UC Santa Barbara
UC Santa Barbara Previously Published Works

Title
Probing the metal-insulator transition of NdNiO3 by electrostatic doping

Permalink
https://escholarship.org/uc/item/38f994b0

Journal
Applied Physics Letters, 99(19)

Authors
Son, Junwoo
Jalan, Bharat
Kajdos, Adam
et al.

Publication Date
2011-11-09

DOI
10.1063/1.3659310

Peer reviewed

eScholarship.org Powered by the California Digital Library
University of California

Probing the metal-insulator transition of $NdNiO_3$ by electrostatic doping

Junwoo Son,[1] Bharat Jalan,[1] Adam P. Kajdos,[1] Leon Balents,[2] S. James Allen,[2] and Susanne Stemmer[1,a)]
[1]*Materials Department, University of California, Santa Barbara, California 93106-5050, USA*
[2]*Department of Physics, University of California, Santa Barbara, California 93106-9530, USA*

(Received 9 September 2011; accepted 18 October 2011; published online 9 November 2011)

Modulation of the charge carrier density in a Mott material by remote doping from a highly doped conventional band insulator is proposed to test theoretical predictions of band filling control of the Mott metal-insulator transition without introducing lattice distortions or disorder, as is the case for chemical doping. The approach is experimentally tested using ultrathin (2.5 nm) $NdNiO_3$ films that are epitaxially grown on La-doped $SrTiO_3$ films. We show that remote doping systematically changes the charge carrier density in the $NdNiO_3$ film and causes a moderate shift in the metal-insulator transition temperature. These results are discussed in the context of theoretical models of this class of materials exhibiting a metal-insulator transition. © *2011 American Institute of Physics*. [doi:10.1063/1.3659310]

Mott insulators defy simple models that predict metallic transport. An early triumph of theory was to recognize that electron-electron repulsion can localize the conduction electrons, causing an insulator to emerge.[1] However, the connection between idealized models and real materials is complicated by structural changes, charge, and magnetic ordering that often accompany the insulating state. A key probe of the Mott insulating state is to add or remove charge, which should cause a transition to the metallic state.[2] In bulk materials, charge modulation is achieved via chemical substitution ("doping"), which, however, also introduces atomic disorder and lattice distortions, making it difficult to isolate the purely electronic contributions. Electrostatic doping avoids these complications, but is challenging because of the large charge carrier concentrations involved—typical Mott materials are characterized by a half-filled *d*-band, corresponding to $\sim$ one unpaired electron per unit cell.[3]

Rare earth nickelates ($RNiO_3$, where R is a trivalent rare earth ion but not La) exhibit a first order phase transition to an insulating state upon cooling. The transition temperature (T_{MIT}) can be strongly modified by chemical doping.[4–6] Initial reports indicated that divalent ions ("hole doping") were more effective in lowering T_{MIT} than quatrovalent ions ("electron doping"),[5] but certain donor dopants also had a large effect on T_{MIT}.[6] Because chemical doping affects the Ni-O bond angles and lengths,[6] an attempt to correct for the structural distortions in Ref. 4 led to estimates that a 1% change in carrier concentration suppressed T_{MIT} by $\sim$25 to 50°K for electron and hole doping, respectively. Separating the influence of structural distortions from band filling is important for the nickelates because the metal-insulator transition temperature (T_{MIT}) is also a strong function of the rare earth ionic radius and of applied pressure,[7–9] which affect the octahedral distortions, the hybridization between O 2*p* and Ni*d*-states, and the bandwidth. Isotope studies point to a strong coupling to the lattice.[10] The $RNiO_3$'s are usually classified as charge-transfer Mott insulators,[8,11] but recent studies indicate that charge ordering may lead to a band gap between the empty e_g band of a weakly magnetic Ni and the fully occupied spin-up band of the strongly magnetic Ni.[12,13]

Recently, electrolyte gating, which can induce carrier densities of the order of $10^{14}\,cm^{-2}$, has been used to induce shifts in T_{MIT} of $NdNiO_3$ films.[14,15] However, electrolytes can chemically alter the underlying channel,[16,17] even in a reversible fashion. Ref. 14 reported that the shift in T_{MIT} was a function of the film thickness, which is not consistent with a purely electrostatic effect that should produce a metallic channel that shunts the bulk of the film.

