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**Epitaxial strain effect in perovskite $RENiO_3$ films ($RE = La-Eu$)
prepared by metal organic decomposition**

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Abstract

We report the synthesis of perovskite $RENiO_3$ films ($RE = La, Pr, Nd, Sm, \text{ and } Eu$) by metal organic decomposition (MOD). The $RENiO_3$ family is an ideal system for studying the metal-insulator transition due to the simplicity of the materials. One of the drawbacks is that the bulk synthesis of the $RENiO_3$ requires processing at high oxygen pressures to stabilize Ni^{3+} . Fundamentally, MOD is similar to solid-state reaction, but it turned out that the MOD synthesis tends to stabilize $RENiO_3$ without the need for high oxygen pressure. The films prepared by MOD show high crystallinity and low resistivity. Furthermore, we have investigated the epitaxial strain effect and observed a dramatic effect in $PrNiO_3$ and $NdNiO_3$ films on $LaAlO_3$ substrates. The metal-insulator transition in the $PrNiO_3$ films on $LaAlO_3$ is fully suppressed, whereas the metal-insulator transition temperature is considerably lowered in the $NdNiO_3$ films on $LaAlO_3$.

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Key words: Nickel oxide, Metal-insulator transition, Epitaxial strain, Metal organic decomposition

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1. Introduction

The metal-insulator (M-I) transition triggered by strong Coulomb correlation (U) in the transition-metal perovskite-related oxides have attracted a considerable interest over the last two decades since the discovery of high- T_c superconductivity in cuprates. The family of the rare-earth nickel oxides, $RENiO_3$, are one of the best candidates to study the M-I transition since the transition temperature varies systematically with the ionic size of RE . Furthermore, the M-I transition is not accompanied by any change in lattice symmetry, unlike the widely studied V_2O_3 or Ti_2O_3 system, but only a slight expansion of the unit cell on cooling into the insulating state, which makes the interpretation of the mechanism simple [1,2]. According to the framework developed by Zaanen, Sawatzky, and Allen [3], there are two general types of U -triggered insulators possible: the Mott-Hubbard type and the charge transfer type. The $RENiO_3$ materials belong to a wider family of charge-transfer-gap compounds, having a p -like valence band and a d -like conduction band, as is the case for high- T_c cuprates [4]. In fact, $RENiO_3$ are located at the boundary that separates “low charge-transfer gap metals” from “charge-transfer insulators” and the charge transfer gap is regulated by the ionic size of RE^{3+} with a larger gap for smaller RE^{3+} [5]. $LaNiO_3$ is metallic with an enhanced Pauli paramagnetism [6] whereas, $LuNiO_3$ is insulating with an antiferromagnetic ordering at $T_N = 145$ K. $RENiO_3$ with $RE = Pr$ to Eu show a M-I transition and the M-I transition temperature (T_{MI}) increase from 135 K for $PrNiO_3$ to 480 K for $EuNiO_3$ [1,7]. For smaller RE^{3+} , the perovskite tolerance factor t , where t is defined as $t = d_{RE-O}/\sqrt{2}d_{Ni-O}$, is substantially smaller than 1.00 ($t = 0.988$ for La versus $t = 0.947$ for Ho , where t , which is evaluated for 12-fold coordinated RE^{3+} , is taken from ref.1), which results in the severe distortion of the structure. In fact, $RENiO_3$ except for $RE = La$ adopts the $GdFeO_3$ structure, orthorhombically distorted perovskite structure ($Pbnm$) with unit cell $\sim \sqrt{2}a_p \times \sim \sqrt{2}a_p \times \sim 2a_p$ (a_p : the pseudo-cubic lattice parameter) at room temperature [1]. The most important feature of this distortion is

the tilting of the NiO_6 octahedra and resultant bending of the Ni-O-Ni bond. The Ni-O-Ni bond angle, θ , deviates from the ideal 180° to 165.2° for La and 151.7° for Ho [5]. With a decrease in θ , the transfer matrix element between $\text{Ni}3d$ and $\text{O}2p$ orbitals is reduced, which makes both of $\text{Ni}3d$ and $\text{O}2p$ bands narrow, resulting in the opening of the charge-transfer gap.

