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ABSTRACT

We proved that the critical thickness for metal-to-insulator transition (MIT) of $LaNiO_3$ could be controlled by substrate orientation. By means of density functional theory calculations, films grown on SrTiO₃ substrates with (001), (110) and (111) orientations have different amount of charge transfer across the interface. Different charge transfer induces different interfacial conductivity behavior and at the same time modifies the carrier density of adjacent LaNiO₃ films. The manipulation of MIT by substrate orientation can be achieved through interfacial charge transfer induced interfacial conductive layer with the modified conductivity of LNO layer.

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The charge-transfer nickelate family ReNiO₃ (Re = rare earth) with dramatic metal to insulator transition (MIT) has been one of the most fascinating systems for designing innovative oxide interface and heterostructures in the past decades.^{1,2} Understanding and controlling of MIT in nickelates is interesting from the fundamental physics aspect, providing great opportunities for future electronic devices.

LaNiO₃ (LNO), a metal paramagnet conductor lacking any ordering phenomena in bulk, has recently become the subject of intense research, as theoretical work predicted orbital ordering and high-*T*c superconductivity.^{3–5} LNO is the most conductive one of the ReNiO₃ family and only exhibits film thicknessdependent MIT. That is, films above a critical thickness of 4 unit cells (u.c.) display metallic behavior while for films below the critical thickness, an insulating behavior is usually observed.⁶ However, it remains difficult to modify the MIT of LaNiO₃ once the materials has been prepared. In our previous work,⁴ we have tried to utilize the ferroelectric polarization of BaTiO₃ films to modify the orbital polarization on a large scale, however, the resistivity of LNO can only be slightly modified. When we turn to other oxide systems for solution, it was reported that the two dimensional electron gas (2DEG) at the (001) LaAlO₃/SrTiO₃ interfaces can be easily tuned by substrate orientation.⁷ In another similar case, LaMnO₃/LaNiO₃ superlattices grown along different substrate orientations have unconventional ferromagnetic behavior.⁸ Meanwhile, oxide thin films grown along unconventional (111)-direction is theoretically proposed to host a variety of exotic states for LNO films.⁹⁻¹¹ All this gives us an important hint that substrate orientation can be used as a tuning knob to tailor the MIT of LNO. As it is frequently reported, the competition of electronic reconstruction and polar distortions is regarded as the main factor that is responsible for the substrate orientation-induced difference in magnetic properties. Nevertheless, the effect of electronic reconstruction is especially dominated for conducting films, as the carrier density directly determines its conductive properties. Thus, it is of great significance to evaluate the effect of electronic reconstruction, namely interfacial charge transfer, on the MIT especially for nickelates.

In this work, we experimentally demonstrate that the critical thickness for metal-to-insulator transition can be controlled by the $SrTiO_3$ substrate orientation. With the aid of density functional theory (DFT) calculation, we further prove that the modification of MIT is due to charge transfer at the interface, which occurs at all three orientations but varies in their concentration. Our results shed new light on the interpretation of charge transfer at the oxide interface and the related transport property.

Prior to deposition, the substrate was heated to 700 $^{\circ}$ C, at which it stayed for half an hour under the deposition pressure for the purpose of releasing unexpected contamination and reducing additional oxygen vacancy on the substrate. LaNiO₃ films were then prepared growing LaNiO₃ from a stoichiometric target on SrTiO₃ (001), (110) and (111) substrates by pulsed laser deposition (PLD). LaNiO₃ films were grown in an atmosphere of 20 mTorr at 700 $^{\circ}$ C. The layer-bylayer growth mode is identified by reflection high-energy electron diffraction (RHEED), one oscillation of which corresponds to one monolayer (ML). The samples were cooled to room temperature under 500 Torr oxygen pressure to avoid oxygen vacancies. Spin polarized DFT calculations were performed using the Vienna abinitio simulation package (VASP)¹² with projector augmented-wave (PAW)¹³⁻¹⁷ pseudopotentials.

