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Permalink
https://escholarship.org/uc/item/91t6195q

Journal
ACS Applied Materials and Interfaces, 6(24)

ISSN
1944-8244

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Publication Date
2014

DOI
10.1021/am506436s

Peer reviewed
Effects of Nonequilibrium Growth, Nonstoichiometry, and Film Orientation on the Metal-to-Insulator Transition in NdNiO₃ Thin Films

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Supporting Information

ABSTRACT: Next-generation devices will rely on exotic functional properties not found in traditional systems. One class of materials of particular interest for applications are those possessing metal-to-insulator transitions (MITs). In this work, we probe the relationship between variations in the growth process, subsequent variations in cation stoichiometry, and the MIT in NdNiO₃ thin films. Slight variations in the growth conditions, in particular the laser fluence, during pulsed-laser deposition growth of NdNiO₃ produces films that are both single-phase and coherently strained to a range of substrates despite possessing as much as 15% Nd-excess. Subsequent study of the temperature-dependence of the electronic transport reveals dramatic changes in both the onset and magnitude of the resistivity change at the MIT with increasing cation nonstoichiometry giving rise to a decrease (and ultimately a suppression) of the transition and the magnitude of the resistivity change. From there, the electronic transport of nearly ideal NdNiO₃ thin films are studied as a function of epitaxial strain, thickness, and orientation. Overall, transitioning from tensile to compressive strain results in a systematic reduction of the onset and magnitude of the resistivity change across the MIT, thinner films are found to possess sharper MITs with larger changes in the resistivity at the transition, and (001)-oriented films exhibit sharper and larger MITs as compared to (110)- and (111)-oriented films as a result of highly anisotropic in-plane transport in the latter.

KEYWORDS: nickelates, epitaxial thin films, stoichiometry, strain, transport

INTRODUCTION

The electronic structure and properties of conducting metal oxides have been a widely investigated topic for many decades because of the exotic phenomena found in these systems.¹ For instance, materials possessing metal—insulator transitions (MITs) have been particularly appealing because of their complex materials physics and potential for applications.²,³ Recently, there has been increasing interest in rare-earth nickelates due to their sharp, temperature-driven, first-order MIT.⁴ The rare-earth nickelates possess the chemical formula RNiO₃, where R is from the lanthanide series of rare earth elements. It has been observed that the onset temperature of the MIT (T_{M1}) scales inversely with the ionic radius of the rare-earth cation with La, the largest ionic radius, resulting in metallic behavior at all temperatures,⁴ and Lu, the smallest ionic radius, possessing the highest T_{M1} ≈ 600 K.⁴ Antiferromagnetic ordering has also been observed (except in LaNiO₃), the onset of which either corresponds to the MIT (for PrNiO₃ and NdNiO₂), or occurs at a lower temperature than T_{M1} (for the remaining RNiO₃ systems).⁵ We note that there exists a deeply complex interplay between the octahedral structure (i.e., bond lengths, angles, rotations, etc.) and the electrical and magnetic properties and that even small structural distortions can induce significant changes in T_{M1} or the magnetic T_N.⁶ Among other applications, this class of materials has been considered for sensors,⁷ electronic switches,⁷ thermochromic coatings,⁸ and nonvolatile memories.⁹

Received: September 19, 2014
Accepted: November 14, 2014
Published: November 14, 2014

ACS Publications
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dx.doi.org/10.1021/am506436s • ACS Appl. Mater. Interfaces 2014, 6, 22436−22444
A number of studies have been performed on both bulk and thin-film samples to study the origin and nature of conductivity in the nickelates. These studies have probed chemical doping, hydrostatic pressure, and epitaxial strain as possible routes to modify the MIT and the character of the MIT by manipulating the angle and spacing of the Ni–O–Ni bond and, in the case of chemical doping, by carrier injection. For instance, using divalent and tetravalent cations (including Ca$^{2+}$, Sr$^{2+}$, Ce$^{4+}$, and Th$^{4+}$) as substitutions for the R$^{3+}$ cation has allowed researchers to explore both electron and hole doping for the nickelate system. In general, carrier doping has a tendency to lower the MIT and damp the magnitude of the transition; with hole doping causing more significant damping than electron doping. One limitation of using chemical doping to affect change on the nature of the MIT is that it is difficult to separate the electronic and strain-related effects that arise from substituting differently sized cations into the lattice. To separate out this factor, others have used top gates to drive charge into or out of the film. These studies have seen similar results, with a general suppression of the MIT.