The T_{MI} in RENiO_3 is also sensitive to applied static pressure as demonstrated by Canfield *et al.* [8] and Obradors *et al.* [9]. One would imagine that the application of physical pressure *might* cause the same effect as chemical pressure, i.e., reducing the size of RE^{3+} . But in fact, the charge transfer gap is reduced by physical pressure whereas it is enhanced by chemical pressure. This is because the tilting of the NiO_6 octahedra arises from a mismatch of the RE^{3+} size and the space between the corner-sharing octahedra: RE^{3+} too small to fill this space causes NiO_6 octahedra to tilt in order to make the space smaller. Pressure reduces the size of the space and consequently reduces the mismatch, leading to the decrease of the NiO_6 tilting and the straightening of the Ni-O-Ni bond. Strain can also be induced in films by the lattice mismatch with substrates (so-called epitaxial strain). Recently there have been several articles reporting that the T_{MI} of RENiO_3 films shows a large shift by epitaxial strain, either compressive or tensile in-plane [10,11,12]. The stress in films is not isotropic but biaxial and thereby the out-of-plane strain is usually opposite to the in-plane strain due the Poisson effect, *e.g.* films compressed in-plane are stretched in the direction perpendicular to the film surface, and vice versa. This may cause a complex effect on the M-I transition and may be responsible for the variations among reported results.

As mentioned earlier, the RENiO_3 family is an ideal system for studying the M-I transition due to the simplicity of the materials and the proposed mechanism responsible for the M-I transition. But there is one problem, i.e., the nickel ions in RENiO_3 exist in the +3 oxidation state. Since this oxidation state is unstable in ambient oxygen pressure, the synthesis of the RENiO_3 materials typically requires either processing at high oxygen

pressures or at low temperatures to stabilize Ni^{3+} . The difficulty in the synthesis of RENiO_3 increases markedly as the RE^{3+} ionic size decreases. However, the intensive efforts over the last decade, have demonstrated that thin film synthesis of RENiO_3 is not as difficult as bulk synthesis due to low-temperature processing and also possibly due to the virtue of epitaxial stabilization. Furthermore single-crystalline films can be obtained, which makes this avenue even more attractive. Most of the past efforts to synthesize RENiO_3 films except for $\text{RE} = \text{La}$ have been performed by either pulsed laser deposition (PLD) [13] or RF magnetron sputtering [10]. In this article, we demonstrate the synthesis of single-crystalline RENiO_3 thin films ($\text{RE} = \text{La, Pr, Nd, Sm, and Eu}$) by metal organic decomposition (MOD) via solid-state epitaxy. Although MOD is fundamentally not different from a solid-state reaction, it appears to stabilize the Ni^{3+} valence state without the need for high oxygen pressure even for smaller RE^{3+} ions. The films prepared by MOD show high crystallinity and low resistivity. The resistivity of LaNiO_3 at 300 K is as low as $100 \mu\Omega\text{cm}$. Furthermore we have investigated the influence of epitaxial strain on the film characteristics and observed a dramatic effect of in-plane compressive strain on the M-I transition in PrNiO_3 and NdNiO_3 films on LaAlO_3 substrates.

2. Experimental

2. 1. Thin film synthesis

RENiO_3 films were prepared by MOD using 2-ethylhexanoate solutions for La and Ni and naphthenate solutions for Pr, Nd, Sm, and Eu. The stoichiometric mixture of solutions was spin-coated on LaAlO_3 (LAO) (001), NdGaO_3 (NGO) (110), and SrTiO_3 (STO) (001) substrates. The lattice constants of the substrates, a_s , are summarized in Table I, together with the lattice constants reported for bulk samples of RENiO_3 . The films were first calcined at 500°C in air to obtain precursors, then fired at $650\text{-}900^\circ\text{C}$ in a tubular furnace with flowing either molecular oxygen or ozone gas from a commercial ozonizer ($\leq 5\%$ ozone

concentration). Subsequently the films were furnace-cooled down to 300 °C. The film thickness was typically 800 Å although it may vary from film to film to some extent. The structure of the films was characterized by ω - 2θ (equivalently θ - 2θ) scans with Cu K $_{\alpha}$ radiation using Rigaku, Smart Lab. From the ω - 2θ scans, the crystallinity was assessed by the peak intensity as well as the rocking curve width ($\Delta\omega$), and also the out-of-plane lattice constant, namely perpendicular to the film surface (hereafter referred as c_f), was determined. Some of the films with high crystallinity were also examined by the four-circle (2θ , ω , ϕ , ψ) X-ray diffractometer (Phillips, X'Pert). The in-plane alignment was determined by the ϕ scan of the (103) and/or (202) reflections and its width ($\Delta\phi$). Also, the in-plane lattice constant (hereafter referred as a_f) was determined from the (110) reflection [14]. The resistivity of the films was measured by a standard four-probe method.