As shown in Fig. 1(a), LNO films grown on STO (001) substrates display good RHEED oscillation, indicating layer-by-layer growth mode and good film quality. The RHEED patterns before growth and after growth manifests that the films remain atomic smooth surfaces as the substrate. The surface topography of films was probed by atomic force microscope (AFM), as shown Fig. 1(b), Fig. 1(c), and Fig. 1(d) with respect to films on (001), (110) and (111) substrates. All the films exhibits atomic flatness, with surface roughness being only 0.256 nm, 0.305 nm and 0.295 nm for films on (001), (110) and (111) substrates.

Figure 2 shows the temperature dependent resistance curves (R-T) for LNO films grown on (001), (110), (111) STO substrates, where ML stands for a monolayer. For films grown on (001) STO substrate (Fig. 2(a)), all the films, even for the thinnest 5 ML film with a thickness of 1.935 nm, exhibits decreasing resistivity with decreasing temperature, characteristic of metallic conductive behavior. That is to say, the critical thickness of insulator-to-metal transition (t_c) for LNO films grown on (001) substrates occurs at 1.9nm. Films grown on (110) STO substrates are much more insulting than those grown on (001) STO substrate. As can be seen in Fig. 2(b), both 7 ML and 11 ML films display an insulating conductive behavior, that is, increasing resistivity with decreasing temperature. Until the film thickness reaches 15 ML, a metallic behavior is observed. This phenomenon is more obvious in films grown on (111) STO substrate seen in Fig. 2(c). Film as thick as 14 ML remains insulating and a metallic behavior is observed for films as thick as 19 ML. An abrupt jump from an insulator to a metallic state is also observed above critical thickness t_c 14 MLs and 19 MLs for (110) and (111) interfaces. Given that 1 ML \approx 2.74 Å for (110) and 1 ML \approx 2.23 Å for (111), t_c for (110) and (111) oriented films are 3.836 nm and 4.25 nm separately, in vast contrast to t_c being lower than 2 nm for (001) oriented film. We depict an orientation dependent transition temperature in Fig. 2(d). The most eminent behavior is that the resistance varies with the orientations of the substrate for films growth. The (001) films are the most metallic one, displaying metallic behavior even for the thinnest 5 ML films. In vast contrast, the (110) films are less conductive with a critical thickness of 15 ML for insulator-to-metal transition, and the (111) films are the most



FIG. 1. (a) RHEED oscillation of LNO growth; AFM image of (b) (001) direction; (c) (110) direction; (d) (111) oriented LNO films.



FIG. 2. (a) Temperature dependent resistance curves (R–T) of LNO films grown along (100) direction; (b) (110) direction; (c) (111) direction; (d) Orientation dependent t_c for (001), (110) and (111) oriented films.

insulting one with a critical thickness of 19 ML. The vast contrast among those films indicates that the orientation of substrate have some fundamental effects on its conductivity and the critical thickness of MIT. As LNO has polar discontinuity as LaAlO₃, different orientated films may have different charge transfer with the substrate, i.e. different electronic reconstruction configuration, which gives rise to substrate orientation dependent conductive behavior.

To elucidate the phenomenon, we employ DFT calculations to examine the electronic structures at LNO/STO interface. For LNO growing on (001)-, (110)- and (111)-oriented STO, slab models are constructed to study the substrate orientation effects. For each direction, STO slabs larger than 2 nm are constructed in order to simulate the substrate effects in experiments. On the other hand, LNO thickness closest to 1.935 nm studied in experiments are modeled, which are 1.973 nm for (001) direction, 1.953 nm for (110) direction, 1.936 nm for (111) direction.

A vacuum space of more than 2 nm is created to guarantee that there is no interaction between the simulation cells and their periodic images. The supercell consist of 2×2 supercell for (001) direction, 1×2 supercell for (110) direction, 1×1 supercell for (111) directions are selected so that three orientations end up with similar cross-sections size for calculations. Spin polarized DFT calculations were performed using the VASP with projector PAW pseudopotentials. A cutoff energy of the plane wave basis set of 500 eV is used in all calculations. Further increase in the cutoff energy up to 800eV will only introduce a tiny energy difference < 0.02eV. A 3×3 Gamma centered *k*-point grid is used in all calculations while the further increase of k points will not affect the energy calculated. For electronic structures, electron localizations are considered using GGA+U scheme. The rotationally invariant approach introduced by Dudarev et al.¹⁸ is applied which takes the form:

$$E_{GGA+U} = E_{GGA} + \frac{(U-J)}{2} \sum_{\sigma} \left[\left(\sum_{m1} n_{m1,m1}^{\sigma} \right) - \left(\sum_{m1,m2} \hat{n}_{m1,m2}^{\sigma} \hat{n}_{m2,m1}^{\sigma} \right) \right]$$
(1)

While on-site Coulomb interaction parameter U and J is set as 8 eV and 1 eV respectively for Ni due to its $3d^84s^2$ electronic configuration since similar parameters provide reasonable predictions in previous studies.¹⁹ Meanwhile, non-collinear magnetic calculations were performed to capture spin orbital coupling (SOC) induced splitting.

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Firstly, our calculation illustrates that there are strong charge transfer among LNO films with STO substrate at the interface. Charge transfer configuration across the interface is depicted in Fig. 3. As demonstrated, the charge transfer at the interface takes place at only O atoms for (100) direction, when comes to (110) directions, it happens at various atoms including O, La, Ni, Ti, however it is still dominated by O atoms. For (111) direction, charge transfer happens though mainly around O atoms as well, the Ti atoms at the center of O hexahedron also contribute certain amount of charge transfer. Thus it can be concluded that charge transfer between LNO and STO dominates at O atoms. It is easy to understand since O atom is the most common bridge atom for charge transfer. Our calculation shows that despite growing direction, charge transfer between STO and LNO happens mainly through O atoms.

To further clarify charge transfer along different growth directions, calculated density of states (DOS) and correspondent ground states of LNO growing on different orientations of STO are shown in Fig. 4. As can be inferred from the DOS calculation, the DOS of LNO near fermi level varies a lot depending on the growing orientation. For (100) direction, the DOS is much larger than those in (110) and





(111) direction. More specifically, it is about 79.2 a.u. in (100) direction while for (110) and (111) directions they are 34.5 a.u. and 22.2 a.u., respectively. This gives a theoretical evidence about the more conductive state of (001) oriented films. And according to experiment results, (001) oriented films have a much lower tc than (110) and (111) oriented films. Since the DOS of (110) oriented films are more conductive than (111) oriented films, (110) oriented films are more conductive than (111) oriented films. Those theoretical calculations are in good agreement with experimental results, meanwhile indicating the DOS near fermi level is at the root of different conductive behaviour for different oriented films.

It is also worthwhile to note that the states near fermi level is mainly contributed by p orbitals for all cases, indicating that porbitals play a significant role in determining interface conducting behaviour. Recalling the charge transfer configuration of Fig. 3, charge transfer between STO and LNO happens mainly through O atoms. Thus it is nature to come to the conclusion that O 2p orbitals play an important role in determining interface DOS near fermi level or further in determining its conductivity. As frequently reported, O 2p orbitals are often the bridge for charge transfer among oxide heterostructures.

On the basis of the above experimental observations and calculation, a possible scenario regarding the interfacial charge transfer can be established. The prerequisite of the Fermi energy continuity at the interface suggests the possible energy alignment, as shown in Fig. 5(a). Ti⁴⁺ possesses an t_{2g}^{0} electron configuration, while Ni³⁺ ions preserve an $t_{2g}^{6}e_{g}^{1}$ electron configuration with nearly degenerate e_{g} band. When it comes to interfacial coupling, strong hybridization between Ni $3z^{2}-r^{2}$ band and the Ti d_{xz} or d_{yz} orbits at the interface would form the lower energy bonding (B) orbits and antibonding (AB) orbits. That is, extended molecular orbits consist of atomic Ni $3z^{2} - r^{2}$ orbits and Ti d_{xz} or d_{yz} orbits with an admixture



FIG. 4. Calculated density of states (DOS) and correspondent ground states of LNO growing on different orientations of STO. (a) (100) direction; (b) (110) direction; (c) (111) direction. The total DOS is illustrated with black lines while the projected DOS contributed by s p d orbitals are colored by red, blue and purple, respectively.