Studies on strain effects generally fall into one of two categories: (1) application of large hydrostatic pressures and (2) epitaxial thin-film strain studies. Hydrostatic pressure studies have universally observed a decrease in the MIT with increasing pressure. The results of experiments on epitaxial strain have been somewhat less consistent and, in some cases, contradictory. For example, in NdNiO$_3$ compressive strain has been shown to increase, decrease, or even completely suppress the MIT. Even from a theoretical approach, researchers have had difficulty in determining how the Ni–O–Ni bonds (i.e., the bond angle and distance) will respond to epitaxial strain and, in turn, impact the properties. For compressive strain, it has been suggested that either an enhanced rotation of the oxygen octahedra (resulting in an increase of the MIT) or a decrease in the Ni–O bond distance and a straightening of the Ni–O–Ni bond angle (resulting in a decrease of the MIT) could be possible. Still other reports have argued that in-plane strain anisotropy is the most important factor, instead of simply the value and sign of the applied strain. A number of first-principles studies have also been performed for the rare earth nickelates and suggest that the symmetry of the underlying substrate has an additional impact on the rotation and shape of the oxygen octahedra, which is responsible for some of the observed differences in the transport profiles. All told, despite extensive studies, there is no general agreement on the interaction between epitaxial strain and transport properties in rare earth nickelate thin films.

The complexity of the situation in films can be further exacerbated by the fact that film stoichiometry, including cation and anion chemistry, can also potentially play a role in the evolution of both structure and properties. Many reports have studied or alluded to the role of oxygen nonstoichiometry to account for discrepancies in reported transport data. Cation nonstoichiometry, however, has been largely ignored with few groups including compositional studies as part of their growth process. Recent work, however, indicates that control over cation stoichiometry is a nontrivial issue, especially for films produced via the most common methods in research and development (including pulsed-laser deposition). Most studies use only X-ray diffraction to probe phase-purity, but such an approach has been shown to be insufficient to accurately assess the chemical state of such complex oxides. It is well-known that the perovskites can remain “phase pure” and exhibit diffraction patterns consistent with what might be expected, despite possessing many atomic percent of nonstoichiometry. Although X-ray diffraction can highlight some telltale signs of nonstoichiometry, such as lattice expansion, extensive studies coupling lattice expansion with chemistry and the associated transport behavior in the nickelates have not been completed. With this in mind, and with a knowledge that many factors, including cation-doping, pressure, epitaxial strain, and so on, can drive dramatic changes in the nature of electronic transport in the nickelate systems, it seems important to assess the role of nonstoichiometry as well. Growing evidence has suggested that even a slight deviation in chemistry can drive a dramatic change of transport properties in conducting oxide systems and thus motivates the current study.

In this work, we undertook a detailed study of the relationship between variations in the growth process, subsequent variations in cation stoichiometry, and ultimately the electronic properties of NdNiO$_3$ thin films. We reveal that by changing the growth conditions, in particular the laser fluence, during pulsed-laser deposition growth of NdNiO$_3$, we can produce films that are, from X-ray diffraction, single-phase despite possessing as much as 15% Nd-excess. For thicknesses <70 nm, regardless of stoichiometry, the films remain coherently strained on a wide range of perovskite substrates. Subsequent study of the temperature-dependence of the electronic transport, however, reveals dramatic changes in both the MIT and the magnitude of the resistivity change at the MIT. In general, increasing cation nonstoichiometry gives rise to a decrease (and ultimately a suppression) of the MIT and the magnitude of the resistivity change associated with the MIT. Armed with the ability to produce nearly stoichiometric NdNiO$_3$ thin films, we proceed to explore epitaxial strain, thickness, and orientation-dependence of the temperature-dependent electronic transport. As the lattice mismatch transitions from tensile to compressive in nature, we observe a systematic reduction of the MIT and a corresponding reduction in the magnitude of the resistivity change across the MIT. In general, thinner films are found to possess sharper MITs with larger changes in the resistivity across the MIT. Finally, studies of film orientation reveal that (001)-oriented films possess both the sharpest and largest change in resistivity associated with the MIT as compared to the (110)- and (111)-oriented films. The smearing of the MIT in the (110)- and (111)-oriented films is found to arise from highly anisotropic transport properties along the in-plane directions of the film, which can give rise to changes in the MIT along different directions as large as ~60 K and differences in the resistance change below the MIT as large as 500%. These variations are connected to the anisotropic strain that is applied to the material.

