

# Chemical strain-dependent two-dimensional transport at $\text{RAIO}_3/\text{SrTiO}_3$ interfaces ( $R = \text{La, Nd, Sm, and Gd}$ )

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Perovskite  $\text{RAIO}_3$  ( $R = \text{La, Nd, Sm, and Gd}$ ) films have been deposited epitaxially on (001)  $\text{TiO}_2$ -terminated  $\text{SrTiO}_3$  substrates. It is observed that the two-dimensional transport characteristics at the  $\text{RAIO}_3/\text{SrTiO}_3$  interfaces are very sensitive to the species of rare-earth element, that is to *chemical* strain. Although electron energy loss spectroscopy measurements show that electron transfer occurs in all the four polar/nonpolar heterostructures, the amount of electrons transferred across  $\text{SmAlO}_3/\text{SrTiO}_3$  and  $\text{GdAlO}_3/\text{SrTiO}_3$  interfaces are much less than those across  $\text{LaAlO}_3/\text{SrTiO}_3$  and  $\text{NdAlO}_3/\text{SrTiO}_3$  interfaces. First-principles calculations reveal the competition between ionic polarization and electronic polarization in the polar layers in compensating the build-in polarization due to the polar discontinuity at the interface. In particular, a large ionic polarization is found in  $\text{SmAlO}_3/\text{SrTiO}_3$  and  $\text{GdAlO}_3/\text{SrTiO}_3$  systems (which experience the largest tensile epitaxial strain), hence reducing the amount of electrons transferred.

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In the last decade, emerging phenomena in complex oxide heterostructures have attracted great interest [1]. For example, a two-dimensional electron gas (2DEG) has been observed on the interface of two insulating oxides,  $\text{LaAlO}_3$  (LaAO) and  $\text{SrTiO}_3$  (STO) [2]. A variety of intriguing properties on the LaAO/STO interface, such as superconductivity [3,4], magnetoresistance [5,6], ferromagnetism [7–9], and even electromechanical responses [10], have been reported, providing opportunities for the development of future oxide electronic devices. For instance, Cen *et al.* demonstrated a field effect device using the LaAO/STO channel [11,12]. Nonvolatile memory functions have been observed in this kind of field effect device by using a ferroelectric gate [13,14] or surface charge injection [15]. Furthermore, surface charges and chemical adsorbates have been found to have a significant influence on the two-dimensional transport [16,17]. Sensors for polar molecules and gas detectors have been achieved based on this effect [18,19].

Although the transport characteristics of metallic LaAO/STO interfaces have been studied theoretically and experimentally for years [2,3,20,21], the physical origin of the interface conductivity is still under debate [22]. It has originally been ascribed to “polar catastrophe” on the LaAO/STO polar/nonpolar interface [23]. However, electron doping by oxygen vacancies in STO [24–26], cation intermixing across the interface [27], and nonstoichiometry in LaAO [28,29] have also been used to explain the 2-dimensional transport on the LaAO/STO interface. In the “polar catastrophe” scenario, the electrostatic energy increases with the increase of LaAO thickness, due to the interface polar discontinuity [23]. This imposes a transfer of electrons from the LaAO layer into the empty conduction band of the STO substrate when the LaAO

thickness is above 4 unit cells (u.c.) [2,23]. However, Hamann *et al.* pointed out that ionic reconstruction (polar lattice distortion) may relieve the electrostatic energy accumulation and retard the electron reconstruction [30,31]. Therefore strain, which couples with ionic polar distortions, may play an important role on the interfacial reconstruction, and hence, the two-dimensional transport—as, e.g., evidenced by the fact that the LaAO/STO interface is insulating under tensile strain [32].

In this study, we systemically investigate the effect of chemical strain (i.e., different rare-earth elements) on the two-dimensional transport at the interface of  $\text{RAIO}_3$  ( $\text{RAO}$ ,  $R = \text{La, Nd, Sm, and Gd}$ ) and  $\text{TiO}_2$ -terminated STO. All RAO materials are band insulators in bulk [33]. Similar to LaAO/STO, all of the other three RAO/STO heterostructures can also be regarded as an alternate stacking of charged  $(\text{RO})^+$  and  $(\text{AlO}_2)^-$  on neutral  $(\text{TiO}_2)^0$  and  $(\text{SrO})^0$  layers. According to the polar catastrophe scenario, electron transfer should occur at all these four polar/nonpolar interfaces. However, we observe that electrons transferred into interfacial Ti 3d orbitals in  $\text{SmAO/STO}$  and  $\text{GdAO/STO}$  are less than those in  $\text{LaAO/STO}$  and  $\text{NdAO/STO}$ . First-principles calculations reveal that chemical strain has a great impact on lattice distortions in the polar overlayer, which influences the electrostatic energy accumulated and the amount of electrons transferred.

The RAO layers were deposited on  $\text{TiO}_2$ -terminated (001) STO substrates by pulsed laser deposition monitored *in situ* by reflective high energy electron diffraction (RHEED). The (001) STO substrates were treated by etching with buffered hydrofluoric acid in an ultrasonic bath, followed by annealing in flowing  $\text{O}_2$  at  $950^\circ\text{C}$  for 60 min, similar to the procedure described by Koster and coworkers [34]. Laser ablation was performed using the 248-nm radiation from a KrF excimer laser (Compex Pro 205 F, Coherent) at a repetition rate of 2 Hz. The laser energy density on the RAO ceramic target was estimated as about  $1.8 \sim 2.2 \text{ J/cm}^2$ . During deposition,

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the substrate temperature and the oxygen chamber pressure were maintained at 750 °C and  $10^{-3}$  mbar, respectively. The thickness of RAO was controlled by counting the intensity oscillations of the specular spot in the RHEED pattern. High-resolution x-ray diffraction (XRD) was performed at BL14B1 beam line of Shanghai Synchrotron Radiation Facility. The surface morphology of the heterostructures was checked by an Asylum Research Cypher-ES atomic force microscope (AFM). Cross-sectional specimens for transmission electron microscopy were prepared by “lift-out” using a focused ion beam system (Helios, FEI). Scanning transmission electron microscopy (STEM) images, collected using a high-angle annular dark field detector, and electron energy loss spectroscopy (EELS) characterizations were performed using a probe aberration-corrected Hitachi HD2700C dedicated STEM operating at 200 kV, with a nominal spatial resolution of 0.9 Å. Transport properties were measured with a Quantum Design physical property measurement system (PPMS-9) in Van der Pauw geometry through aluminum electrical contacts to the RAO/STO interface, achieved by direct wire bonding (7476D, West Bond). Interface sheet carrier density was obtained from Hall measurement by scanning a magnetic field from  $-0.2$  to  $0.2$  T then back to  $-0.2$  T.

The surface of RAO films show a clear step-and-terrace structure. XRD patterns recorded around the (002) reflection of STO substrates show only (002) diffraction peaks from the RAO layers with thickness fringes. Cross-sectional STEM images show atomically abrupt interfaces in all the samples, in absence of interfacial dislocations. EELS line scans across the RAO/STO interfaces show that the transmission layers in RAO/STO are less than 1 nm. These results demonstrate the high quality of RAO/STO epitaxy [35].

Figure 1(a) shows the sheet resistance as a function of temperature for LaAO/STO, NdAO/STO, SmAO/STO, and GdAO/STO interfaces, in which all the RAO overlayers are of 10 u.c. in thickness. It is clear that both LaAO/STO and NdAO/STO heterostructures exhibit room-temperature metallic interfaces with the sheet resistance decreasing with decreasing temperature. The sheet resistance of the two metallic interfaces shows a slight upturn at low temperatures, which may be ascribed to variable range hopping transport due to carrier localization [36]. For the NdAO/STO interface, the larger tensile strain may cause a stronger localization, which limits the carrier mobility and thus results in the clear low-temperature resistance upturn observed. Hall coefficients obtained from these two metallic interfaces are negative, revealing that the dominant carriers at both interfaces are electrons. This is consistent with previous reports for LaAO and NdAO deposited on  $\text{TiO}_2$ -terminated STO substrates [21,36]. The mobility and density of the interfacial electrons are shown in Fig. 1(b). The values of carrier mobility and sheet carrier density at 7 K are  $2.9 \times 10^{13} \text{ e/cm}^2$  and  $520 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for LaAO/STO and  $1.5 \times 10^{13} \text{ e/cm}^2$  and  $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for NdAO/STO, similar to those reported previously [21,36]. In contrast, the two interfaces with heavier A site rare-earth elements in the aluminate overlayer, SmAO/STO, and GdAO/STO, are both insulating. As shown in Fig. 1(a), the sheet resistances are 5–6 orders higher than those of metallic LaAO/STO and NdAO/STO interfaces at room temperature and increases rapidly with decreasing temperature

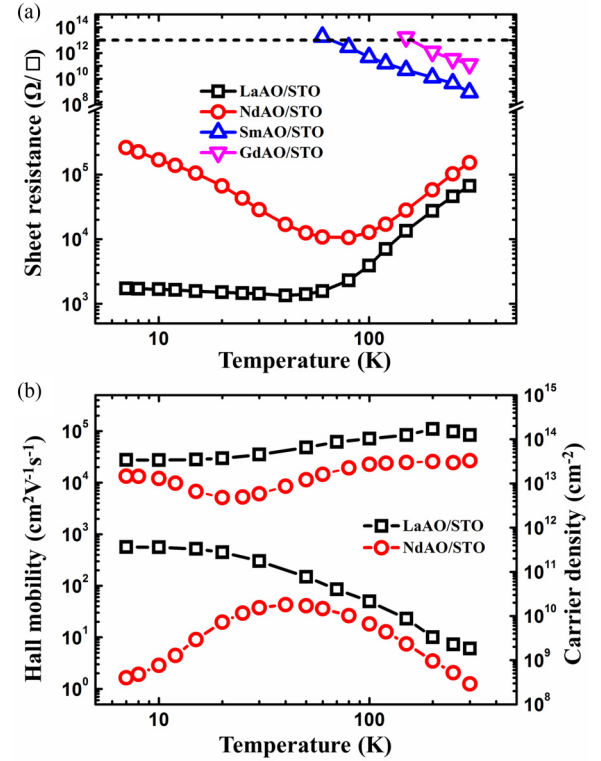


FIG. 1. (a) Temperature dependence of interface sheet resistance of 10 u.c. RAO/STO samples. (b) Carrier mobility and sheet carrier density of 10 u.c. LaAO/STO and NdAO/STO samples as functions of temperature.

to values beyond the measurement capability of our facilities ( $\sim 10^{13} \Omega/\square$ ).

According to the polar catastrophe scenario [2], all the RAO/STO interfaces might be metallic because electrons should be transferred into the empty Ti 3d orbitals at the interface to avoid the dispersion of electrostatic potential as a result of interface polar discontinuity. To explain the difference in RAO/STO interfacial transport characteristics, we then probe the filling of Ti 3d orbitals using subtle changes in the fine structure of the EELS Ti  $-L_{2,3}$  edge as an indicator. Abbate *et al.* [37] observed, in soft x-ray absorption spectra, that the valley between Ti  $2p_{1/2} \rightarrow 3d_{t_{2g}}$  and Ti  $2p_{1/2} \rightarrow 3d_{e_g}$  components vanishes as more and more electrons are doped into Ti 3d orbitals. Verbeeck *et al.* [38] have observed a reduction of the valley in LaAO/STO heterostructures by comparing the spectrum acquired well within the STO substrate with the one acquired from the interface. Figure 2 shows the Ti- $L_{2,3}$  EELS spectra collected from atomic layers across the RAO/STO interface. Regarding the STEM image of GdAO/STO in Fig. 2(e) as an example, the number labeled on each spectrum indicates the distance of the atomic layer from the interface, which is labeled with “0.” Spectra with negative numbers are taken from inside the STO substrate and those with positive numbers are taken from within the RAO overlayer. For all the four RAO/STO heterostructures, there is a clear valley between the Ti  $2p_{1/2} \rightarrow 3d_{t_{2g}}$  and Ti  $2p_{1/2} \rightarrow 3d_{e_g}$  components inside the STO substrate. This is consistent with the empty Ti 3d orbitals

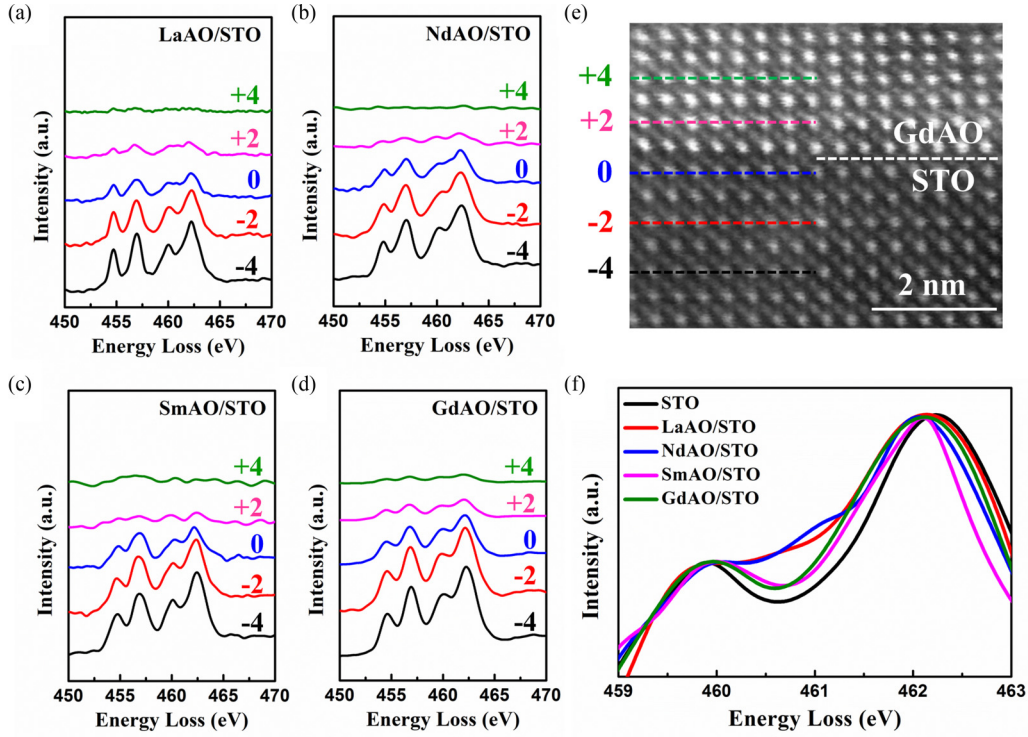


FIG. 2. EELS spectrum of Ti- $L_{2,3}$  edge of (a) LaAO/STO, (b) NdAO/STO, (c) SmAO/STO, and (d) GdAO/STO samples. The number labeled on each spectrum indicates the distance of the atomic layer from the interface, which is labeled with “0,” as indicated in the STEM image of GdAO/STO interface as an example in (e). (f) Normalized EELS spectra of Ti- $L_{2,3}$  at the interface layer of these four RAO/STO heterostructures and the STO substrate.

in STO. For LaAO/STO and NdAO/STO interfaces, as shown in Figs. 2(a) and 2(b) respectively, the valley reduces as the electron probe approaches close to the interface from the STO side. This indicates the filling of Ti 3d orbitals. However, for SmAO/STO and GdAO/STO interfaces, as shown in Figs. 2(c) and 2(d), respectively, clear valleys can still be observed in the spectra taken from the interface. Comparison of the normalized EELS fine structure of these four RAO/STO heterostructures are shown in Fig. 2(f). It is clear that, compared with LaAO/STO and NdAO/STO interfaces, Ti 3d spectra acquired from SmAO/STO and GdAO/STO interfaces are closer to that acquired from STO interior. The electron reconstruction, which moves electrons from the O 2p orbitals in the polar overlayers into the interfacial Ti 3d orbitals [21,39], occurs in SmAO/STO and GdAO/STO. However, the transferred electrons are less than those in LaAO/STO and NdAO/STO interfaces. The Ti -  $L_{2,3}$  core level shift to lower energy is also an indicator of the reduced Ti ions. It is indeed observed. In LaAO/STO and NdAO/STO, the spectra acquired from interfacial Ti is shifted about 0.4 ~ 0.5 eV from those inside the STO substrate, while the shift is only 0.1 ~ 0.2 eV in SmAO/STO and GdAO/STO [35]. This again indicates that less electrons are transferred in the latter case. Comparisons between EELS spectra of O-K edges acquired from inside the STO substrate and from various RAO/STO interfaces lead to the same conclusion [35].

Let us try to understand these effects. For that, it is important to reiterate that, in RAO/STO heterostructures, RAO layers contain oppositely charged  $(RO)^{+1}$  and  $(AlO_2)^{-1}$  layers [40,41]. This yields a build-in polarization  $P_{RAO}^0 = e/2a^2$  in

RAO layers along the [001] direction, where  $a$  is the in-plane lattice constant and  $e$  the electronic charge. In contrast, the build-in polarization is zero in STO substrate because of neutral  $(SrO)^0$  and  $(TiO_2)^0$  layers. Polarization in the two sides of the heterointerfaces is discontinuous. As discussed in the literature,[39,40], this polarization discontinuity between the STO and RAO layers can be compensated by two different mechanisms that are not mutually exclusive: (1) electrons on the RAO surface may transfer to the RAO/STO interface, which is usually coined as an electronic reconstruction and that provides a charge density denoted as  $\sigma^e$  here in the interface; and (2) the RAO layers may adopt ionic distortions, which generates a polarization along the growth direction, termed as  $P^i$ , which can be estimated from the Born effective charge tensor and the atomic displacements [35]. As a result, we have

$$P_{RAO}^0 = \frac{e}{2a^2} = \sigma^e + P^i. \quad (1)$$

$\sigma^e$  and  $P^i$  are competitive mechanisms to compensate the build-in polarization  $P_{RAO}^0$ . In one limit,  $\sigma^e = 0$  (no electrons are transferred from the surface to the interface), the ionic polarization  $P^i$  fully compensates the built-in polarization  $P_{RAO}^0$ . This happens when the number of RAO layers  $n \leq 3$ , as reported in both experiments and first-principles calculations for the insulating LaAO/STO interface [31,39–43]. In the opposite limit of infinite RAO thickness,  $\sigma^e = P_{RAO}^0 = e/2a^2$  (corresponding to a metallic interface with an interfacial carrier density of  $3.3 \times 10^{14} \text{ e/cm}^2$ ), and there is no polar ionic distortion in RAO layers. With the increase of A-site atomic number, the lattice mismatch between RAO and STO increases



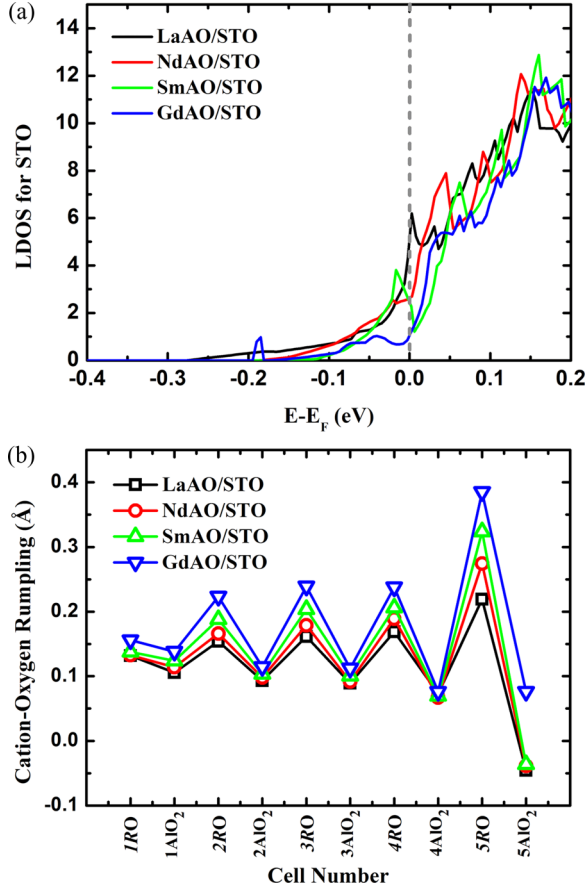


FIG. 3. (a) Local density of states in the interface STO layers and (b) cation-oxygen rumpling in RAO layers in  $(\text{RAO})_5/(\text{STO})_9$  heterostructures.

from 2.9% in LaAO/STO to 4.5% in GdAO/STO. The large epitaxial strain in ultrathin SmAO and GdAO overlayers may have a great impact on the lattice distortion and  $P^i$ , and hence, on  $\sigma^e$ , the density of electrons transferred [44].

In order to determine the amount of electronic reconstruction and polar ionic polarization in RAO/STO heterostructures,  $(\text{RAO})_5/(\text{STO})_9$  model heterostructures are investigated in the framework of first-principles calculations [35]. RAO/STO heterostructures with thinner RAO layers were also studied. It is observed that the interfaces are metallic when RAO is thicker than 3 u.c. for  $R = \text{La, Nd, and Sm}$  and 4 u.c. for  $R = \text{Gd}$ . We focus on  $(\text{RAO})_5/(\text{STO})_9$  for the calculations because transport measurements generate identical results on  $(\text{RAO})_{10}/\text{STO}$  and  $(\text{RAO})_5/\text{STO}$  heterostructures. The details of the model heterostructures and calculation parameters can be found in Ref. [35]. Figure 3 reports the local density of states (LDOS) of STO layers and the cation-oxygen rumpling in RAO layers in  $(\text{RAO})_5/(\text{STO})_9$ . As shown in Fig. 3(a), electron transfer from the RAO surface to the RAO/STO interface occurs in all the four RAO/STO heterostructures. The resulted  $\sigma^e$  can be computed by summing up the LDOS on all the atoms of STO integrated from the conduction band minimum up to the Fermi energy. As shown in Fig. 3(b), all the RAO layers show distinct cation-oxygen rumpling, indicating obviously ionic compensation to the built-in polarization  $P_{\text{RAO}}^0$  due to the polar discontinuity at the interface [41].

TABLE I. Interfacial electron density  $\sigma$  (in  $\text{e}/\text{\AA}^2$ ), ionic polarization  $P^i$  (in  $\text{e}/\text{\AA}^2$ ) in RAO layers, average out-of-plane lattice constant  $c$  (in  $\text{\AA}$ ) in RAO layers of the  $(\text{RAO})_5/(\text{STO})_9$  heterostructures.  $\Delta$  represents the potential (in eV) across the RAO layers.

$(\text{RAO})_5/(\text{STO})_9$	LaAO	NdAO	SmAO	GdAO
$\sigma^e$	0.110	0.092	0.078	0.045
$P^i$	0.295	0.330	0.370	0.429
$c$	3.766	3.681	3.649	3.627
$\Delta$	2.84	3.11	3.24	3.54

Table I summarizes the interface electron density  $\sigma^e$ , the ionic polarization  $P^i$  and average out-of-plane lattice constant  $c$  of RAO in RAO/STO heterostructures obtained from first-principles calculations. It is clear that  $\sigma^e$  decreases with  $R$  going from La to Gd (with increasing tensile strain in polar RAO overlayers). The carrier densities, derived from first-principles calculations, for LaAO/STO ( $0.110\text{e}/\text{\AA}^2 = 7.2 \times 10^{13} \text{ e}/\text{cm}^2$ ) and NdAO/STO ( $0.092\text{e}/\text{\AA}^2 = 6.1 \times 10^{13} \text{ e}/\text{cm}^2$ ) are close to the values measured experimentally (see Fig. 1). Furthermore, the computed transferred electrons in SmAO/STO and GdAO/STO are much less than those in LaAO/STO and NdAO/STO, in agreement with EELS results in Fig. 2. Bark *et al.* [32] pointed out that a large tensile strain may result in defects in LaAO/STO heterostructures, and these defects, as reported, may limit the electron mobility at LaAO/STO interfaces [40,45]. Therefore defects formed due to the large tensile strain in SmAO/STO and GdAO/STO interfaces may play a role on the insulating behavior observed.

Interestingly and as shown in Table I, the ionic polarization  $P^i$  increases with  $R$  going from La to Gd, as the tensile strain in polar RAO overlayers increases (note that the  $P^i$  may be underestimated by the calculated Born effective charge tensor). This is in drastic contrast with cases of typical (001) ferroelectric films, such as  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ , and  $\text{BiFeO}_3$ , in which the out-of-plane polarization decreases with the increase of tensile strain [46–49]. To further understand this increase of  $P^i$  in  $(\text{RAO})_5/(\text{STO})_9$ , it is informative to recall that one can also write that  $P^i = \epsilon_0 \epsilon_r E$ , where  $\epsilon_r$  is the dielectric constant and  $E$  is the electric field within the RAO layers. For all the  $(\text{RAO})_5/(\text{STO})_9$  supercell we considered, the RAO thickness (5 u.c.) is larger than the critical thickness for charge transfer. Therefore  $E$  decreases as a function of RAO thickness, according to  $E = \frac{\Delta}{nce}$  [40], where  $n$  is the number of u.c. layers along the growth direction of RAO and  $\Delta$  is the energy difference between the valence band of RAO and the conduction band of STO—which is also the potential across the RAO layers in RAO/STO, as well as the difference between the band gap of STO and the band offset between STO and RAO. As a result, one has

$$P^i = \frac{\epsilon_0 \epsilon_r \Delta}{nce}. \quad (2)$$

Table I reports the values of  $\Delta$ , as obtained by subtracting the band offset between STO and RAO (as computed from first principles) from the experimental band gap of STO, for the  $(\text{RAO})_5/(\text{STO})_9$  heterostructures that we considered. One can see that  $\Delta$  increases when  $R$  goes from La to Gd, which, along with the concomitant decrease of  $c$ , explains the increase

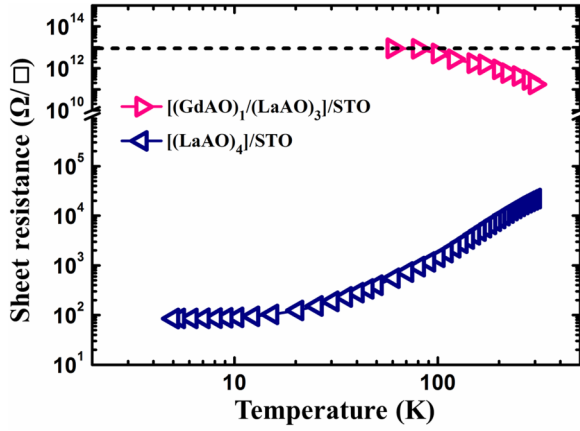


FIG. 4. Two-dimensional transport characteristics of  $[(\text{GdAO})_1/(\text{LaAO})_3]/\text{STO}$  and  $[(\text{LaAO})_4]/\text{STO}$  heterostructures.

of  $P^i$  in RAO, with  $R$  going from La to Gd—since  $\epsilon_r$  is rather similar in the different RAO materials [33,50].

Moreover, it is well known that the LaAO/STO interface is metallic only when the LaAO layer thickness exceeds a critical value, 4 u.c. in most reports [11,51]. As shown in Fig. 4, the 4 u.c. LaAO/STO interface is metallic. However, when the top u.c. of the LAO layer is replaced by a u.c. of GdAO, the interface becomes insulating. The large strain in the GdAO layer induces a large ionic rumpling. Therefore the ionic polarization  $P^i$  in the  $(\text{GdAO})_1/(\text{LaAO})_3$  composite polar overlayer is stronger than that in  $(\text{LaAO})_4$ . The large ionic compensation to the build-in polarization retards the electron transfer in the  $[(\text{GdAO})_1/(\text{LaAO})_3]/\text{STO}$  interface. To further verify the chemical strain effect on the interfacial electronic reconstruction,  $(\text{La}_{0.5}\text{Gd}_{0.5})\text{AlO}_3$  (LaGdAO) thin films, 10 u.c. in thickness, were deposited on STO and the 2-dimensional transport characteristics of the LaGdAO/STO interface were measured. The lattice constant of LaGdAO is about 3.77 Å, very close to that of NdAO (3.76 Å) [35]. Figure 5 shows the sheet resistance, carrier density and mobility of the LaGdAO/STO and NdAO/STO interfaces as functions of temperature. As expected, the transport characteristics of LaGdAO/STO interface is identical to those of NdAO/STO interface, as a result of similar epitaxial strain in LaGdAO and NdAO polar overlayers.

In summary, a series of RAO ( $R = \text{La}, \text{Nd}, \text{Sm}, \text{and Gd}$ ) thin films, 10 u.c. in thickness, have been deposited on  $\text{TiO}_2$ -terminated STO substrates. It is observed that LaAO/STO and NdAO/STO interfaces are metallic, whereas SmAO/STO and GdAO/STO interfaces are insulating. TEM characterizations reveal that less electrons are transferred into interfacial Ti 3d orbitals in SmAO/STO and GdAO/STO heterostructures, although electron transfer occurs in all the four interfaces. First-principles calculations demonstrate that the ionic polarization increases with increasing  $R$  atomic

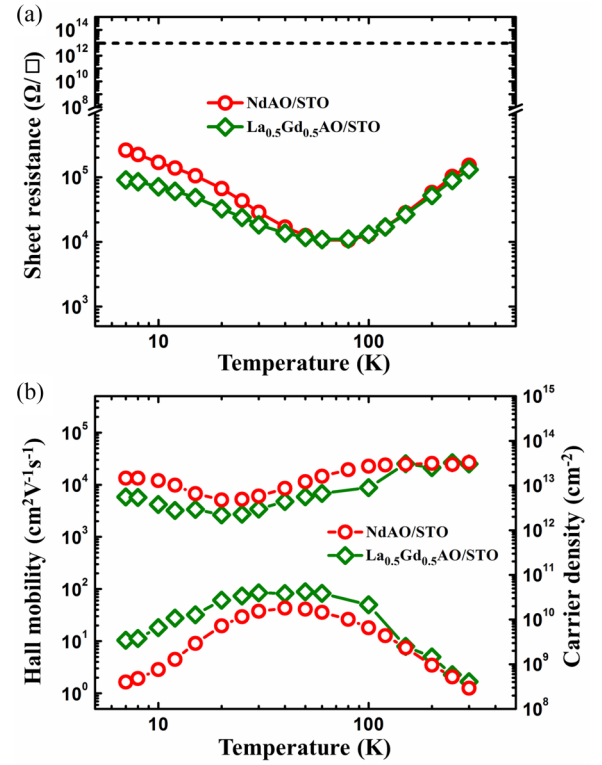


FIG. 5. Sheet resistance (a) and carrier mobility and sheet carrier density (b) of the 10 u.c. LaGdAO/STO interface as functions of temperature, compared with those of the NdAO/STO interface.

number in the polar layer. As a consequence, the large ionic compensation to the build-in polarization reduces the amount of electron transferred. The insulating behavior in SmAO/STO and GdAO/STO interfaces may be ascribed to carrier localization or defect scattering. Our results demonstrate, and explain why, chemical strain is an additional and novel handle in the control of properties at the interface of complex oxides.

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