Exposition of semiconducting and ferromagnetic properties of pulsed-laser-deposited thin films of $LaFe_{1-x}Ni_xO_3$ (x=0.3, 0.4, and 0.5)

R. J. Choudhary and Ravi Kumar[a)]
Materials Science Division, Nuclear Science Center, N. Delhi-110067, India

M. Wasi Khan and J. P. Srivastava
Department of Physics, Aligarh Muslim University, Aligarh-202002, India

S. I. Patil
Department of Physics, University of Pune, Pune-411007, India

S. K. Arora and I. V. Shvets
SFI Nanoscience Laboratories, Physics Department, Trinity College Dublin-2, Ireland

(Received 21 March 2005; accepted 2 August 2005; published online 20 September 2005)

We have explored the possibility of ferromagnetic semiconducting property in the epitaxial thin films of $LaFe_{1-x}Ni_xO_3$ (x=0.3, 0.4, and 0.5) grown on (001) oriented $LaAlO_3$ substrate. We observe that substitution of Ni in the series leads to the increase in conductivity of the samples with conduction being controlled by the disorder-induced localization of charge carriers. All these samples show ferromagnetic behavior at room temperature while their magnetization decreases with increase in Ni concentration in the composition. The results have been explained on the basis of the close interplay between the electrical and magnetic properties. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2058218]

Over the last few years, there has been extensive study in the direction of search for the materials possessing ferromagnetic property as well as the semiconducting property because of their potential applications in the spintronics devices, wherein the spin-controlled electrical, optical, and magnetic properties are desired.[1,2] The study has yielded several systems such as magnetic multilayers,[3] Fe_3O_4,[4] perovskite-based transition metal oxides etc.[5] Study of transition metal oxides (TMOs), has revealed an impressive diversity of exciting physical properties such as dielectric, magnetic, optical, and transport properties because of the strong electron correlation effect in the system. The TMOs exhibit high-T_c superconductivity in cuprate systems; metal-insulator (MI) transition, colossal magnetoresistance, and charge ordering in manganites; and many other phenomena in other TMO systems.[5–8]

Among several TMO-based systems of $LaTO_3$ (T=Fe, Co, Cr, Ni, and Mn), $LaNiO_3$ has rhombohedral perovskite structure and is a Pauli-paramagnetic metal with high electrical conductivity at room temperature,[9] while the other TMO systems are generally antiferromagnetic insulators, except for $LaFeO_3$, which shows ferrimagnetic transition at Néel temperature $T_N \sim 750$ K.[10–14] Therefore, the series of $LaNi_{1-x}Fe_xO_3$ samples provides an ideal opportunity to observe an interesting co-occurrence of MI transition accompanied with a paramagnetic to ferrimagnetic transition in the same member of the series at a critical substitution concentration of Fe/Ni ions. This presents a prospect to investigate the Mott's criterion of the dependence of MI transition on the critical charge carrier density by examining in such series from its one end member ($LaNiO_3$) to the one at the other end ($LaFeO_3$).

There are several reports available on bulk samples of $LaNi_{1-x}Fe_xO_3$ series by various groups including ours, where disorder-induced MI transition, structural transition from rhombohedral ($LaNiO_3$) to orthorhombic ($LaFeO_3$) at Fe concentration of ~50%, and the inverse dependence of itinerancy of d electrons with the Fe concentration have been observed.[15–18] It is suggested that in these systems the MI transition is due to the potential mismatch between the substituent metal ion and Ni^{+3} ion, which causes the transfer of hole states from near E_F to an energy state above E_F. Most of these observations have been made on polycrystalline bulk samples, where the contribution from grain boundaries could not be avoided. In the present work, we report our observations on the correspondence among the structural, electrical, and magnetic properties of thin films of $LaFe_{1-x}Ni_xO_3$ (x =0.3, 0.4, and 0.5) and propose that this system may prove to be a good candidate from the spintronics point of view. To the best of our knowledge, no report is available on the thin films of this series. We focus our present study on these x values because for a lower x value, the films become insulating enough to show any transport. Moreover, our intention is to establish the regime where the composition may show the semiconducting ferromagnetic behavior. Beyond x=0.5, there is possibility of structural transition and the structure is found to become unstable.