2. 2. Optimizing the growth parameters

First of all, the growth parameters (firing temperature and atmosphere (O₂ or O₃)) for the synthesis of $RENiO_3$ were optimized for each RE . Figure 1 summarizes the optimization process. The XRD peak intensity of the (002) reflection (Fig. 1 (a)) and the resistivity at room temperature, $\rho(295\text{ K})$ (Fig. 1 (b)), are plotted as a function of the firing temperature, T_f , for typical $RENiO_3$ films on NGO substrates prepared under either O₂ or O₃. For $RE = \text{La}$, the O₂ growth and the O₃ growth are not much different and hence the films were prepared mostly under O₂. For the film preparation under O₂, the (002) peak intensity increases with T_f from 650°C to 900°C whereas the $\rho(295\text{ K})$ decreases gradually with increase in T_f . For $RE = \text{Pr}$ and Nd , the film growth under O₃ is slightly better than that under O₂. For PrNiO_3 films prepared under O₃, the film quality improves monotonically with T_f from 650°C to 800°C as evident from the increase in the (002) peak intensity and the decrease in $\rho(295\text{ K})$. However, the $\rho(295\text{ K})$ increases for $T_f \geq 850^\circ\text{C}$. For $RE = \text{Nd}$, although the data are scattered, the optimum T_f appears to be lower than for $RE = \text{Pr}$. The optimization for PrNiO_3

and NdNiO₃ has been carried out not only from a viewpoint of the XRD peak intensity and $\rho(295\text{ K})$, but also from the sharpness of the M-I transition. Figure 2 compares the M-I transition for PrNiO₃ films on NGO fired at various T_f under O₃ flow. One can see an overall tendency that lower T_f yields a sharper M-I transition.

For $RE = \text{Sm}$ and Eu , the films were prepared mostly with O₃. Even with O₃, SmNiO₃ films prepared with $T_f = 900^\circ\text{C}$ show broad XRD peaks with the appearance of an impurity phase, Sm₂O₃, and also have high resistivity values. For $RE = \text{Eu}$, firing at $T_f \geq 850^\circ\text{C}$ yields mainly Eu₂O₃. The optimum synthesis conditions are summarized in Table II. The RE dependence of the synthesis conditions for $RENiO_3$ seems to indicate that the thermodynamic boundary conditions become more stringent for smaller RE^{3+} ions, indicating that stronger oxidation and/or lower firing temperature are required. But in general, the reaction activity is lower for smaller RE^{3+} , which makes it difficult to promote crystal growth at low T_f .

3. Results and discussion

3.1. $RENiO_3$ films on NdGaO₃ substrates

First, we discuss our results of $RENiO_3$ films on NdGaO₃ substrates. NdGaO₃ is nearly lattice-matched with $RENiO_3$ ($RE = \text{La, Pr, Nd}$), and most frequently used substrate for thin film growth of these compounds. Taking a closer look at the lattice constants as shown in Table I, it is clear that the a_s of NdGaO₃ is a little larger than the pseudo-cubic perovskite lattice constant, $a_p(\text{bulk})$, of $RENiO_3$, which should introduce in-plane tensile strain into $RENiO_3$ films. Figure 3 shows the out-of-plane XRD patterns (a) and resistivity-temperature (ρ - T) curves (b) of $RENiO_3$ films with $RE = \text{La, Pr, Nd, Sm, and Eu}$, synthesized under optimized conditions. All the peaks in the XRD patterns except for the substrate peaks could be indexed to the (00 l) reflections of the $RENiO_3$ perovskite structure, indicating that the films are single-phase and c -axis textured. However, the peak intensity becomes weaker and

