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<td>Wang, Le; Chang, Lei; Yin, Xinmao; Rusydi, Andrivo; You, Lu; Zhou, Yang; Fang, Liang; Wang, Junling</td>
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Localization-driven metal-insulator transition in epitaxial hole-doped Nd$_{1-x}$Sr$_x$NiO$_3$ ultrathin films

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Keywords: metal-insulator transition, nickelates thin films, weak localization, dimensional crossover

Abstract:

Advances in thin film growth technologies make it possible to obtain ultra-thin perovskite oxide films and open the window for controlling novel electronic phases for use in functional nanoscale electronics, such as switches and sensors. Here, we study the thickness-dependent transport characteristics of high-quality ultrathin Nd$_{0.9}$Sr$_{0.1}$NiO$_3$ (Sr-NNO) films, which were grown on LaAlO$_3$ (001) single-crystal substrates by using pulsed laser deposition method. Thick Sr-NNO films (25 unit cells) exhibit metallic behavior with the electrical resistivity following the $T^n$ ($n<2$) law corresponding to a Non-Fermi liquid system, while a temperature driven metal-insulator transition (MIT) is observed with films of less than 15 unit cells. The transition temperature increases with reducing film thickness, until the insulating characteristic is observed even at room temperature. The emergence of the insulator ground state can be attributed to weak
localization driven MIT expected by considering Mott-Ioffe-Regel limit. Furthermore, the magneto-transport study of Sr-NNO ultrathin films also confirms that the observed MIT is due to the disorder-induced localization rather than the electron-electron interactions.

1. Introduction

The intense research activities on perovskite oxides (ABO$_3$) have revealed various strongly correlated electron phenomena, including metal-insulator transition (MIT), multiferroism, and high temperature superconductivity. Understanding these unusual electronic behaviors has been a long-standing task in modern physics. Many perovskite oxides have very complex electronic structures, with charge, spin, orbital orders arising from the strong correlation among the transition-metal 3$d$ electrons and their hybridization with oxygen 2$p$ electrons. As a key member of the perovskite oxides family, rare earth nickelates (RNiO$_3$, where R represents rare earth lanthanide elements) are believed not to be of the Mott-Hubbard class but of a charge transfer type [1-3], characterized by an oxygen 2$p$-like valence band and a 3$d$-like upper Hubbard conduction band (separated by an energy $\Delta$, known as the charge transfer energy). Within the Sawatzky–Allen–Zaanen scheme [3], RNiO$_3$ have been classified as small or negative charge transfer systems. Small or negative $\Delta$ is one key property of compounds that can produce a superconducting state by doping [4]. This has motivated researchers to explore the possibility of superconductivity in RNiO$_3$-based compounds or heterostructures [5,6]. However, no experimental observation of superconductivity in this system has been reported. On the other hand, most RNiO$_3$ heterostructures or ultrathin films undergo a MIT at room temperature with a critical thickness of 3-5 monolayers [7-13].

Many possible mechanisms have been proposed to explain this insulating ground state, such as orbital ordered Mott insulator [5,14], Fermi surface nesting effect and orbital reconstruction [10], charge and/or spin order [11], and weak localization [8]. However, no consensus has been reached. It appears essential to understand the nature of the insulating ground state in the ultrathin film limit for future investigation of RNiO$_3$-based heterostructures. In this letter, we present the thickness-dependent transport investigation on the Nd$_{0.9}$Sr$_{0.1}$NiO$_3$ (Sr-NNO) films
with thickness ranging from 3 to 25 unit cells (u.c.). For 25 u.c. thick films, the temperature-driven MIT in un-doped NdNiO$_3$ (NNO) is completely suppressed by Sr$^{2+}$ doping on A site. Evolution from metallic to insulating behavior is observed as the Sr-NNO film thickness decreases from 25 to 3 u.c.. The possible mechanism is discussed.

2. Experimental details

High-quality epitaxial Sr-NNO thin films with thicknesses ranging from 3 to 25 u.c. were deposited on (001)-LaAlO$_3$ (LAO, $a_{\text{LAO}}$~3.79 Å) substrates using pulsed laser deposition (PLD) method. The laser pulse (248 nm) energy density was ~2 J/cm$^2$ and the repetition rate was 3 Hz. The Sr-NNO films were grown at 630 °C under an oxygen pressure of 40 Pa. After deposition, we raised the oxygen pressure to 10 kPa and cooled the samples to room temperature.