Modulation doping using a heterointerface is an attractive approach for electrostatic control of large carrier densities of Mott materials and to probe the sensitivity of the transition to band filling without introducing disorder or lattice distortions.[18–20] For a 1 eV band offset, which is realistic for $RNiO_3/SrTiO_3$ interfaces[21,22] and no interface traps, estimates[23] show that the *interfacial* carrier concentration in a $RNiO_3$ film can be modulated greater than 20%, if interfaced with $SrTiO_3$ doped with $10^{21}\,cm^{-3}$ electrons, far exceeding the few percent required for substantial changes in T_{MIT} that the bulk doping studies indicate. Although the transferred charge drops rapidly away from the interface,[23] the average doping in a 2.5 nm film is $\sim$6% and thus substantial in terms of modulation of T_{MIT}, by the bulk doping experiments. Carrier concentrations as high as $10^{21}\,cm^{-3}$ are easily achievable in high-quality $SrTiO_3$.[24] Although some charge will likely be lost to interface traps, $RNiO_3/SrTiO_3$ interfaces are ideal to evaluate the influence of carrier modulation on the transition. In this letter, we demonstrate substantial modulation of the carrier concentration in $NdNiO_3$, using charge transfer from a $SrTiO_3$ film and study its influence on the metal-insulator transition.

$LaAlO_3$ substrates impose a compressive strain, which stabilizes the metallic phase of ultrathin $NdNiO_3$ films.[25,26] 5-nm-thick $SrTiO_3$ doped with different amounts of La were grown on 5 nm undoped $SrTiO_3$ buffers on (001) $LaAlO_3$ by molecular beam epitaxy (MBE).[27] The La-dopant concentrations (N_{La}) were 0, 10^{19}, 10^{20}, and $10^{21}\,cm^{-3}$, respectively. The total thickness of $SrTiO_3$ was limited to

a)Author to whom correspondence should be addressed. Electronic mail: stemmer@mrl.ucsb.edu.

 © 2011 American Institute of Physics

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

10 nm to ensure coherently strained films. A 5-nm-thick La-doped $SrTiO_3$ should not contribute to in-plane transport, because for carrier concentrations up to $10^{21}\,cm^{-3}$, the depletion width w is greater than the doped film thickness

$$w = \sqrt{\frac{2\varepsilon_{STO}\varphi_{STO}}{eN_{La}}}, \tag{1}$$

where ε_{STO} is the dielectric constant of $SrTiO_3$ ($\sim 300\varepsilon_0$ at room temperature), φ_{STO} is the band-bending ($\sim$1 V), and e is the elemental charge. Confirmation of the fully depleted nature is described below. Epitaxial $NdNiO_3$ thin films were then grown using RF magnetron sputtering with a gas pressure of 200 mTorr and a substrate temperature of 700 °C. The Ar/O_2 sputter gas ratio was 75/25, and the growth rate was $\sim$12 nm/h. Samples were annealed for 30 min under flowing oxygen at 600 °C after growth. All films were epitaxial.[23] Sheet resistance and Hall coefficient were measured in Van der Pauw and Hall bar geometries, respectively. The hall resistance r_H needed to be symmetrized to remove contributions from the magnetoresistance, i.e., $r_H = [V_H(B) - V_H(-B)]/2I$, where $V_H(B)$ and $V_H(-B)$ are the Hall voltages at positive and negative magnetic fields B, respectively, and I is the current.

Due to the large carrier density and short screening length of $NdNiO_3$, ultrathin films are required to substantially modulate the charge in the film. As the sheet resistance of the thin films exceeds the Mott minimum conductivity for metallic conductivity ($R_S < 10\ k\Omega/\square$), localized characteristics are expected at all temperatures and are observed.[25] Figure 1 shows resistivity of $NdNiO_3$ films grown directly on $LaAlO_3$ as a function of temperature 12 nm-thick $NdNiO_3$ films show a first order transition with hysteresis at $T_{MIT} \sim 100$ K, similar to the literature.[14,26] Thin $NdNiO_3$ films show higher resistivity at room temperature and a narrower hysteresis that eventually vanishes for the 3 nm thick $NdNiO_3$ film. However, even the localized films show a sharp rise (two orders of magnitude) in resistance at T_{MIT} that is not characteristic for a disorder-induced transition. The robustness of the transition to a highly resistive state even in ultrathin films makes them thus suitable to study the influence of carrier modulation.[14,15]