broader with decrease in the RE^{3+} ionic radius, i.e., going from La to Eu. Figure 4 summarizes the variation c_f of the films with the ionic radius of 12-fold coordinated RE^{3+} . The c_f of the films on NdGaO₃ for $RE = \text{La, Pr, and Nd}$ are smaller than the $a_p(\text{bulk})$ reported for bulk specimens, implying that an in-plane tensile strain is induced in these films. In order to confirm this speculation, the in-plane structural characterizations were carried out using the four-circle X-ray diffractometer. Table III presents a summary of all the structural data. Figure 5 demonstrates the ϕ scan of the (103) reflection for the PrNiO₃ film on NdGaO₃ as a typical example. The four-fold symmetry observed in the ϕ -scan XRD pattern of the films indicates that the films are indeed in-plane aligned. The full width at half maximum, $\Delta\phi$, is 0.66° , a fairly good value for complex oxide thin films. Furthermore, the in-plane lattice constant, a_f , of the films was evaluated from the ω - 2θ scan of the (110) reflection. As shown in Table III, the a_f of the films on NdGaO₃ for $RE = \text{La, Pr, and Nd}$ estimated from the maximum of the peak are indeed larger than the $a_p(\text{bulk})$, confirming the in-plane tensile strain induced in these films by solid-state epitaxy. However, the ω - 2θ scan of the (110) reflection for the PrNiO₃ films on NGO is fairly broad (Fig. 6(a)) indicating that there is a substantial variation of the a_f in the film, probably along the thickness direction. The a_f may be close to a_s near the interface between a film and a substrate, but the strain is relaxed toward the film surface. Therefore Δa_f , calculated from the full width ($\Delta(2\theta)$) at the half maximum for the (110) reflection, is included in Table III.

The resistivity value above the T_{MI} increases monotonically from La to Nd as shown in Fig. 3(b). This trend in the resistivity is partly due to the poorer crystallinity and predominantly due to the larger bending of the Ni-O-Ni bond for smaller RE^{3+} . LaNiO₃ film exhibits low resistivity, $\rho(295 \text{ K}) = 100 \text{ } \mu\Omega\text{cm}$, and a high residual resistivity ratio, RRR ($\equiv \rho(295 \text{ K})/\rho(4.2 \text{ K})$), of ~ 18 , both of which are comparable to or even better than the best values ever reported [8,15]. PrNiO₃ and NdNiO₃ films show a M-I transition at 125 K and 210 K respectively, which roughly agree with the T_{MI} reported for the bulk polycrystalline

ceramics ($T_{\text{MI}} = 130\text{-}135$ K for Pr, and $T_{\text{MI}} = 200$ K for Nd) [1,16]. According to the previous reports [1,5,7], the T_{MI} 's of SmNiO_3 and EuNiO_3 are 400 K and 480 K, respectively. Therefore we observed only a semiconducting temperature dependence of resistivity below the M-I transition for these two compounds in the measured temperature range (300 – 4.2 K).

The T_{MI} of RENiO_3 films is affected by several factors such as epitaxial strain, crystallinity, *etc.* In-plane compressive strain reduces the T_{MI} whereas tensile strain raises it. Poor crystallinity reduces the T_{MI} and broadens the transition. Our T_{MI} (= 210 K) for NdNiO_3 may be slightly higher but our T_{MI} (= 125 K) for PrNiO_3 is slightly lower than the bulk T_{MI} reported for these compounds. It has been reported that the NdNiO_3 films as thin as 200 Å prepared by PLD on NGO show $T_{\text{MI}} = 240$ K [12], but this is an exceptional case as the film thickness is very low. In our observations, the increase of T_{MI} by tensile strain was not that prominent.

As mentioned in introduction section, RENiO_3 except for $RE = \text{La}$ adopts the orthorhombic GdFeO_3 structure. But another form of NdNiO_3 with a rhombohedral unit cell has been synthesized by low-temperature ($\sim 650^\circ\text{C}$) bulk synthesis at $p_{\text{O}_2} = 1$ atm [17]. This phase has a somewhat larger lattice constant ($a_{\text{p}}(\text{bulk}) = 3.85$ Å for the pseudo-cubic cell), and shows a much more broader M-I transition with a much larger transition hysteresis on cooling and heating ($\Delta T_{\text{MI}} \sim 100$ K) than orthorhombic NdNiO_3 ($a_{\text{p}}(\text{bulk}) = 3.81$ Å, $\Delta T_{\text{MI}} \leq 8\text{-}12$ K) [8, 18]. It should be noted that our MOD preparation conditions for NdNiO_3 films are almost identical to the bulk synthesis conditions for rhombohedral NdNiO_3 . However, a sharp M-I transition and a small hysteresis ($\Delta T_{\text{MI}} \leq 10$ K) observed in our NdNiO_3 films (Fig. 7) seems to indicate that our NdNiO_3 films may be orthorhombic NdNiO_3 . The bulk synthesis of orthorhombic NdNiO_3 requires oxygen pressures of 150-200 bars [1] whereas its MOD synthesis requires only 1 atm of oxygen [19], which is remarkable. This large difference in oxygen pressure during synthesis to stabilize orthorhombic NdNiO_3 is puzzling.