The polycrystalline bulk targets of $LaFe_{1-x}Ni_xO_3$ (x =0.3, 0.4, and 0.5) were synthesized using standard solid state reaction technique, whose details are provided in Ref. 18. Using these well-characterized polycrystalline bulk targets of $LaFe_{1-x}Ni_xO_3$ (x=0.3, 0.4, and 0.5), pulsed-laser deposition technique [KrF excimer laser (λ=248 nm, t_p =20 ns)] was employed to grow thin films. The substrate preferred for the purpose was (001) oriented $LaAlO_3$ (LAO) single crystal in view of the close proximity of its lattice parameters with those of the target. LAO has rhombohedral structure with a=3.788 Å and shows a very good lattice

a)Author to whom correspondence should be addressed; electronic mail: ranade@nsc.ernet.in

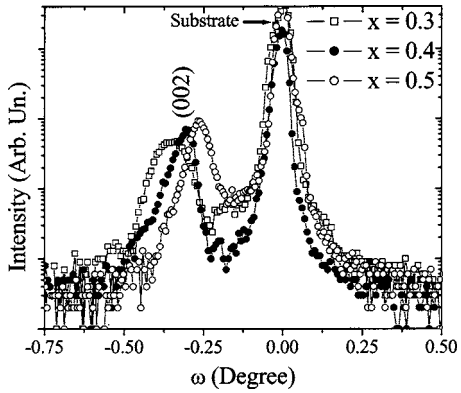

FIG. 1. The rocking curve for the (004) peak for $LaFe_{1-x}Ni_xO_3$ (x=0.3, 0.4, and 0.5) thin films along with the (002) ($LaAlO_3$) substrate peak.

match with $LaFe_{1-x}Ni_xO_3$ (a=3.884 Å). However, LAO inflicts an in-plane compressive strain ($\Delta a/a_{\text{subst.}} \sim 2.5\%$ for x=0.3) on the film. Prior to deposition, the chamber was evacuated to the base pressure of 10^{-5} Torr. During deposition, the oxygen partial pressure was kept at 300 mTorr and substrate temperature was maintained at 750 °C while the target to substrate distance was kept at 5 cm and laser energy density was 1.8 J/cm^2. After deposition, the deposited films were cooled down to room temperature in the ambient oxygen pressure at the rate of 20 °C/min. The films thickness was 150 nm. These films were characterized by various techniques such as x-ray diffraction (XRD), isothermal dc magnetization hysteresis using an alternating gradient force magnetometer (Micromag-3900, Princeton Measurements, USA), and four-probe electrical resistivity measurement in the temperature range of 77 to 300 K.

The XRD θ-2θ data (not shown here) of these films suggest the single phase, c-axis growth of the film. In Fig. 1 we show the x-ray rocking curve for the (002) peak for all the samples. From the separation between film and substrate Bragg peak we determine the perpendicular lattice constant for the films. We notice that the peak separation decreases with the increase in Ni concentration indicating a decrease is lattice mismatch.[18] The full width at half-maximum (FWHM) of the thin-film peak for x=0.3, 0.4 and 0.5 is 0.05°, 0.04°, and 0.03°, respectively. Small values of FWHM observed for these films indicate the high crystalline quality of the film. From the structural characterization, we infer that the films grown on (001) LAO substrate are under in-plane compressive strain and are highly c-axis-oriented single-phase epitaxial films.

Figure 2(a) shows the electrical resistivity behavior as a function of temperature for all the samples (x=0.3, 0.4, and 0.5). All the samples show semiconducting properties. It is clearly evident in the plots that the resistivity at room temperature is decreasing with increasing Ni substitution and for 50% Ni substitution it drops to 20 mΩ cm at room temperature, as compared to 5 Ω cm (for x=0.3). These resistivity values in thin films are lower by an order of magnitude as compared to the values of their corresponding bulk samples.[18] Indeed, the lower values of resistivity in thin films suggest that the grain boundary density in thin films are much lesser than those in the bulk samples, as also indicated by the small FWHM values for these films. It is generally recognized that the Ni substitution in the $LaFeO_3$ leads to carrier doping, which consequently decreases the energy gap