### Experimental Section

We grew 10–120 nm thick NdNiO$_3$ (which possesses an orthorhombic structure with lattice parameters $a = 5.389$ Å, $b = 5.382$ Å, and $c = 7.610$ Å and a pseudocubic lattice parameter $a_{pc} = 3.807$ Å) thin films on LaAlO$_3$ (001), (110), and (111) (cubic, $a = 3.79$ Å), 0.3(LaAlO$_3$)$_x$–0.7(SrTiO$_3$)$_{0.8}$ (LSAT) (001) (cubic, $a = 3.87$ Å), NdGaO$_3$ (110) (orthorhombic, $a = 5.433$ Å, $b = 5.503$ Å, and $c = 7.716$ Å, $a_{pc} = 3.86$ Å), and SrTiO$_3$ (001) (cubic, $a = 3.905$ Å) single-crystal substrates. The films were grown via pulsed-laser deposition using a KrF excimer laser (LPX 305, Coherent) in 200 mTorr of O$_2$ at a frequency of 5 Hz at 750 °C (measured by a thermocouple embedded in the heater block; samples attached via Ag paint). A ceramic, stoichiometric NdNiO$_3$ target was used for all growths. The...
We have explored laser grown films, high-quality (exhibiting Laue fringes), and show a systematic variation in the out-of-plane lattice parameter of the NdNiO₃ film as a function of laser fluence during growth. X-ray reciprocal space mapping studies about the 332-diffraction condition of the film and substrate for films grown at a laser fluence of (b) 0.9, (c) 1.3, (d) 1.7, and (e) 2.1 J/cm². In all cases, the films and substrates reveal the same in-plane lattice parameter (i.e., Q-value) indicating that all films are coherently strained to the substrate.

However, for the films studied here, an additional expansion of the out-of-plane lattice parameter (from the predicted coherently strained peak position) of 0.2–1.6% is observed as we move from high to low laser fluences. This matches closely with the results observed previously for SrTiO₃ films and, considering the Nd-rich phases observed at lower fluence, seems to indicate a fluence dependence of the film stoichiometry with lower fluence favoring Nd-excess. The expansion of the out-of-plane lattice parameter is indicative of the presence of lattice-distorting cation defects, likely vacancies or vacancy complexes, which are known to expand the lattice. Despite this fact, the quality of the films appears to be quite high, as all films reveal relatively sharp diffraction peaks and clear Laue oscillations, which are indicative of excellent film and interface quality. Similar results have been found for growth on the other substrates, and additional X-ray diffraction θ-2θ and reciprocal space mapping studies are provided (Supporting Information, Figure S2).

The in-plane lattice constants and the strain state of the films was investigated by reciprocal space mapping studies about the 332-diffraction conditions of both the NdNiO₃ film and the NdGaO₃ substrate. Focusing again on the films grown between 0.9 and 2.1 J/cm² (Figure 1b-e), the reciprocal space mapping studies reveal that all films, regardless of laser fluence, are coherently strained to the substrate and possess identical in-plane lattice parameters, as indicated by the film and substrate peaks having the same Q₁ values. Additionally, consistent with the θ-2θ scans, the out-of-plane lattice parameter of the films in the Q₂ direction is found to decrease as the laser fluence increases. The combination of the θ-2θ and reciprocal space mapping studies indicates that the changes in the out-of-plane lattice parameter are not the result of some complex strain.