It is worthwhile to point out that the c_f values for SmNiO_3 and EuNiO_3 films on NGO

are longer than the NdNiO_3 films on NGO (please see Fig. 4) and also longer than the $a_p(\text{bulk})$ by $\sim 0.5\%$. This cannot be explained by epitaxial strain. The longer c_f values observed for $RE = \text{Sm}$ and Eu might be attributed to rhombohedral distortion as in the case of rhombohedral NdNiO_3 . Our oxidation condition, even with O_3 , during synthesis may not be strong enough to stabilize the orthorhombic phase of SmNiO_3 and EuNiO_3 .

3.2. $RE\text{NiO}_3$ films on LaAlO_3 substrates

We now examine our results for the films on LAO. LAO has smaller a_s than $a_p(\text{bulk})$ of $RE\text{NiO}_3$ ($RE = \text{La}, \text{Pr}, \text{Nd}$), so it should introduce in-plane compressive strain into $RE\text{NiO}_3$ films. Indeed, there are several recent articles demonstrating a large epitaxial strain effect on the M-I transition in the PrNiO_3 and NdNiO_3 films on LAO [11,20]. The structural data in Fig. 4 and Table III show that our MOD-grown PrNiO_3 and NdNiO_3 films on LAO have smaller a_f and larger c_f compared to their respective $a_p(\text{bulk})$, indicating that these films are well strained via solid-state epitaxy. As shown in Fig. 6(b), the peak width of the (110) reflection in the ω - 2θ scan for the PrNiO_3 film on LAO is relatively small as compared to the PrNiO_3 film on NGO (Fig. 6(a)) or on STO (Fig. 6(c)). The peak is asymmetric with a tail at lower angles, implying the existence of portions with larger a_f in the film due to probable strain relaxation.

Figure 8 compares the ρ - T curves of $RE\text{NiO}_3$ films for $RE = \text{La}, \text{Pr}, \text{Nd}$, and Sm prepared on LAO, NGO and STO substrates. For $RE = \text{La}$, the substrate dependence is minimal, but a better lattice-matched NGO gives the lowest resistivity and highest RRR values. On the other hand, for $RE = \text{Pr}$, the substrate dependence of the resistivity is dramatic. The M-I transition of the PrNiO_3 films on LAO is completely suppressed and the film shows a RRR value as high as 15. In the case of $RE = \text{Nd}$, the T_{MI} is also reduced substantially from 210 K to 140 K although the transition is even sharper for the films on LAO than on NGO. For $RE = \text{Sm}$, again the substrate dependence is small. The reduction of T_{MI} in PrNiO_3 and

NdNiO₃ is roughly equal to the reduction by static isotropic pressure of ~15 kbar.

3.3. *RENiO₃* films on SrTiO₃ substrates

STO has been the most common substrate for oxide film growth. It has substantially larger a_s than $a_p(\text{bulk})$ of *RENiO₃*, which should introduce in-plane tensile epitaxial strain into *RENiO₃* films. Since the lattice mismatch of *RENiO₃* with STO is larger than that of NGO, a more dramatic epitaxial strain effect *would* be expected. However, the structural data in Fig. 4 and Table III, show that the situation is not that straightforward. The c_f should be reduced by the in-plane tensile strain via the Poisson effect. The c_f of LaNiO₃ is indeed smaller on STO than on NGO. In contrast, the c_f of PrNiO₃ and NdNiO₃ is larger on STO than on NGO contrary to the expectation. Furthermore, the a_f of PrNiO₃ is larger on STO than on NGO as expected whereas the a_f of LaNiO₃ and NdNiO₃ is smaller on STO than on NGO as opposed to expectation. This complex behavior seems to imply that the epitaxial strain is relaxed, at least partially, on STO due to too large lattice mismatch. This scenario is supported by the ω - 2θ scan (Fig. 6(c)) for the PrNiO₃ film on STO where the peak width of the (110) reflection on STO is considerably larger than on LAO or NGO.

In line with the structural observations, the ρ - T curves show an unusual behavior. The in-plane tensile strain is expected to raise the T_{MI} . Contrary to this expectation, the T_{MI} of the PrNiO₃ films on STO is reduced from 130 K to ~100 K and the transition is also substantially broadened. This tendency is more prominent in the case of NdNiO₃ films on STO where the M-I transition is quite smeared. Because of this smearing, the T_{MI} is difficult to determine precisely but seems to be lower than T_{MI} of the films on NGO. In general, the critical thickness for the relaxation of epitaxial strain is inversely proportional to the lattice mismatch α ($= \Delta a/a_p(\text{bulk})$) where $\Delta a = a_s - a_p(\text{bulk})$. The value of α is listed in Table III. For PrNiO₃, the α is +2.36% for STO, +1.17% for NGO, and -0.45% for LAO. The film thickness of about 800 Å in the present study may be under the critical thickness for LAO but

over the critical thickness for STO, with NGO on the border. The α of STO is +2.36% for PrNiO₃ and +2.56% for NdNiO₃. The larger α may explain that NdNiO₃ films on STO show a more smeared M-I transition than PrNiO₃ films on STO.

3.4. Comparison of *RENiO₃* films by MOD with films by other thin film techniques

Now we would like to make a comparison of the properties of our MOD films with those grown by other thin film techniques such as MBE [21,24], PLD [13,12,22,11,26], RF magnetron sputtering [23,27], and MOCVD [25], which is summarized in Table IV [28]. In the literature, most of the earlier works on the growth of LaNiO₃ films were by MBE, PLD, and sputtering, and MBE and PLD grown films have high $\rho(295\text{ K})$ and low *RRR* values. Only the LaNiO₃ films prepared by sputtering have $\rho(295\text{ K})$ and *RRR* values comparable to our MOD synthesized films.

The PrNiO₃ films have been grown by MBE, PLD, and MOCVD. The M-I transition is fully suppressed in the well-strained films grown on LAO either by MBE or PLD whereas only slight reduction of T_{MI} is seen in the MOCVD grown films, which may be due to partial strain-relaxation. In spite of full suppression of the M-I transition in MBE and PLD grown films, the films have lower *RRR* than our MOD grown films (2 ~ 4 in MBE or PLD versus 15 in MOD), indicating that PrNiO₃ films by MOD may be superior to those by MBE or PLD.

The NdNiO₃ films have been grown by PLD and sputtering. On LAO substrates, the films shows the reduction of T_{MI} due to in-plane compressive strain although T_{MI} ranges from 80 K to 140 K, depending on several factors such as thickness, crystallinity, etc. On NGO substrates, the increase of T_{MI} to 240 K was observed due to in-plane tensile strain in very thin (200 Å) films grown by PLD, but this is rather exceptional. In most other reports, the T_{MI} on NGO is reduced to 150-170 K, possibly due to poor crystallinity, which is known to reduce the T_{MI} and broaden the M-I transition, as mentioned earlier. Judging from this

criterion, our NdNiO₃ films ($T_{MI} = 210$ K) on NGO are fair, at least. Taking into account the simplicity and low cost of MOD, it is a quite attractive method to synthesize high-quality *RENiO₃* thin films. We have also demonstrated that these MOD films are suitable as precursors for topotactic transformation to infinite-layer *RENiO₂* [29].

4. Summary

We have carried out the systematic synthesis of *RENiO₃* films ($RE = \text{La, Pr, Nd, Sm, and Eu}$) by MOD on NGO, LAO, and STO substrates and the influence of epitaxial strain on various properties was investigated from the structural characterization and transport measurements. The results are summarized as follows.

(1) *RENiO₃* films on NGO – in-plane tensile strain

The LaNiO₃ films on NGO show high crystallinity due to large La³⁺ as well as good lattice matching with the substrate. The best film exhibits $\rho(295 \text{ K}) = 100 \text{ } \mu\Omega\text{cm}$, and a large *RRR* value of ~ 18 . The PrNiO₃ and NdNiO₃ films on NGO have slight in-plane tensile strain, and they show a M-I transition at 125 K and 210 K respectively. The $T_{MI} = 210$ K for NdNiO₃ films prepared by MOD is slightly higher than the T_{MI} reported for bulk samples, which could be attributed to tensile strain.

(2) *RENiO₃* films on LAO – in-plane compressive strain

The PrNiO₃ and NdNiO₃ films on LAO experience in-plane compressive strain. The structural characterization of the MOD-grown PrNiO₃ and NdNiO₃ films revealed that the films are well strained on LAO via solid-state epitaxy. The M-I transition of the PrNiO₃ films on LAO is fully suppressed and the films are metallic down to 4.2 K with a *RRR* value as high as 15. The T_{MI} of the NdNiO₃ films is also reduced significantly from 210 K to 140 K besides having a sharp transition.

(3) *RENiO₃* films on STO – strain relaxation

In-plane tensile strain is introduced into the *RENiO₃* films but is partially relaxed due to too

large lattice mismatch. The T_{MI} of the PrNiO_3 films on STO is reduced from 130 K to ~ 100 K with the transition substantially broadened. This effect is more prominent in the NdNiO_3 films on STO and the M-I transition is quite smeared.

