044(62)
	NTO-20	1.861(57) x3 2.081(57) x3	R : 0.074 σ^2 : .0009 Δr : 0.003(57)	R : 0.058 σ^2 : .0009 Δr : -0.047(83)
	NTO-25	1.864(73) x3 2.084(73) x3	R : 0.254 σ^2 : .0009 Δr : 0.005(73)	R : 0.309 σ^2 : .0009 Δr : -0.027(91)

*Starting model - Ni-K: 2.059 x3

2.117 x3 (2 x 3 bonds for 6 coordination)

Ti K: 1.858 x3

2.079 x3

Figure A1: AC magnetic susceptibility measurements of a $\text{Ni}_{1-x}\text{Ti}_{1-y}\text{O}_3$ sample with an Ni/Ti ratio of 1.33 showing different Néel temperatures (T_N) for the zero-field-cooled and the field-cooled experiments.

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Table I: Summary of the reported lattice parameters for ilmenite (ILM)-NiTiO₃, sapphire Al₂O₃, calculated lattice parameters for the two (ILM- and LNO-type) NiTiO₃ phases, and the measured and calculated parameters for the present NiTiO₃ films. Nearest-neighbor distances are also included where available.

Material	Comment	c (Å)	a, b (Å)	Ni – O (Å)	Ti – O (Å)
ILM-NiTiO ₃ [22]	Bulk, reported	13.790	5.030	2.088	1.985
ILM-NiTiO ₃	Bulk, measured (this study)	-	-	2.074(18)	1.936(37)
ILM-NiTiO ₃	Bulk, calculated (this study)	13.662	4.984	2.05 (2.02-2.08)	1.965 (1.85-2.08)
LNO-NiTiO ₃	Bulk, calculated (this study)	13.654	4.983	2.045 (2.02-2.07)	1.975 (1.84-2.11)
LNO-NiTiO ₃	Film, calculated (this study)	13.77486	4.98995	2.045 (2.01-2.08)	1.995 (1.87-2.12)
NiTiO ₃ /Al ₂ O ₃ film (NTO-3)	Measured (this study); thickness: 16.6 nm	13.851(3)	5.042(9)	2.052(26)	1.945(38)
NiTiO ₃ /Al ₂ O ₃ film (NTO-25)	Measured (this study); thickness 50 nm	13.840(4)	5.021(4)	2.150(20)	1.974(73)
NiTiO ₃ /Al ₂ O ₃ film (NTO-20)	Measured (this study); thickness 115 nm	13.767(4)	5.048(9)	2.098(22)	1.971(57)
Al ₂ O ₃ substrate [33]	-	12.991	4.759	-	-

Figure captions

Fig. 1. (Color online) (a) Representative high-resolution 2θ - θ XRD pattern of a $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ film showing a (001)-oriented epitaxial film. Inset: (006) rocking curve for the same NiTiO_3 film; (b) In-plane (116) ϕ scan for the same NiTiO_3 film and the sapphire substrate; (c) (1010) reciprocal space map for the same $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ film sample. Data collected using $\text{Cu K}\alpha$ (1.54056 Å) radiation.

Fig. 2. (Color online) (a) Lower magnification TEM image of the $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ interface. The carbon (C) and platinum (Pt) coating are from the sample preparation step.; (b) High-magnification TEM image of $\text{NiTiO}_3/\text{Al}_2\text{O}_3$ interface.

Fig. 3. (Color online) (a) Representative fitting of the (006) film + substrate ($\text{NiTiO}_3 + \text{Al}_2\text{O}_3$) peaks simultaneously to obtain strain information in BEDE RADS [34]; (b) Strain-dependence of the in-plane (a) and out-of-plane (c) lattice parameters of NiTiO_3 films grown on Al_2O_3 . Data collected using $\text{Cu K}\alpha$ (1.54056 Å) radiation.

Fig. 4. (a) Dependence of strain from lattice mismatch on film thickness; (b) Variation of lattice parameter a with film thickness. The dotted line serves as a guide to the eye.; (c) Variation of lattice parameter c with film thickness. Inset: The 5-30 nm thickness range magnified, and a linear line fitted to the data.

Fig. 5. (a) Variation of the FWHM of the (006) rocking curve peak of thin-film NiTiO_3 with film thickness; (b) Variation of FWHM of the (116) rocking curve peak of thin-film NiTiO_3 with film thickness. Data collected using $\text{Cu K}\alpha$ (1.54056 Å) radiation.

Fig. 6. (Color online) (a) Ni *K*-edge XANES spectra of NiTiO₃ thin films and bulk NiTiO₃; (b) Ti *K*-edge XANES spectra of NiTiO₃ thin films and bulk NiTiO₃; (c) Ti *K*-edge XANES spectra of NiTiO₃ thin films compared with that of rutile TiO₂.

Fig. 7. (Color online) (a) Fourier-transformed *R*-space spectra at the Ni *K*-edge for NiTiO₃ films of different thicknesses and bulk NiTiO₃; (b) Fourier-transformed *R*-space spectra at the Ti *K*-edge for NiTiO₃ films of different thicknesses and bulk NiTiO₃.

Fig. 8. (a) Variation of the FWHM of the (006) rocking curve peak of thin-film NiTiO₃ with substrate temperature; (b) Variation of FWHM of the (116) rocking curve peak of thin-film NiTiO₃ with substrate temperature. Data collected using Cu K α (1.54056 Å) radiation.

Fig. 9. Field-dependent magnetization curves for NiTiO₃/Al₂O₃ film above (300 K) and below (10 K) the Néel temperature indicating residual magnetization at low *T*.

Fig. 10. Dependence of the Néel temperature on the Ni/Ti ratio in NiTiO₃/Al₂O₃ films. Recorded in AC mode at 10 G field. For the Ni/Ti=1.3 sample the mean of the values measured in the ZFC and FC experiments was used; 140 K.

Fig. 11. (Color online) Optical SHG images of three NiTiO₃/Al₂O₃ films of different thicknesses. Images recorded under identical conditions for the strongly polar ferroelectric LiNbO₃ and the non-polar sapphire Al₂O₃ substrate are also shown as reference.

Fig 1

Fig 2a

Fig 2b

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

Fig 8

Fig 9

Fig 10

Fig 11