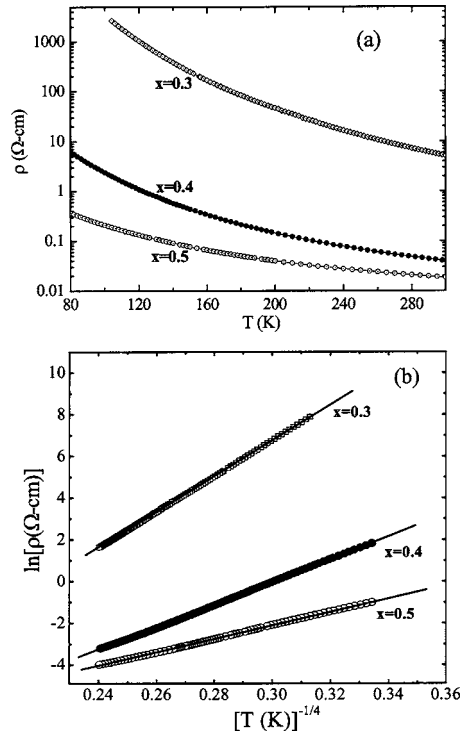

FIG. 2. (a) Resistivity as a function of temperature for $LaFe_{1-x}Ni_xO_3$ (x=0.3, 0.4, and 0.5) thin films. (b) Plot of ln ρ versus $T^{-1/4}$ of the resistivity data for $LaFe_{1-x}Ni_xO_3$ (x=0.3, 0.4, and 0.5) thin films. Line plus dot indicates the experimental data, while solid line shows the calculated linear fit in the VRH model.

and hence the resistivity of the composition. However, carrier doping by chemical substitution generally brings in disorder in the system, which may tend to localize the carriers at the doping site. The carriers in the localized states move by a phenomenon known as variable-range hopping (VRH).[17] In order to understand the effect of disorder induced localization on the electrical transport behavior, we have fit our data with Mott's VRH model $\rho(T)=\rho_0 \exp(T_0/T^{1/4})$ in the measured temperature range of 77 to 300 K. Figure 2(b) shows the ln ρ versus $T^{-1/4}$ plot for all the samples. These plots reveal that the data fit very well with the VRH model in the entire temperature range of measurement, suggesting the conduction to be governed by the disorder induced localization of charge carriers.[17] We also observe that with increase in the Ni concentration, the slope of the curve decreases. This further confirms that Ni substitution in $LaFeO_3$ decreases the activation energy or overall hopping potential via carrier doping.

In Fig. 3 we show magnetic hysteresis loops at room temperature for all the samples. A well-defined hysteresis loop with coercivity ~110 Oe is seen in each case. However, it is observed that the saturation magnetization decreases with an increase in the Ni concentration. The constant coercivity in one series of members of ferromagnetic semiconductors having different saturation magnetization is not new.[19] However, it should be pointed out here that coercivity of a magnetic thin film depends on various factors, such as micromagnetic structure of the film, magnetic anisotropy constant, magnetic exchange energy, saturation magnetization, intergrain domain wall, grain size, microstructural defects, etc. To estimate the contribution from each of these factors is beyond the scope of the present work. The saturation magnetic moment for x=0.3 sample is 5 emu/cm^3,

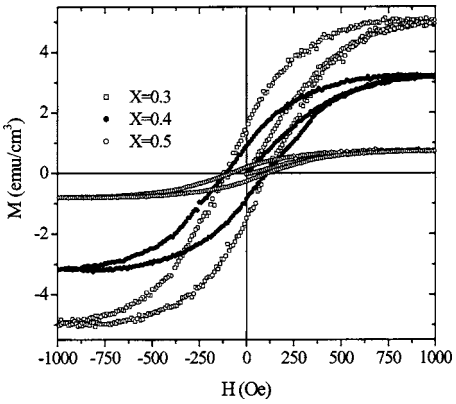

FIG. 3. The magnetic hysteresis loops for $LaFe_{1-x}Ni_xO_3$ ($x=0.3$, 0.4, and 0.5) thin films at 300 K.

while for the $x=0.5$ sample, it decreases to 0.85 emu/cm^3. Such a sharp decrease in the magnetization with increase in the Ni concentration suggests the delocalization of *d*-electrons participating in the conduction mechanism via exchange interaction between Fe and Ni ions. Indeed, in our resistivity data we observed that the increase in Ni concentration lead to lower resistivity values and a decrease in the energy gap. The M_S value for $x=0.3$ and the clear hysteresis behavior establish the strong ferromagnetic interaction which decreases with increase in Ni concentration. It should be recalled here that the magnetic and electronic properties in these transition metal oxides account for the simultaneous presence of strong electron-electron interaction potential within the transition metal *d*-orbital and a sizeable hopping interaction between the transition metal *d*- and oxygen *p*-orbitals. In view of these observations it seems that increase in Ni concentration increases the number of itinerant *d* electrons participating in the hopping interaction and decreases the number of localized *d*-orbital moments leading to decrease in the saturation magnetic moment. The magnetization data together with the electrical resistivity data favor this system strongly for its application as a ferromagnetic semiconductor.

In conclusion, we have studied the structural, electrical, and magnetic properties of highly *c*-axis-oriented single-phase epitaxial pulsed-laser-deposited thin films of $LaFe_{1-x}Ni_xO_3$ ($x=0.3$, 0.4, and 0.5) grown on (001) oriented LAO substrate. All these samples exhibit semiconducting behavior, while their resistivity values decrease with increase in the Ni concentration in the composition due to decrease in the energy gap. The resistivity behavior fits well for all the samples with the VRH model signifying the conduction is controlled by the disorder-induced localization of charge carriers. We observe a clear magnetic hysteresis loop with coercivity $\sim$110 Oe for all the samples at room temperature establishing their ferromagnetic nature. Their magnetization decreases with increase in the Ni concentration in the composition because of increase in the number of itinerant *d*-electrons participating in the hopping interaction and decreases the number of localized *d*-orbital moments. The correlation between the electrical and magnetic properties in the present system formulates it to be a potential aspirant for the spintronics oriented devices wherein the communication between the charge and spin is desired.

This work is supported by the Department of Science and Technology under project No. SP/S2/M-07/98. One of the authors (R.J.C.) would like to thank CSIR for financial support.

[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. Von Molnar, M. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).
[2] S. D. Sarma, Nature (London) **2**, 292 (2003).
[3] M. N. Baibich, J. M. Broto, A. Fert, F. N. Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
[4] K. Ghosh, S. B. Ogale, S. P. Pai, M. Robson, E. Li, I. Jin, Z. Dong, R. L. Greene, R. Ramesh, T. Venkatesan, and M. Johnson, Appl. Phys. Lett. **73**, 689 (1998).
[5] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 362 (1990).
[6] J. G. Bednorz and K. A. Muller, Z. Phys. B: Condens. Matter **64**, 189 (1986).
[7] R. von Helmont, J. Wecker, B. Holzaphel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
[8] J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719 (2003).
[9] K. Sreedhar, J. M. Honig, M. Darwin, M. McElfresh, O. M. Shand, J. Xu, B. C. Crooker, and J. Spalck, Phys. Rev. B **46**, 6382 (1992).
[10] A. E. Bocquet, A. Fujimori, T. Mizokawa, T. Saitoh, H. Namatame, S. D. Suga, N. Kimizuka, Y. Takeda, and M. Takano, Phys. Rev. B **45**, 1561 (1992).
[11] Y. Okimoto, T. Katsufuji, T. Ishikawa, A. Urushibara, T. Arima, and Y. Tokura, Phys. Rev. Lett. **75**, 109 (1995).
[12] D. D. Sarma, N. Shanthi, and Priya Mahadevan, Phys. Rev. B **54**, 1622 (1996).
[13] I. Vobornik, L. Perfetti, M. Zacchigna, M. Grioni, G. Margaritondo, J. Mesot, M. Medarde, and P. Lacorre, Phys. Rev. B **60**, R8426 (1999).
[14] D. D. Sarma, N. Shanthi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, Phys. Rev. Lett. **75**, 1126 (1995).
[15] P. Ganguly, N. Y. Vasanthacharya, C. N. R. Rao, and P. P. Edwards, J. Solid State Chem. **54**, 400 (1984).
[16] D. D. Sarma, O. Rader, T. Kachel, A. Chainani, M. Mathew, K. Holldack, W. Gudat, and W. Eberhardt, Phys. Rev. B **49**, 14238 (1994).
[17] D. D. Sarma, A. Chainani, S. R. Krishnakumar, E. Vescovo, C. Carbone, W. Eberhardt, O. Rader, Ch. Jung, Ch. Hellwig, W. Gudat, H. Srikanth, and A. K. Raychaudhuri, Phys. Rev. Lett. **80**, 4004 (1998).
[18] Ravi Kumar, R. J. Choudhary, M. Wasi Khan, J. P. Srivastava, C. W. Bao, H. M. Tsai, K. Asokan, and W. F. Pong, J. Appl. Phys. **97**, 093526 (2005).
[19] S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. Das Sarma, H. D. Drew, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **91**, 077205 (2003).