The film thickness was determined using x-ray reflectivity (XRR) and the crystal structure was examined using the X-ray Demonstration and Development (XDD) beamline at the Singapore Synchrotron Light Source (SSLS). The surface morphology was analyzed using an atomic force microscope (AFM) (Asylum Research MFP-3D). Resistance, magnetoresistance, and Hall measurements were performed using a physical properties measurement system (PPMS-14T, Quantum Design) at temperatures ranging from 10 to 300 K at a cooling/warming rate of 3 K/min. We use linear four point geometry with Pt top electrodes to make Ohmic contacts. The magnetoresistance of the NNO films are measured with a perpendicular magnetic field.

3. Results and discussion

X-ray Diffraction (XRD) $\theta$-2$\theta$ scans confirm that the Sr-NNO films are single phase. To obtain the crystal structure of the Sr-NNO film on LAO substrate, L-scan XRD and reciprocal space mapping (RSM) are conducted. As shown in figure 1(a), the (002) peak of LAO corresponds to the out-of-plane lattice constant of $c = 3.79$ Å. After Gaussian fitting, the $c$ lattice constant of Sr-NNO film is calculated to be about 3.85(1) Å. Figure 1(b) shows a typical RSM collected around the (-203) peak of a 25 u.c. thick film grown on LAO. It clearly reveals that the in-plane lattice
parameter of the Sr-NNO film is identical to that of the substrate, indicating that the film is coherently grown on LAO. As shown in figure 1(c), a typical AFM topography image of Sr-NNO film on LAO shows clear step-edges with small roughness of ~0.15 nm.

The temperature dependence of electrical resistivity ($\rho$-$T$) was measured in the temperature range of 5-300 K. As shown in figure 2(a), the 25 u.c. thick Sr-NNO film exhibits metallic behavior in the entire temperature range. Compared with the $\rho$-$T$ curve of un-doped NNO films of the same thickness (blue curve in figure 2(a)), the temperature-driven MIT is completely suppressed and thermal hysteresis disappears in the hole-doped Sr-NNO film. It is likely that the doped holes change the electronic states from $\alpha|d^7\rangle + \beta|d^8 L\rangle$ ($\alpha^2 + \beta^2 = 1$) to mainly $d^7 L$ character [15], where $L$ stands for a ligand hole. In the following, we take a close look at the metallic state of the hole-doped Sr-NNO films. Linear relation $\rho(T) \sim T$ fails to describe the experimental data, especially for the low temperature region. Recent studies on nickelate films reveal that non-Fermi liquid (NFL) behavior can exist in this system [16]. For NFLs, $\rho_{NFL}(T)$ follows a power law relationship with an exponent $n<2$

$$\rho_{NFL}(T) = \rho_0 + AT^n,$$

where the residual resistivity $\rho_0$ is a temperature independent value attributed to the electron-impurity scattering caused by defects, and A is the temperature coefficient. However, eq. (1) alone cannot completely describe our experimental observation either. $\rho(T)$ can only be accurately described when we account for the resistivity saturation ($\rho_{SAT}$) as following [17]

$$\rho^{-1}(T) = \rho_{NFL}^{-1}(T) + \rho_{SAT}^{-1},$$

where $\rho_{SAT}$ acts as a parallel resistor, which is applied to many materials that show resistivity saturation [18-21]. The red dashed line in figure 2(a) is the fitting result using eq. (2). The fitting yields $\rho_0=3.98\times10^{-5}$ $\Omega$.cm, $\rho_{SAT}=4.64\times10^{-4}$ $\Omega$.cm, n=4/3, and A=3.85$\times10^{8}$ $\Omega$.cm/K$^{3/4}$. Figure 2(b) shows the Hall measurement results in the temperature range of 5-300 K. The carriers are found to be holes, consistent with previous reports [22-24]. As the temperature decreases from
room temperature, the concentration $p$ decreases slightly from $\sim 4 \times 10^{-22}$ cm$^{-3}$ at 300 K to $1 \times 10^{-22}$ cm$^{-3}$ at 5 K, while the hole mobility $\mu$ increases from 1.6 cm$^2$/Vs at 300 K to 14.5 cm$^2$/Vs at 5 K.