Progress in the methods of computational material science may now allow first-principle calculations of the coupling between structure and electronic properties. Some attempts have started toward understanding the epitaxial strain effect on the electronic structure in RENiO_3 , although still rather crude [30,31]. It will require state-of-the-art computational routes to explain the dramatic changes in the physical properties caused by a change in the lattice constants as small as $\pm 1\%$.

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Table I. Crystal structure and the lattice parameters of $RENiO_3$ [1,7] and the substrate materials used in this work. The pseudo-cubic perovskite lattice constant, $a_p(\text{bulk})$, for $RENiO_3$ and, a_s , for the substrates are calculated by assuming the materials as a pseudo-cubic system.

Material or substrate	Structure	a (Å)	b (Å)	c (Å)	$a_p(\text{bulk})$ or a_s (Å)
LaNiO ₃	rhombohedral	5.3954			3.830
		$(\alpha=60^\circ 78')$			
PrNiO ₃	GdFeO ₃	5.4154	5.3755	7.6192	3.813
NdNiO ₃	GdFeO ₃	5.3888	5.3845	7.6127	3.805
SmNiO ₃	GdFeO ₃	5.3283	5.4374	7.5675	3.782
EuNiO ₃	GdFeO ₃	5.2938	5.5460	7.5359	3.768
SrTiO ₃ (001)	Perovskite				3.905
NdGaO ₃ (110)	GdFeO ₃	5.417	5.499	7.717	3.858
LaAlO ₃ (001)	rhombohedral	5.356			3.796
		$(\alpha=60^\circ 06')$			

Table II. Summary of the optimal synthesis condition for $RENiO_3$ ($RE = \text{La, Pr, Nd, Sm, and Eu}$) films on NGO.

RE	T_f (°C)	O_2 or O_3
La	850	O_2
Pr	700-800	O_3
Nd	650-750	O_3
Sm	750-850	O_3
Eu	700-800	O_3

Table III. X-ray crystallographic data for $RENiO_3$ ($RE = \text{La, Pr, and Nd}$) films. The a_f and c_f were determined from positions of the (110) and (002) reflections in the ω - 2θ scans, respectively. The Δa_f is calculated from the full width ($\Delta 2\theta$) at the half maximum of the (110) reflection. The $\Delta\omega$ and $\Delta\phi$ denote the full width at the half maximum for the ω scans and ϕ scans, respectively.

RE	La			Pr			Nd		
	STO	NGO	LAO	STO	NGO	LAO	STO	NGO	LAO
$a_p(\text{bulk}) (\text{\AA})$	3.830			3.813			3.805		
Substrate	STO	NGO	LAO	STO	NGO	LAO	STO	NGO	LAO
$a_s (\text{\AA})$	3.905	3.858	3.796	3.905	3.858	3.796	3.905	3.858	3.796
$\alpha (\%)$	1.92	0.72	-0.90	2.36	1.17	-0.45	2.56	1.37	-0.24
$a_f \pm \Delta a_f (\text{\AA})$	3.854 ± 0.042	3.860 ± 0.026	3.827 ± 0.023	3.841 ± 0.028	3.831 ± 0.021	3.805 ± 0.014	3.826 ± 0.020	3.842 ± 0.016	3.805 ± 0.014
$c_f (\text{\AA})$	3.805	3.812	3.845	3.800	3.787	3.831	3.800	3.782	3.822
$\Delta\omega (0\ 0\ 2) (\text{degree})$	0.30	0.098	0.27	0.45	0.15	0.15	0.73	0.11	0.13
$\Delta\phi (1\ 0\ 3) (\text{degree})$	1.66	0.43	1.46	2.51	0.66	0.77	2.61	0.49	0.70
$\Delta\phi (2\ 0\ 2) (\text{degree})$	1.22	<u>0.19</u>	1.33	1.01	0.34	0.32	1.69	0.28	0.27
$\Delta\phi (1\ 1\ 0) (\text{degree})$	0.69	0.43	0.74	0.61	0.48	0.54	0.88	0.5	0.26

Table IV. The properties of LaNiO_3 , PrNiO_3 , and NdNiO_3 films prepared by MOD (present work) and by other thin-film techniques. For reference, the data of bulk samples are also included.