Figure 1. (a) θ-2θ X-ray diffraction patterns about the 220-diffraction conditions of the NdNiO₃ film and NdGaO₃ substrate, respectively. Films are single-phase, of high-quality (exhibiting Laue fringes), and show a systematic variation in the out-of-plane lattice parameter of the NdNiO₃ film as a function of laser fluence during growth. X-ray reciprocal space mapping studies about the 332-diffraction condition of the film and substrate for films grown at a laser fluence of (b) 0.9, (c) 1.3, (d) 1.7, and (e) 2.1 J/cm². In all cases, the films and substrates reveal the same in-plane lattice parameter (i.e., Q₁-value) indicating that all films are coherently strained to the substrate.

■ RESULTS AND DISCUSSION

We begin by examining the structure of the NdNiO₃ films as determined by X-ray diffraction studies. For brevity, we focus here on the evolution of structure in 70 nm NdNiO₃/NdGaO₃ (110) heterostructures as an illustrative example. X-ray diffraction θ-2θ studies reveal that the films grown at laser fluences of 0.9 J/cm² and higher are single-phase (Supporting Information, Figure S1a) with films grown at lower fluences showing the presence of parasitic, Nd-rich phases Nd₃NiO₅ and Nd₅NiO₈ (which belong to the A₁B₂O₅⁺ᵢ series, which is related to, but distinct from, the Ruddlesden-Popper series). Close inspection of the single-phase NdNiO₃ films reveals that the out-of-plane lattice parameter of the films gradually contracts as the fluence is increased (Figure 1a and Supporting Information, Figure S1c). From epitaxial strain and Poisson effects, a decrease in the c-axis lattice parameter by 0.8% as compared to bulk is expected,
relaxation process in the films, but are indicative of changes in the volume of the unit cell of the NdNiO$_3$ as the growth conditions are varied. Regardless of the laser fluence, the films are found to be coherently strained and this results in a systematic decrease in the out-of-plane lattice parameter as the laser fluence is increased. Based on these structural studies alone, it is clear that the structure of the NdNiO$_3$ films is acutely sensitive to the growth parameters. To determine the cause of the observed structural changes and their ramifications on the MIT behavior, we performed studies of both the film chemistry and physical properties of these films.

A characteristic RBS spectrum for a NdNiO$_3$/YAlO$_3$ film grown at 2.1 J/cm$^2$ is provided (Figure 2a). RBS studies focused on films grown on YAlO$_3$ for practical considerations because clear separation of peaks in the spectra simplifies and improves the quality of the compositional analysis. No correlation between substrate selection and chemistry was found (within the error of the measurement); in other words, regardless of substrate selection, the growth conditions were found to dominate the stoichiometry that was obtained. Consistent with our hypothesis, dramatic variations in the cation chemistry, here reported as a percentage of Nd excess or deficiency as calculated by $\text{[Nd]}/([\text{Nd}]+[\text{Ni}]) \times 100$, are observed as the laser fluence is varied (inset, Figure 2a). We note that we cannot uniquely differentiate between Nd excess and Ni deficiency, but for simplicity, we refer to the chemical state in terms of the Nd content. By comparing our experimental data to multiple calculated fits, we have determined that the accuracy of our compositional data is ±0.7% (a more in-depth determination of the error of the RBS studies is provided in the Supporting Information, Figure S3).

Stoichiometric films, within the error of the RBS studies, are found to be produced at relatively high laser fluences (2.1 J/cm$^2$). Upon decreasing the laser fluence, the films trend toward more and more Nd excess and when one reaches a laser fluence of 0.9 J/cm$^2$ a single-phase, epitaxial, high-quality thin film of 15% Nd excess NdNiO$_3$ is observed. Such trends in cation nonstoichiometry are consistent with results from the growth of both SrTiO$_3$ and LaAlO$_3^{23,24,30}$ where lower laser fluence tended to favor excess of the A-site cation, and higher laser fluence tended to favor excess of the B-site cation. Such effects also help explain the observed lattice distortion (Figure 1 and Supporting Information, Figure S1c), as we observe increasing Nd content to produce an increasing out-of-plane lattice parameter. Again, we would like to reemphasize the fact that these films grown at 0.9 J/cm$^2$, despite possessing 15% Nd-excess, exhibited no signatures of secondary phases in the X-ray diffraction studies (Supporting Information, Figure S1a).

Somewhat surprisingly, this indicates that 15% Nd excess is either within the effective solubility limit (given the kinetic and epitaxial constraints on the system) or that the fraction of any Nd-excess phases are below the sensitivity of the diffraction experiments. These results are crucial because they show that observing single-phase, epitaxial, high-quality diffraction peaks, even those possessing telltale signs of high-quality (i.e., sharp peaks, Laue oscillations), is insufficient evidence of a stoichiometric or “ideal” film. Armed with this information, we determined the impact that the observed deviations in film stoichiometry have on the electronic transport properties.

The resulting temperature-dependent electronic transport profiles for 70 nm thick stoichiometric 3, 6, and 15% Nd-excess films are provided (Figure 2b). Stoichiometric films (black data, Figure 2b) exhibit a sharp MIT whereby the resistivity increases by 2000% over a 15 K wide temperature range about the transition (the onset of which occurs at ∼161 K). Below the phase transition, the resistivity further increases by another 1.5 orders of magnitude by the time the temperature reaches 50 K. Overall, the system shows a 34 000% change in resistivity within the range of temperatures (50–250 K) probed here. This behavior is (roughly) consistent with prior studies of epitaxially strained NdNiO$_3$/NdGaO$_3$ (110) heterostructures. Upon deviation from stoichiometry and the introduction of Nd excess, we observe an increase (decrease) in the resistivity of the metallic (insulating) states, resulting in a systematic damping of the magnitude of the resistivity changes associated with the MIT, a reduction in the $T_{\text{MI}}$ and a broadening of the transition region in temperature. Even just 3% Nd excess in the films (purple data, Figure 2b) results in a suppression of the exhibited $T_{\text{MI}}$ (∼144 K) and a reduction of the resistivity change across the MIT (a 500% increase in resistivity over a 17 K wide temperature range) and only a 4800% change in resistivity across the entire temperature range studied. For films possessing >6% Nd excess (blue and red data are for 6 and 15% Nd excess, respectively, Figure 2b), the films exhibit a semiconducting-like temperature-dependence of resistivity across all temperature ranges probed. Weak or unresolvable MITs are observed in films in this stoichiometry range. For the 6% Nd-excess film, a weak hysteresis is observed between 80

![Figure 2](https://example.com/fig2.png)

**Figure 2.** (a, ●) Characteristic Rutherford backscattering spectrometry (RBS) data set and (red line) a corresponding fit to the data for a nearly stoichiometric film grown at 2.1 J/cm$^2$; (inset) stoichiometry (here, in Nd percentage) as a function of laser fluence. (b) Temperature dependence of the resistivity of NdNiO$_3$ films controlled to possess (black, stoichiometric) 0, (purple) 3, (blue) 6, and (red) 15% Nd-excess showing dramatic dependence of the MIT on film chemistry.
and 160 K. Overall, the 6 and 15% Nd-excess films exhibit only 500 and 180% changes in resistivity across the entire temperature range studied.

There are several important points to make in summarizing these findings. First, we have shown that cation stoichiometry is a pivotal parameter for controlling the character of the MIT in NdNiO₃ films. Second, by using laser fluence to tune the cation stoichiometry of the system, we have managed to fabricate films with different $T_{\text{MIT}}$ values on the same substrate. This indicates that without carefully controlling the growth process, it is difficult to know whether observed changes in NdNiO₃ transport properties are purely the result of substrate-strain-induced effects. It is instead possible that a non-negligible percentage of experimental observations for the NdNiO₃ system have probed defect-induced, extrinsic effects. Finally, even though the NdNiO₃ phase is capable of handling up to 15% Nd-excess, the transport properties of such films deviate substantially from those of the stoichiometric samples. For this reason, phase purity is a necessary but insufficient condition for achieving sharp, first-order MIT properties. These insights may be instrumental in clearing up some of the experimental inconsistencies in prior works on epitaxially strained RNiO₃ films.^[7,11,12]