Figure 3(a) shows the evolution of $\rho(T)$ curves with Sr-NNO film thickness. Reducing thickness causes an increase in the resistivity in the entire temperature range. Clear metallic behavior down to 5 K is observed for the 25 u.c. Sr-NNO film. Films with thickness less than 15 u.c. exhibits a temperature driven MIT characterized by an upturn in resistivity at the transition temperature $T_{MI}$ (indicated by arrows in figure 3(a)). The $T_{MI}$ shifts to higher temperature upon reducing film thickness. At about 3 u.c., insulating behavior is observed in the entire temperature range. Epitaxial strain imposed by substrates strongly affects the electronic properties of nickelates films [13]. However, all the Sr-NNO films in this study are coherently strained on the LAO substrate, so strain is not responsible for the metal-insulator transition of the Sr-NNO films upon reducing thickness. The thickness dependent transport property of the Sr-NNO films is similar to that of LaNiO$_3$ studied by photoemission, which suggests a gradual loss of quasiparticle weight at 10 u.c., and its total suppression by $\sim 4$ u.c. [9]. Such a slow crossover behavior was attributed to gradual localization [9].

Below we try to clarify the origin of the insulating ground state. We use eq. (2) to describe the metallic state of all the Sr-NNO films. The fitting parameters are listed in table 1. Although the exponent $n$ is an adjustable parameter in the fitting, only one value ($n=4/3$) is obtained from the fittings (figure 3(b) and 3(c)), indicating NFL behavior [16]. Figure 3(d) and 3(e) show $(\sigma(T) - \sigma_{SAT})^{-1} - \rho_0$ vs. $T^{4/3}$ plots for 6, 8, 15 and 25 u. c. Sr-NNO films and $(\sigma(T) - \sigma_{SAT})^{-1} - \rho_0$ vs. $T^{4/3}$ plots for 5 and 4 u. c. Sr-NNO films, respectively. From table 1, it can be seen that $\rho_0$ increases with decreasing film thickness. In contrast, $\rho_{SAT}$ is basically thickness-independent. $\rho_0$ increases with decreasing film thickness because of the increased scattering by the surface, while $\rho_{SAT}$ is often linked to the maximum resistivity ($\rho_{MIR}$) that approaches the Mott-Ioffe-Regel limit [17,25].

$$\rho_{MIR} = \frac{3\pi^2\hbar}{q^2k_T^2\eta_{min}},$$  \hspace{1cm} (3)
where $l_{\text{min}}$ is the minimum carrier mean free path, which equals the interatomic spacing. If we set the interatomic spacing as the pseudocubic lattice constant ($\sim 3.8$ Å), $\rho_{\text{MIR}}$ can be calculated by using eq. (3) with $k_F = (3\pi^2 N)^{1/3}$ and a total carrier density $N \sim 10^{22}$ cm$^{-3}$. With these estimates, we obtain a $\rho_{\text{MIR}}$ value of about 0.5 mΩ.cm (black dash line in figure 3(a)) [26]. Therefore, $\rho(300K)$ increases with $\rho_0$ for the thicker films, and $\rho(300K)$ will be dominated by $\rho_{\text{SAT}}$ (or $\rho_{\text{MIR}}$) when $\rho_0$ becomes so large that $\rho_0^{-1}$ is smaller than $\rho_{\text{SAT}}^{-1}$. The Sr-NNO film will become insulating at all temperature when $\rho(300K) \approx \rho_{\text{SAT}}$ (or $\rho_{\text{MIR}}$) due to Mott-Ioffe-Regel limit. According to the data shown in figure 3(a) and the table 1, the critical thickness corresponding to $\rho(300K) \approx \rho_{\text{SAT}}$ is close to 3 u.c., which is consistent with the experimental result (figure 3(a)).

Therefore, the emergence of the insulating ground state can be attributed to weak localization driven MIT expected by considering Mott-Ioffe-Regel limit.

The strong localization induces the insulating behavior for 3 u.c. Sr-NNO film across the whole temperature range studied. In this case, electrons hop between localized states at low temperatures. The transport characteristics will follow the Mott variable range hopping (VRH) model [27,28]. And the hopping conductance is given by:

$$\sigma = C \exp\left[-\left(\frac{T_0}{T}\right)^{1/(d+1)}\right], \quad (4)$$

where $T_0$ is a constant associated with the density of localized states at the Fermi level, $T$ is the temperature and $d$ is the dimensionality of the system. The two dimensionality (2D) VRH equation fits the low T data from 10 to 130 K well as can be seen in figure 3(d), suggesting 2D behavior in these ultra-thin films. The slope and $T_0$ value obtained by fitting are 27 and 1.968×10$^4$ K. Large deviations exist if we fit the data with $d=3$, indicating that 3 u.c. Sr-NNO film is largely suppressed. According to the VRH theory, the mean hopping distance $R_{\text{hop}}$, $R_{\text{hop}} = (T_0 / T)^{1/3} a / 3$ [29], must be larger than the localization length $a$. We calculated the ratio of $R_{\text{hop}}/a$ to be larger than 1.9 within the temperature range, which satisfies the requirement for applying the VRH theory.