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FIG. 5. (a) Schematic of covalent bond at the interface of STO and LNO. (b) Schematic of the interface between STO and LNO.

of the p_z orbits on the apical oxygen. In this scenario, the electrons are transferred from the degenerate band to the molecular $3z^2-r^2$ orbits at the interface, as sketched in Fig. 5(a). In other words, the electrons at the molecular obits are possessed both by STO and LNO, which naturally lowers the valence state of Ti⁴⁺ to Ti³⁺, i.e. electrondoped SrTiO₃ at the interface. As indicated by the 2DEGs at the interface of LAO/STO, electron-doped STO has some metallic conductive behavior, which will contribute to the overall conductivity of our heterostructure. As for LNO as a hole conductive films,⁶ less electron transferred means more hole for conducting.

Thus, it is easy to explain the different conductive behavior for films grown along different orientations. For (001) oriented films, more electrons are transferred from LNO to STO, with electron doped STO being conductive and hole doped LNO being more conductive compared with other oriented films. (110)-oriented films have less electrons transferred from LNO to STO, thus being less conductive. (111)-oriented films have the least electron transfer and is the most insulting one. Our results are similar to the reported different conductive behavior of different oriented LAO on STO substrates.7 However, our case is somewhat different. LNO is a conductor itself, the hole doping level of which will influence the overall conductivity in addition to the conductive interface, and thus display a more significant difference among different oriented films. In LAO/STO system, LAO is an insulator with only the interface being conductive. Here, in our heterostructures, parallel conductive model is applied since both interfacial electron doped STO and the overlayer LNO will make a contribution to the overall conductivity. (001) oriented films with more electron transferred not only possess a more conductive hole doped LNO film but also with the interfacial electron doped STO, which also contributes to the overall conductivity. (110) oriented films with less electron transferred surely has less conductive LNO and interfacial STO, being less conductive. And (111) oriented films with the least electron transferred is the most insulting one of the three oriented films.

One question worth noting is why different oriented films have different charge transfer. Rajesh V. Chopdekar observed orientation dependence magnetization at the La_{0.7}Sr_{0.3}MnO₃/STO interfaces and regarded crystal surface orientation as well as epitaxial strain play an important role in tailoring their properties.²⁰ The theoretical calculation by N. Sivadas indicates both electronic reconstruction and polar distortions must be taken into account when analyzing the 2DEG behavior for (111) and (110) interfaces.²¹ In the polar catastrophe scheme, the (110) case has no charge transfer at the interface. As suggested by our theoretical calculations, charge transfer take places regardless of substrate orientation, excluding polar catastrophe. Thus the tailoring of transport behavior of different oriented films is a matter concerning crystal surface orientation, electronic reconstruction, strain state and polar distortion, which may be independently responsible for charge transfer at the interface. Or rather, the combined effect of those factors causes charge transfer at the interface. The exact determination needs further systematical characterization.

To summarize, different charge transfer on different oriented substrates may have different effect both on LNO films and interfacial layer. For (001) oriented films, strong charge transfer makes LNO more conductive and the largest of DOS of the interfacial layer; For (110) oriented films, charge transfer is not so strong as that on (001) oriented films, bringing about less conductive LNO films and lower DOS and eventually less conductive. For (111) oriented films, charge transfer effect is the least with the smallest DOS at the interface. In other words, substrate orientation has tailored the MIT transition of LNO film. Our work gives both experimental and theoretical proof of substrate induced conductive behavior of LNO films.

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