As we attempt to understand the behavior that we have observed, it is illustrative to compare these results to effects observed in both electronic gating and chemical alloying studies of NdNiO₃. Upon application of voltages using an ionic liquid contact, researchers observed a reduction of the $T_{\text{MIT}}$ (~45 K for application for 4 V) and a reduction in the resistivity change associated with the MIT as the applied electric field drives an increase in the carrier concentration and stabilizes the metallic state of the material.^[7] Likewise, by alloying with 5% of either Ca²⁺ or Sr²⁺ (corresponding to the addition of holes) or 5% of Th⁴⁺ (corresponding to the addition of electrons), researchers have observed a reduction of $T_{\text{MIT}}$ by as much as ~130 K and a corresponding reduction in the magnitude of the resistivity change across the MIT by upward of 3 orders of magnitude.^[15] These seemingly contradictory observations were explained by a combination of size effects from the inclusion of different cations (resulting in a change in Ni–O–Ni bond angle and distance) and the fact that all dopants introduce extra carriers (because it is thought that both electrons and holes can be directly incorporated into the Ni–O bands of such Ni³⁺ compounds). For the films studied here, we demonstrate that it is possible to introduce as much as 15% Nd-excess (likely as point defects) via the growth process while maintaining a single-phase thin film. These excess Nd cations provide two possible mechanisms by which to suppress the $T_{\text{MIT}}$ and drive a reduction in the magnitude of the resistivity change associated with the MIT. Such point defects generally result in (1) an expansion of the lattice and (2) the production of excess charge (assuming the charged defects are not totally compensated by other charged defects), which can both impact the nature of electronic transport. This said, we hypothesize that, in these samples, the majority of the effect potentially arises from structural (not charge) mechanisms for the following reasons. First, the production of free charge carriers as a result of the cation nonstoichiometry likely has less influence (although it cannot be totally neglected) on the system as compared to the massive structural changes observed. Although it is impossible to completely exclude doping effects thus far, the individual and clustered charged point-defects can be readily accommodated electronically by other charged defects without the need for the production of free charge carriers. The lattice expansion observed in the films corresponds to a 0.2–1.6% deviation from ideal, a considerably larger value than the lattice expansion observed in the case of bulk chemical doping which was on the order of ~0.01%.^[13] On the other hand, these values are similar to the lattice distortions provided by coherent epitaxial growth on substrates, providing an interesting opportunity for comparison. We believe that this expansion of the lattice, resulting from the presence of the defects induced by the growth process, likely changes the structure of the NdNiO₃ in particular the nature of the bond angles, bond lengths, and/or octahedral tilts, and therefore stabilizes the metallic phase to lower temperatures. Thus, we have gone on to grow films with ideal stoichiometry on several single-crystal substrates, offering a variety of strain conditions, in order to compare the response of the MIT to similar values of defect-induced strain and coherent epitaxial strain.

Additional 70 nm thick films were grown on SrTiO₃ (2.5% lattice mismatch), LSAT (1.6% lattice mismatch), and LaAlO₃ (−0.47% lattice mismatch) substrates to compare to those grown on NdGaO₃ (1.3% lattice mismatch). Wide angle X-ray θ–2θ and reciprocal space mapping studies (Supporting Information, Figure S2) confirm single phase, coherently strained NdNiO₃ films on NdGaO₃ and LSAT substrates and (potentially) partially relaxed films on LaAlO₃ and SrTiO₃ substrates. High-resolution θ–2θ studies (Figure 3a) exhibit sharp film peaks with clear Laue fringes for all films except...
While we observed a broadening of the hysteresis for samples observed to necessarily diminish the sharpness of the MIT. We hypothesize that the effects of strain on the MIT based on a reference in symmetry in the substrates (orthorhombic for NdGaO$_3$ and cubic for LSAT) results in single-structural variant films (with either $ab$-oriented films or $c$-oriented) on NdGaO$_3$ and multistructural variant films on LSAT. In the latter, the crystallographic boundaries between the competing phases could lead to diminished transport character and ultimately causes the magnitude of the MIT to be reduced. Finally, tensile strain is associated with an expansion of the Nd−O bond, which serves to straighten the octahedral buckling angle and can stabilize the metallic phase, decreasing the $T_{MI}$ as compared to bulk. This is supported by recent studies, which have indicated that orthorhombic nickelates, such as NdNiO$_3$, have a strong tendency to accommodate tensile strain via bond elongations.

With an understanding of the effect of defect-induced strain and epitaxial strain on the MIT, we conclude by investigating a route to apply strain differently to the NdNiO$_3$ unit cell by changing the orientation of the substrate. Prior work on this topic has investigated NdNiO$_3$ on NdGaO$_3$, noting a damped MIT hysteresis for films grown on (001)- and (100)-oriented substrates. This was correlated to changes in substrate strain anisotropy arising from the orthorhombic distortion of the NdGaO$_3$ substrate. To probe similar effects for a substrate without in-plane anisotropy to the lattice parameters, we grew a series of films on (001)-, (110)-, and (111)-oriented LaAlO$_3$ substrates. Films were grown to two thicknesses, 10 and 70 nm, to enable us to probe the role of thickness. X-ray diffraction

Figure 4. Temperature dependence of resistivity for (a) 10 and (b) 70 nm thick NdNiO$_3$ films grown on (black) (001)-, (blue) (110)-, and (red) (111)-oriented LaAlO$_3$ substrates. Note the dramatic thickness and orientation dependence to the sharpness and magnitude of the MIT.
studies of the various films reveal single-phase, epitaxial films that are coherently strained to the substrate in all cases (Supporting Information, Figures S4 and S5). Let us first begin with the resistivity profiles for these films (Figure 4a,b). The 10 nm NdNiO₃/LaAlO₃ (001) heterostructures (black data, Figure 4a) exhibit a sharp transition at ∼100 K, with a 100 000% change in resistivity across the MIT hysteresis. This is consistent with prior results for NdNiO₃ grown on LaAlO₃ and confirms the high quality of our films. On the other hand, 70 nm NdNiO₃/LaAlO₃ (001) heterostructures (black data, Figure 4b) exhibit slightly reduced TMI and significant suppression of the magnitude of the resistivity change across the MIT. This could be due to partial relaxation effects in the film (Supporting Information, Figure S2b), as misfit and threading dislocations can induce local variations in the strain state.¹¹ In turn, such strain relaxation processes can broaden the MIT and modify the TMI.¹¹ In both 10 and 70 nm thick NdNiO₃/LaAlO₃ (001) heterostructures, however, the resistivity of the high-temperature metallic state is quite low, with values of 100−200 μΩ-cm at 300 K.

Investigation of the transport properties of both the (110)- (blue data, Figure 4a,b) and (111)- (Figure 4a,b) oriented films, however, reveals broad transitions with very small hysteresis associated with the MIT. Focusing first on the 10 nm thick heterostructures, we observe increased resistivity for the high-temperature metallic states and the TMI appears to be reduced to ∼50 and ∼70 K for (110)- and (111)-oriented heterostructures, respectively. The magnitude of the transition in both cases was greatly diminished, with resistivity changes of only ∼100% between 50 and 70 K. We observe very similar profiles for the 70 nm thick heterostructures on both (110)- and (111)-oriented substrates (Figure 4b), although the TMI has shifted to ∼120 K. This could indicate relaxation effects;¹¹ although, it is interesting that, for these orientations, the TMI was seen to increase with increasing thickness, while the opposite was observed for (001)-oriented heterostructures. Such results hint at a complex interplay between orientation and relaxation effects. Additionally, we remind the reader that these profiles are derived from the van der Pauw approach, which relies on roughly isotropic transport profiles along the two in-plane directions. Quick inspection of the raw, unprocessed data, however, reveals highly anisotropic transport properties along the in-plane directions of the (110)- and (111)-oriented heterostructures including changes in the TMI along different directions as large as ∼60 K and differences in the resistance change below TMI as large as 500%. This is not entirely unprecedented and can be seen as a result of the biaxial nature of the strain (as opposed to hydrostatic).¹⁴ When the strain is applied diagonally to the Ni−O−Ni bond, the distortion can be expected to be different than if it were applied in-line with the Ni−O−Ni bond. This is an important consideration because when NdNiO₃ is grown on, for example, LaAlO₃ (110), the two in-plane directions are [001] and [110]. The epitaxial strain is applied in-line with the Ni−O−Ni bond for the [001] direction but diagonally for the [110] direction (Figure 5). Clearly, additional detailed studies of the transport along the different in-plane crystallographic directions may be necessary to fully understand the relationship between epitaxial strain and transport in these systems.