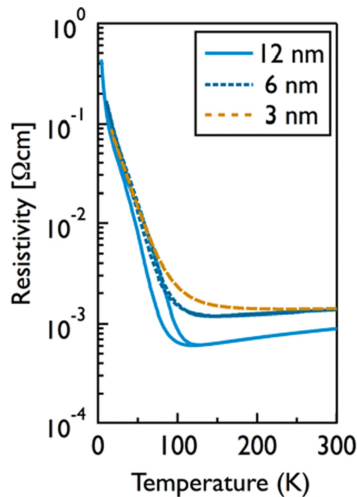

FIG. 1. (Color online) Resistivity of epitaxial $NdNiO_3$ thin films grown on $LaAlO_3$ as a function of temperature and $NdNiO_3$ film thickness.

Figure 2(a) shows the temperature-dependent sheet resistance of 2.5 nm-thick $NdNiO_3$ films grown on La:$SrTiO_3$ with the different La doping concentrations. The resistance between Hall bar structures after etching the $NdNiO_3$ was measured to confirm that no conduction occurred through the La:$SrTiO_3$ layers. The $NdNiO_3$ sheet resistance systematically decreases as the doping in the $SrTiO_3$ is increased, consistent with electron transfer from the La:$SrTiO_3$ and the schematic band alignment shown in Fig. 2(b). The $NdNiO_3$ films on La:$SrTiO_3$/$LaAlO_3$ with the highest La dopant concentration show a decrease in resistance on cooling above T_{MIT}. This is consistent with the sheet resistance of these films being significantly below 10 k$\Omega/\square$. To quantify the electron transfer, Fig. 3 shows the room-temperature Hall resistance as a function of magnetic field for the three $NdNiO_3$ films on differently doped La:$SrTiO_3$. The Hall coefficient is positive, i.e., the Hall resistivity increases linearly with magnetic fields up to 7 T for all films. The $R$$NiO_3$'s show semimetallic characteristics above T_{MIT}.[8,12] The positive Hall coefficient is due to a large hole Fermi surface around the R point.[28,29] The Hall coefficient for a relatively simple, semiconductor like material, with free electron and hole band dispersion, is given by

$$R_H = \frac{-n\mu_n^2 + p\mu_p^2}{e(n\mu_n + p\mu_p)^2}, \tag{2}$$

Where n and p are the electron and hole concentrations, respectively and μ_i their mobilities. Despite the limitations of Eq. (2), the observed positive Hall coefficient for the undoped material suggests that $p\mu_p^2 > n\mu_n^2$ and its Hall coefficient is consistent with transport dominated by holes at a carrier concentration of approximately 1 carrier per Ni. The

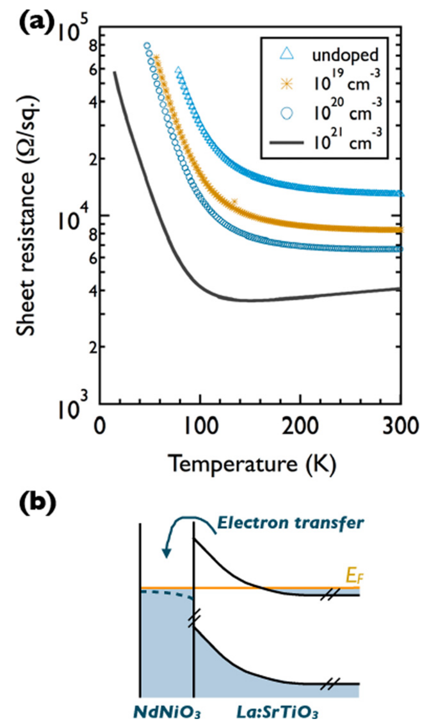

FIG. 2. (Color online) (a) Sheet resistance of epitaxial, 2.5-nm thick $NdNiO_3$ thin films on La-doped $SrTiO_3$ as a function of La-dopant concentration in the $SrTiO_3$ (see legend). (b) Schematic of the expected band lineup at the interface between metallic $NdNiO_3$ and La:$SrTiO_3$. The dashed lines indicate the position of a half filled d-band for an ideal Mott insulator.

