Strain-mediated metal-insulator transition in epitaxial ultra-thin films of NdNiO$_3$

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We have synthesized epitaxial NdNiO$_3$ ultra-thin films in a layer-by-layer growth mode under tensile and compressive strain on SrTiO$_3$ (001) and LaAlO$_3$ (001) respectively. A combination of X-ray diffraction, temperature dependent resistivity, and soft X-ray absorption spectroscopy has been applied to elucidate electronic and structural properties of the samples. In contrast to the bulk NdNiO$_3$, the metal-insulator transition under compressive strain is found to be completely quenched, while the transition remains under the tensile strain albeit modified from the bulk behavior.

PACS numbers:

Since the Mott metal-insulator transition (MIT) is the hallmark of strongly correlated electron systems, understanding it in the ultra-thin limit is fundamentally and technologically important. The bulk nickelate family, RENiO$_3$ (RE = rare earth, e.g. La, Pr, Nd ...), is a prototypical strongly correlated system exhibiting fascinating bandwidth-controlled MIT that is largely attributed to the decrease (increase) in the Ni-O-Ni bond angle with smaller (larger) RE cation [1]. In this family, NdNiO$_3$ (NNO) possesses a rich set of properties such as proximity to localized-to-itinerant behavior, an unusual antiferromagnetic structure, and a charge-ordered insulating ground state [2–4]. With increasing temperature, NNO undergoes a first order insulator-metal transition and becomes a paramagnetic metal, accompanied by a structural phase transition from monoclinic to orthorhombic [5]. It is thereby an ideal candidate to investigate the behavior of MIT when subjected to confinement, lattice misfitm and broken symmetry at the interface (surface).

However, due to the low thermodynamic stability of rare earth nickelates, the synthesis of NdNiO$_3$ single crystals requires high temperature and high oxygen pressure (>100bar) and yields only micron size samples [6]. Although, by virtue of the epitaxial stabilization, thin film deposition with relatively low oxygen pressure is now possible, any partial relaxation or 3D island formation during the growth immediately causes oxygen deficiency and secondary phase formation [7]. In the absence of the layer-by-layer (LBL) growth, the relaxation and the induced non-stoichiometry severely hinders the quantitative interpretation of the effect of epitaxial strain on the electronic structure and is largely responsible for the disagreement among reported results [8]. For instance, tensile strain has been reported to either suppress[9, 10] or enhance[11] the MIT temperature. Similarly controversial results have been reported for compressive strain [9, 12]. As a result, to obtain fully epitaxial stoichiometric NNO thin films and quantify the role of strain, perfect epitaxy characteristic of the LBL growth is critical. In addition, LBL growth is crucial in achieving the high morphological quality necessary for hetero-junctions and devices with atomically flat surfaces and interfaces.

In this letter, we report on the fabrication of NNO ultra-thin films on SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) substrates with a LBL growth mode by pulsed laser deposition. Characterization by atomic force microscopy (AFM), synchrotron based X-ray diffraction (XRD), and resonant X-ray absorption spectroscopy (XAS) reveals full epitaxy and proper stoichiometry. Temperature dependent transport measurements and XAS clearly demonstrate that tensile strain preserves the MIT globally and locally while compressive strain suppresses the insulating phase.

High-quality epitaxial NNO ultra-thin films (10-15uc) were grown on STO (001) and LAO (001) single crystal substrates by pulsed laser deposition with in-situ monitoring by Reflection High Energy Electron Diffraction (RHEED). Due to the lattice mismatch, NNO (3.80 Å) is subjected to a tensile strain of 2.6% on STO (3.90 Å), whereas a compressive strain of -0.3% is applied on LAO (3.79 Å). STO substrates were prepared by our recently developed chemical wet-etch proce-
procedure ('Arkansas treatment') to attain an atomically flat TiO$_2$-terminated surface with a minimal number of surface bound electronic defects\cite{13}. The growth temperature was in the range of 670-730°C, while the oxygen partial pressure was maintained at 75-120 mTorr. After deposition, in order to maintain the proper oxygen content, samples were post-annealed in-situ for 30 minutes and cooled down to room temperature in 1 atmosphere of ultra-pure oxygen.

To maintain the perfect epitaxy, LBL growth is achieved by the interrupted deposition\cite{14}, which requires a rapid laser ablation cycle (up to 30Hz) followed by a prolong time-delay between two successive unit cells. Figure 1(a) shows a representative time-dependent RHEED specular intensity (RSI), where the full recovery of RSI, characteristic of the perfect LBL growth, can be seen after each unit-cell layer. Smooth surface morphology is also evident from the well-defined spots of the (00) specular and (01) and (0\bar{1}) off-specular reflections with streaks in the resulting RHEED pattern (see Fig. 1(b)). AFM imaging (Fig. 1(c)) showed that the sample surface is atomically flat with preserved vicinal steps and typical surface roughness <80nm.