On the basis of these findings, it is clear that the transport character is highly dependent on substrate orientation. In previous work on NdNiO₃/NdGaO₃ heterostructures, the relationship between orientation and transport was explained by strain anisotropy.¹⁵ We observe similar responses to changes in substrate orientation, however, and the strain values in the NdNiO₃/LaAlO₃ system are not especially anisotropic. We remind the reader that NdNiO₃ possesses an orthorhombic structure with lattice parameters a = 5.389 Å, b = 5.382 Å, and c

![Figure 5](image-url)
= 7.610 Å, while LaAlO₃ possesses a rhombohedral structure with \( a = 3.79 \) Å. It is unclear which orientation the orthorhombic NdNiO₃ structure prefers to take on LaAlO₃ if there is a preference at all. As a result, there are two scenarios for in-plane strain, depending on the orientation of the film unit cell direction (Figure 5). In either scenario, the strain values fall between 0.39 and 0.47% for all orientations, and the anisotropy of the two in-plane directions only decreases when transitioning to (110)- and (111)-oriented films. For this reason, the anisotropy of the strain does not seem to be the key, most important parameter. Rather, the orientation of the oxygen octahedra within the strain field appears to be of more importance. A schematic of the orientation of the octahedra for each orientation is provided (Figure 5, bottom). Note that for (001)-oriented heterostructures (Figure 5a), there is a compression along the two in-plane directions and an expansion along the out-of-plane direction. For the (110)-oriented heterostructures, on the other hand, there is a compression along one set of vertices of the octahedra, compression along one set of edges of the octahedra, and expansion along the out-of-plane octahedra edge (Figure 5b). Finally, for (111)-oriented heterostructures, there is a compression along the in-plane faces with an expansion along the out-of-plane octahedra face (Figure 5c). Given the importance of octahedral tilts and bond lengths in the RNiO₃ system, the orientation of the octahedra within the strain field is a highly important detail, and a theoretical precedent for this has been set in literature. Indeed, it has been previously predicted that the biaxial nature of epitaxial strain could be expected to induce anisotropy in the transport properties of the rare earth nickelate systems.¹⁴ This, it was suggested, arises from the different buckling angles associated with the application of strain along different directions, though the net effect is not intuitive or simple to model.

**CONCLUSIONS**

We have demonstrated that laser fluence has a marked effect on the composition of NdNiO₃ films and, in turn, their physical properties. Deviations in the cation stoichiometry by up to 15% were seen to be soluble in the NdNiO₃ perovskite phase. Both structural and electrical properties were found to be highly sensitive to such deviations. Expansions to the out-of-plane lattice parameter were found, indicating the presence of lattice-distorting cation defects. The transport properties (as compared to stoichiometric and bulk effects) were observed to be diminished in the presence of nonstoichiometry, illustrating the importance of understanding and controlling the growth process to synthesize ideal films. Separating out the impact of extrinsic effects, we were able to conclusively determine the role that epitaxial strain plays in controlling the MIT for NdNiO₃. We found that both compressive and tensile strain yield \( T_{MI} \) values diminished from bulk, although films under compressive strain were found to possess lower values. Finally, we investigated the influence of substrate orientation on transport properties for the (110)- and (111)-oriented films. These results indicate the importance of understanding how the complex interplay between stoichiometry, strain, and orientation impact the structure of the oxygen octahedra and subsequent transport profiles.

**ASSOCIATED CONTENT**

**Supporting Information**

Laser optics setup; determination of laser fluence; additional X-ray diffraction studies and data for fluence and substrate effects; Rutherford backscattering spectrometry fitting; and additional X-ray diffraction data for orientation effects. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. E.B. synthesized and characterized the materials. Z.C. and A.R.D. provided help with sample characterization and data analysis. L.W.M. supervised the work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

E.B. acknowledges the support of the National Science Foundation under grant DMR-1124696. Z.H.C. acknowledges the support of the Air Force Office of Scientific Research under grant FA9550-12-1-0471. A.R.D. acknowledges support from the Army Research Office under grant W911NF-14-1-0104. L.W.M. acknowledges support from the Department of Energy under grant DE-SC0012375.

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