Synthesis method	Ref.	Material (thickness)	$\rho(300\text{K})$ ($\mu\Omega\text{ cm}$)	RRR	T_{MI} (K)
MBE	21	$\text{LaNiO}_3/\text{STO}$	300	6	–
PLD	22	$\text{LaNiO}_3/\text{STO}$	500	2.4	–
Sputtering	23	$\text{LaNiO}_3/\text{LAO}$	130	8	–
MOD	this work	$\text{LaNiO}_3/\text{NGO}$	100	18	–
MOD	this work	$\text{LaNiO}_3/\text{LAO}$	130	16	–
MOD	this work	$\text{LaNiO}_3/\text{STO}$	140	10	–
bulk (cold press)	15	LaNiO_3	100	15	–
MBE	24	$\text{PrNiO}_3(120\text{\AA})/\text{LAO}$	250	3.6	0
PLD	11	$\text{PrNiO}_3(750\text{\AA})/\text{LAO}$	74	2	0*
MOCVD	25	$\text{PrNiO}_3(1000\text{\AA})/\text{LAO}$	700	–	80
MOD	this work	$\text{PrNiO}_3/\text{NGO}$	440	–	125
MOD	this work	$\text{PrNiO}_3/\text{LAO}$	320	15	0
bulk	8	PrNiO_3	500	–	130
PLD	13	$\text{NdNiO}_3/\text{NGO}$	($\sim 6\Omega$)***	–	170
PLD	13	$\text{NdNiO}_3/\text{LAO}$	($\sim 10\Omega$)***	–	120
PLD	12	$\text{NdNiO}_3(200\text{\AA})/\text{NGO}$	200	–	240
PLD	26	$\text{NdNiO}_3(500\text{\AA})/\text{NGO}$	(400)**	–	160
Sputtering	27	$\text{NdNiO}_3(120\text{\AA})/\text{NGO}$	300	–	150
Sputtering	27	$\text{NdNiO}_3(120\text{\AA})/\text{LAO}$	300	–	80
MOD	this work	$\text{NdNiO}_3/\text{NGO}$	550	–	210
MOD	this work	$\text{NdNiO}_3/\text{LAO}$	400	–	140
bulk(cold press)	15	NdNiO_3	300	–	200
bulk	8	NdNiO_3	1100	–	200

* Resistivity measurements were carried out in the limited temperature range 25-300 K.

** Resistivity value at 200 K.

*** No resistivity but resistance is presented in this article.

Figure caption

Figure 1. Structural and transport data for $RENiO_3$ films prepared under various growth parameters: (a) variation of the (002) peak intensity and (b) $\rho(295\text{ K})$ as a function of firing temperature, T_f . The films were prepared on NGO at various $T_f = 650\text{--}900^\circ\text{C}$ under either O_2 or O_3 flow.

Figure 2. Temperature dependence of resistivity for $PrNiO_3$ films on NGO fired at various temperature $T_f = 650\text{--}850^\circ\text{C}$ in an O_3 flow.

Figure 3. (a) XRD patterns and (b) ρ - T curves of the $RENiO_3$ films ($RE = \text{La, Pr, Nd, Sm, and Eu}$) on NGO obtained after optimizing synthesis conditions. In the XRD patterns, all peaks can be indexed for the (00 l) reflections of the perovskite structure.

Figure 4. c -axis length (c_f) of $RENiO_3$ films ($RE = \text{La, Pr, Nd, Sm, and Eu}$) grown on NGO, LAO, and STO plotted against the ionic size $r_i^{\text{XII}}(RE^{3+})$ of RE . The open circles represent the bulk $a_p(\text{bulk})$ of $RENiO_3$.

Figure 5. ϕ scan of the (103) reflection of the $PrNiO_3$ film on NGO: (a) overall view and (b) enlarged view for a single peak.

Figure 6. ω - 2θ scans of the (110) reflection for the $PrNiO_3$ films on (a) NGO, (b) LAO, and (c) STO, respectively. The substrate peak can be seen together with the film peak, but its intensity depends on the alignment. The substrate peak is large on NGO whereas it is only discernible on LAO. The dotted line in (a) is a guide to the eye. The arrows indicate the position of the (110) reflection expected for a bulk specimen.

Figure 7. Hysteresis of the ρ - T curve for the NdNiO₃ film on NGO measured on cooling (open circles) and heating (solid circles). The transition hysteresis, ΔT_{MI} , on cooling and heating is ≤ 10 K, indicating that our NdNiO₃ films may be orthorhombic.

Figure 8. Comparison of ρ - T curves of the $RE\text{NiO}_3$ films ($RE = \text{La, Pr, Nd, and Sm}$) on LAO, NGO, and STO.

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