Film structure was determined with synchrotron-based XRD performed at the 6ID-B beamline of the Advanced Photon Source (APS). Temperature dependent resistivity was measured using a van der Pauw geometry. To probe the local electronic state, detailed spectroscopic measurements were carried out in the soft X-ray regime in both fluorescence yield (FY) mode and total electron yield (TEY) mode at the Ni L-edge with 100 meV resolution at the 4ID-C beamline at APS. To obtain precise information on the Ni valence state, all the spectra were aligned to a NiO (Ni$^{2+}$) standard which was measured simultaneously with the samples.

Figure 2 shows the XRD scans around the (003) reflection for NNO (15uc) on STO and LAO. Total thickness fringes are clearly seen, indicating coherently grown films. In addition, their size corresponds to a thicknesses of 15 monolayers, which is in excellent agreement with the number of unit cells deduced from RHEED. The out-of-plane lattice parameters are 3.75Å and 3.84Å on both STO and LAO, respectively. Compared to the bulk, they are consistent with the expected compression and expansion of the c-axis under bi-axis tensile and compressive strains, respectively. The insets in Figure 2 shows the H=K scans across the (113) off-specular reflection of the films. As seen, the in-plane components are perfectly matched to the substrates, confirming the films are fully epitaxial.

Temperature dependent resistivity curves are shown in Figure 3. As clearly seen, the sample grown on STO maintains metallicity at high temperatures, even though it has only a few monolayers. This is in contrast to the previously reported results which show a breakdown of metallicity around few hundred angstroms\cite{9}. With lowering temperature, a resistivity minimum is reached at around 180K followed by a rapid increase of resistivity with a thermal hysteresis at lower temperatures. This behavior is characteristic of a broadened first order MIT. Notice, the overall increase of resistivity is over three orders of magnitude and consistent with a bulk-like insulating ground state\cite{8}. This is opposed to the previous reports, where the resistivity increase under tensile strain was found to be suppressed to only two orders or less as the film thickness reduces to 10-20nm\cite{9,15,16}. On the other hand, compared to the bulk, the observed increase of resistivity within the hysteresis is more gradual in the ultra-thin structure\cite{2}. In addition to strain, this could also be related to the ultra-thin nature of the film, which has been shown to inhibit and broaden phase transitions of other oxide films\cite{17,18}. In marked variance to STO, samples grown on LAO are highly metallic within the entire temperature range without any sign of hysteric behavior. This indicates that the bulk MIT is completely quenched by application of the compressive strain.

To elucidate a possible modification of the local Ni electronic structure, XAS spectra of films on STO and LAO were obtained at 300K and 10K, i.e. well below the bulk MIT temperature of ~210K. Due to the overlapping La M$_{4,5}$-edge, the spectra of films on LAO at the Ni L$_{3}$-edge is strongly dis-
der sample has revealed the presence of a charge-order (CO) insulating phase \[20\]. Previous extensive work on the appearance of a strong multiplet, which is also observed in other temperature, the bulk and film grown on STO show the appearance of a strong multiplet, which is also observed in other members of the Ni\(^{3+}\) series with smaller rare-earth ions in the insulating phase\[19\]. At low temperature, the bulk and film grown on STO show the appearance of a strong multiplet, which is also observed in other members of \(\text{RENiO}_3\) series with smaller rare-earth ions in the insulating phase\[20\]. Previous extensive work on the powder sample has revealed the presence of a charge-order (CO) ground state below the MIT. In contrast to this observation, no temperature dependent evolution of the line-shape associated with CO is seen for the sample on LAO which is consistent with the maintained metallic phase even at low temperature.

In the bulk, it has been established that the evolution of MIT is due to the opening of a charge transfer gap with the reduction of the d-band bandwidth \[21, 22\]. By close analogy, the results above imply, that the suppression of the MIT under compressive strain is likely associated with the closing of the charge transfer gap. It is interesting to note, that the MIT can also be suppressed by application of hydrostatic pressure and a complete quenching would require more than 40kBar \[23\]. When under tensile strain, the presence of the MIT with a hysteresis and the bulk-like magnitude of MIT strongly implies that a sizable charge transfer gap remains in the ground state, despite the existence of electronic modification due to strain and the ultra-thin geometry.