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

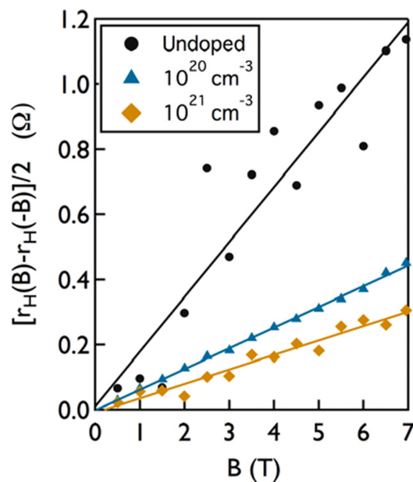

FIG. 3. (Color online) Symmetrized Hall resistances for 2.5-nm thick $NdNiO_3$ thin films on La-doped $SrTiO_3$ as a function of La dopant concentration in the $SrTiO_3$. The slope (lines) gives the Hall coefficient, which is positive and decreases with increasing La dopant concentration.

Hall coefficient changes by about a factor of four (from 4.2×10^{-4} to 1.1×10^{-4} cm^3/C) between the films on undoped $SrTiO_3$ and those on $SrTiO_3$ doped with 10^{21} cm^{-3} La. This indicates a large compensation of the hole transport by electrons. Thus, both resistivity and Hall measurements demonstrate highly effective remote doping of an ultrathin, rare earth nickelate by interfacing it with highly doped $SrTiO_3$.

The results provide insights into the metal-insulator transition of the rare earth nickelates. In particular, Figure 2 shows that (1) $NdNiO_3$ films transition to a highly resistive state below ~100 K even when heavily doped and (2) T_{MIT} is only weakly dependent on doping. A plot of $d(\ln R)/dT$ shows a ~20–30 K shift for the film on $SrTiO_3$ doped with 10^{21} cm^{-3} La relative to films on undoped $SrTiO_3$,[23] *despite* the large change in Hall coefficient. This can be compared with the much larger effects of comparable chemical doping (a ~120 K shift for 10% doping[4]) but is similar to the shifts obtained with electrolyte gating.[14,15] The first observation is the most challenging to understand. Theoretically, a defect-free material with a finite deviation from an integral number of electrons per unit cell must be conducting at zero temperature, owing to the presence of partially filled bands. A possible explanation of the robust insulating state in the nickelates is that the stoichiometric charge and spin order of undoped $NdNiO_3$ (Refs. 11–13, 29, and 30) evolves into an *incommensurate* ordered state in concert with doping. If the wavevector of the charge order tracks the change in carrier density, an insulating ground state can be achieved. For example, bulk nickelates $La_{2-x}Sr_xNiO_4$ form insulating "stripe" states with an incommensurability which is proportional to x.[31] The robustness of the T_{MIT} with doping is also striking. This provides further evidence that the metal-insulator transition in the rare earth nickelates is closely tied to the spontaneous symmetry breaking and charge/spin ordering below T_{MIT}.[30] In contrast, a Mott material in the strong U limit described using only single-site physics would respond to substantial doping by exhibiting a crossover, as distinct from a phase transition, to a metallic phase. Finally, the modulation doping approach presented here is entirely general and could be applied to elucidate the nature of metal-insulator transitions in other materials systems, as well as allow for new Mott field-effect devices.[32]

This work was supported by a MURI program of the Army Research Office (Grant No. W911-NF-09-1-0398). We thank SungBin Lee and Andy Millis for many useful discussions.