Since external magnetic field can break the time-reversal symmetry and result in a decrease in resistance by destructing the weak localization [30,31]. We have also carried out
magnetoresistance (MR) measurements with the magnetic field perpendicular to the film surface at various temperatures. Here, \( MR = 100\% \times \frac{R_H - R_0}{R_0} \), where \( R_H \) and \( R_0 \) are resistance values measured with and without magnetic field, respectively. As shown in figure 4(a) and figure 4(b), negative MR effect is observed which decreases with increasing temperature and film thickness, consistent with the characteristics of weak localization systems [32]. This can be ascribed to the increased density of localized electrons in thinner films. The negative MR also suggests that the dominant mechanism in Sr-NNO thin films at low temperatures is not electron-electron interactions, which will lead to a positive MR in the disordered electronic system [33,34], since the magnetic field can suppress the hopping process.

4. Summary

Transport properties of high-quality Sr-NNO thin films on LAO substrates have been investigated. Thick Sr-NNO films (25 u.c.) exhibit metallic behavior in the entire temperature range, different from that of un-doped NNO films, which is likely that the doped holes change the electronic states. The temperature driven MIT is induced in Sr-NNO ultrathin films of less than 15 u.c.. Based on the fitting results, we conclude that the origin of the insulator ground state is attributed to weak localization driven MIT expected by considering Mott-Ioffe-Regel limit. Furthermore, the magneto-transport study of Sr-NNO ultrathin films also confirms that the observed MIT is due to the disorder-induced localization rather than the electron-electron interactions.

Acknowledgment

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References


Figures and Figure captions:

Figure 1 (Color figure online). (a) L-scan XRD around (002) peak, (b) the reciprocal space mapping around (-203) peak, and (c) AFM topography image of a 25 u.c. thick Sr-NNO film. The AFM scan size is $3 \times 3 \mu m^2$.

Figure 2 (Color figure online). (a) $\rho$-T curves of 25 u.c. thick undoped NNO and Sr-NNO films grown on LAO substrates. Solid lines are experimental data and red dashed line is fitting using Eq. 2. (b) Temperature dependence of carrier concentration ($\rho$) and mobility ($\mu$) from Hall measurements for the 25 u.c. thick Sr-NNO film.

Figure 3 (Color figure online). (a) $\rho$-T curves for Sr-NNO films with thickness ranging from 25 u.c. to 3u.c.. Arrows indicate the local minima in resistivity, namely the metal-insulator transition point ($T_{MI}$). The black dash line represents the Mott-Ioffe-Regel limit according to Eq. 3. Temperature dependence of resistivity for Sr-NNO films with thicknesses of (b) 15 u.c., 8 u.c., 6 u.c. and (c) 5 u.c., 4 u.c.. Solid lines are experimental data and dashed lines are fittings using Eq. 2. (d) $(\sigma(T)-\sigma_{SAT})^{-1}-\rho_0$ vs. $T^{-4/3}$ plots for 6, 8, 15 and 25 u. c. films. (e) $(\sigma(T)-\sigma_{SAT})^{-1}-\rho_0$ vs. $T^{-4/3}$ plots for 5 and 4 u. c. films. (f) Logarithm of conductance as a function of $1/T^{1/3}$ for a 3 u.c. thick Sr-NNO film for temperatures between 10 to 300 K. The red dash line is the linear fit to the data between 10 and 130 K.

Figure 4 (Color figure online). (a) Perpendicular magnetic field dependence of the MR of a 6u.c. thick Sr-NNO film at different temperatures. (b) Thickness dependence of the MR at 5 K.
Figure 1
Figure 3
Figure 4

(a) 

(b) 

MR (%) vs. Magnetic field (T)

- 5 K
- 7 K
- 10 K
- 15 K
- 20 K
- 50 K

- 8 u.c.
- 6 u.c.
- 5 u.c.
- 4 u.c.
**Tables and Table captions**

**Table 1.** Transport properties of Sr-NNO films with various thicknesses deposited on the LAO substrates.

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<th>Film thickness (u.c.)</th>
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<th>ρ₀ (Ω cm)</th>
<th>ρ_{SAT} (Ω cm)</th>
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