In conclusion, we have developed the LBL growth and synthesized high-quality fully epitaxial ultra-thin film of NNO on STO and LAO. Metallicity is maintained on both substrates for films even as thin as 10 unit cells. RHEED, AFM imaging, synchrotron-based XRD and XAS studies have confirmed the excellent morphology and bulk-like stoichiometry of the samples. Temperature dependent d.c. resistivity and resonant XAS at the Ni L-edge have revealed that the MIT is quenched under the compressive strain of LAO, while the metal-insulator transition remains under the tensile strain. These findings demonstrate the possibility of a strain-controlled MIT by ultra-thin film epitaxy for future applications based on heterojunctions of correlated oxides.

The authors acknowledge fruitful discussions with D. Khomskii, A. Millis and G.A. Sawatzky. J.C. was supported by DOD-ARO under the grant No. 0402-17291 and NSF grant No. DMR-0747808. Work at the Advanced Photon Source, Argonne is supported by the U.S. Department of Energy, Office of Science under grant No. DEAC02-06CH11357.

*References*

1. M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
2. J.-S. Zhou, J. B. Goodenough, B. Dabrowski, P. W. Klamut, and Z. Bukowski, Phys. Rev. B 61, 4401 (2000).
3. J. L. Garcia-Munoz, J. Rodriguez-Carvajal, and P. Lacorre, Phys. Rev. B 50, 978 (1994).
4. V. Scagnoli, U. Staub, M. Janousch, A. M. Mulders, M. Shi, G. I. Meijer, S. Rosenkranz, S. B. Wilkins, L. Paolasini, J. Karpinski, S. M. Kazakov, and S. W. Lovesey, Phys. Rev. B 72, 155111 (2005).
5. J. L. Garcia-Munoz, M. A. G. Aranda, J. A. Alonso, and M. J. Martinez-Lope, Phys. Rev. B 79, 134432 (2009).
6. P. Lacorre, J. B. Torrance, J. Panneier, A. I. Nazzal, P. W. Wang, and T. C. Huang, J. Solid State Chem. 91, 225 (1991).
7. O. Yu. Gorbenko, S. V. Samoilenkov, I. E. Graboy, and A. R. Kaul, Chem. Mater. 14, 4026 (2002).
8. G. Catalan, Phase Transitions 81, 729 (2008).
9. G. Catalan, R. M. Bowman, and J. M. Gregg, Phys. Rev. B 62, 7892 (2000).
10. M. A. Novojilov, O. Yu. Gorbenko, I. E. Graboy, A. R. Kaul, H. W. Zandbergen, N. A. Babushkina, and L. M. Belova, Appl. Phys. Lett. 76, 2041 (2000).
11. R. Eguchi, Y. Okamoto, Z. Hiroi, S. Shin, A. Chainani, Y. Tanaka, M. Matsunami, Y. Takata, Y. Nishino, K. Tamasaku, M. Yabashi, and T. Ishikawa, Appl. Phys. Lett. 105, 056103 (2009).
12. A. Tiwari, C. Jin, and J. Narayan, Appl. Phys. Lett. 80, 4039 (2002).
13. M. Kareev, S. Prosandeev, J. Liu, C. Gan, A. Kareev, J. W. Freeland, Min Xiao, and J. Chakhalian, Appl. Phys. Lett. 93, 061909 (2008).
14. D. H. A. Blank, G. Koster, G. A. H. M. Rijnders, E. van Setten, P. Slycke, and H. Rogalla, J. Cryst. Growth 211, 98 (2000).
15. Y. Kozuka, T. Susaki, and H. Y. Hwang, Appl. Phys. Lett. 88, 142111 (2006).
16. F. Goudeau, P. Laffez, M. Zaghrioui, E. Elkahim, and P. Ruello, Crystal Engineering 5, 317 (2002).
17. M. Ziese, H. C. Semmelhack, K. H. Han, S. P. Sena, and H. J. Blythe, J. Appl. Phys. 91, 9930 (2002).
18. M. Huijben, G. Koster, D. H. A. Blank, and G. Rijnders, Phase...
[19] M. Medarde, A. Fontaine, J. L. Garcia-Munoz, J. Rodriguez-Carvajal, M. de Santis, M. Sacchi, G. Rossi, and P. Lacorre, Phys. Rev. B 46, 14975 (1992).
[20] C. Piamonteze, F. M. F. de Groot, H. C. N. Tolentino, A. Y. Ramos, N. E. Massa J. A. Alonso, and M. J. Martinez-Lope, Phys. Rev. B 71, 020406(R) (2005).
[21] J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansaldo, and C. H. Niedermayer, Phys. Rev. B 45, 8209 (1992).
[22] J. L. Garcia-Munoz, J. Rodriguez-Carvajal, P. Lacorre, and J. B. Torrance, Phys. Rev. B 46, 4414 (1992).
[23] J.-S. Zhou, J. B. Goodenough, and B. Dabrowski, Phys. Rev. Lett. 95, 127204 (2005).