[1] N. F. Mott, Proc. Phys. Soc. London, Sect. A **62**, 416 (1949).
[2] J. Orenstein and A. Vishwanath, Nature Phys. **6**, 566 (2010).
[3] C. H. Ahn, A. Bhattacharya, M. Di Ventra, J. N. Eckstein, C. D. Frisbie, M. E. Gershenson, A. M. Goldman, I. H. Inoue, J. Mannhart, A. J. Millis, A. F. Morpurgo, D. Natelson, and J. M. Triscone, Rev. Mod. Phys. **78**, 1185 (2006).
[4] J. L. García-Muñoz, M. Suaaidi, M. J. Martínez-Lope, and J. A. Alonso, Phys. Rev. B **52**, 13563 (1995).
[5] S. W. Cheong, H. Y. Hwang, B. Batlogg, A. S. Cooper, and P. C. Canfield, Phys. B **194**, 1087 (1994).
[6] J. A. Alonso, M. J. Martinezlope, and M. A. Hidalgo, J. Solid State Chem. **116**, 146 (1995).
[7] J. B. Goodenough, Rep. Prog. Phys. **67**, 1915 (2004).
[8] J. B. Torrance, P. Lacorre, A. I. Nazzal, E. J. Ansaldo, and C. Niedermayer, Phys. Rev. B **45**, 8209 (1992).
[9] P. C. Canfield, J. D. Thompson, S. W. Cheong, and L. W. Rupp, Phys. Rev. B **47**, 12357 (1993).
[10] M. Medarde, P. Lacorre, K. Conder, F. Fauth, and A. Furrer, Phys. Rev. Lett. **80**, 2397 (1998).
[11] T. Mizokawa, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **61**, 11263 (2000).
[12] I. I. Mazin, D. I. Khomskii, R. Lengsdorf, J. A. Alonso, W. G. Marshall, R. A. Ibberson, A. Podlesnyak, M. J. Martinez-Lope, and M. M. Abd-Elmeguid, Phys. Rev. Lett. **98**, 176406 (2007).
[13] M. Medarde, C. Dallera, M. Grioni, B. Delley, F. Vernay, J. Mesot, M. Sikora, J. A. Alonso, and M. J. Martinez-Lope, Phys. Rev. B **80**, 245105 (2009).
[14] S. Asanuma, P.-H. Xiang, H. Yamada, H. Sato, I. H. Inoue, H. Akoh, A. Sawa, K. Ueno, H. Shimotani, H. Yuan, M. Kawasaki, and Y. Iwasa, Appl. Phys. Lett. **97**, 142110 (2010).
[15] R. Scherwitzl, P. Zubko, I. G. Lezama, S. Ono, A. F. Morpurgo, G. Catalan, and J.-M. Triscone, Adv. Mater. **22**, 5517 (2010).
[16] J. D. Yuen, A. S. Dhoot, E. B. Namdas, N. E. Coates, M. Heeney, I. McCulloch, D. Moses, and A. J. Heeger, J. Am. Chem. Soc. **129**, 14367 (2007).
[17] K. Ueno, H. Shimotani, Y. Iwasa, and M. Kawasaki, Appl. Phys. Lett. **96**, 252107 (2010).
[18] M. Nakamura, A. Sawa, H. Sato, H. Akoh, M. Kawasaki, and Y. Tokura, Phys. Rev. B **75**, 155103 (2007).
[19] T. Higuchi, Y. Hotta, T. Susaki, A. Fujimori, and H. Y. Hwang, Phys. Rev. B **79**, 075415 (2009).
[20] W. C. Lee and A. H. MacDonald, Phys. Rev. B **74**, 075106 (2006).
[21] T.-B. Wu and H.-J. Shy, Ceram. Int. **26**, 599 (2000).
[22] Y. Kozuka, T. Susaki, and H. Y. Hwang, Appl. Phys. Lett. **88**, 142111 (2006).
[23] See supplementary material at http://dx.doi.org/10.1063/1.3659310 for structural data, depletion lengths, the transferred carrier concentration, and plots of d(lnR)/dT for $NdNiO_3$ films on La-doped $SrTiO_3$ with different La concentrations.
[24] B. Jalan and S. Stemmer, Appl. Phys. Lett. **97**, 042106 (2010).
[25] J. Son, P. Moetakef, J. M. LeBeau, D. Ouellette, L. Balents, S. J. Allen, and S. Stemmer, Appl. Phys. Lett. **96**, 062114 (2010).
[26] G. Catalan, R. M. Bowman, and J. M. Gregg, Phys. Rev. B **62**, 7892 (2000).
[27] J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N. J. Wright, R. Engel-Herbert, and S. Stemmer, Nature Mater. **9**, 482 (2010).
[28] R. Eguchi, A. Chainani, M. Taguchi, M. Matsunami, Y. Ishida, K. Horiba, Y. Senba, H. Ohashi, and S. Shin, Phys. Rev. B **79**, 115122 (2009).
[29] S. Lee, R. Chen, and L. Balents, Phys. Rev. Lett. **106**, 016405 (2011).
[30] U. Staub, G. I. Meijer, F. Fauth, R. Allenspach, J. G. Bednorz, J. Karpinski, S. M. Kazakov, L. Paolasini, and F. d'Acapito, Phys. Rev. Lett. **88**, 126402 (2002).
[31] J. M. Tranquada, D. J. Buttrey, and V. Sachan, Phys. Rev. B **54**, 12318 (1996).
[32] J. Son, S. Rajan, S. Stemmer, and S. J. Allen, J. Appl. Phys **110**, 084503 (2011).

Author complimentary copy. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp