Introduction

The conducting interface between two insulating perovskite materials LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) has aroused great interest from researchers since Ohtomo and Hwang discovered it in 2004.\textsuperscript{1–11} The LaAlO$_3$/SrTiO$_3$ (LAO/STO) heterointerface has exhibited many unexpected properties such as superconductivity,\textsuperscript{2–5} magnetism,\textsuperscript{6–8} disorder and localization ground states,\textsuperscript{9,10} and Rashba spin–orbit interaction etc.\textsuperscript{11,14} Although the origins of this conducting interface were debated between different groups,\textsuperscript{15} the so called ‘polarization catastrophe’ theory is widely recognized by most researchers.\textsuperscript{1,14,17} This theory suggests that the discontinuity of the polarization between the polarized layer structure LAO (with sub-layers AlO$_2$ -/LaO$^+$) and non-polarized layer structure STO (with sub-layers TiO$_2$/SrO) at the interface could induce the charge transfer from LAO to STO, which should cause the conduction. It successfully explained the phenomenon that a minimum thickness of 4 unit cells (u.c.) LAO layers was required to induce the conduction. In addition to this theory, oxygen vacancies, interfacial strain and atomic mixing were also proposed to possibly induce the interface conductance.\textsuperscript{18–21} Furthermore, an enhancement of charge carrier density was found by doping LaTiO$_3$ layers into the interface.\textsuperscript{24,25} The transport properties can be also modified by doping LAO with magnetic elements.\textsuperscript{26}

Magnetotransport studies have revealed that the magnetism of LAO/STO originated from the interface between non-magnetic LAO and STO.\textsuperscript{8} The origination of magnetism is unknown yet. Quantum properties such as weak localization, Kondo effect and weak anti-localization have been studied under low temperature.\textsuperscript{4–11} and the intrinsic mechanisms are always associated with the electron–electron scattering, electron-local magnetic moment scattering, spin-orbital scattering etc. Disorder and localization play the important roles in these quantum effects at low temperature.

The previous investigations mainly focused on the ground state of the heterostructure to seek for the quantum properties
near the temperature of absolute zero. Under such a purpose researchers only concerned with the heterointerface during cooling, not the inverse warming process. STO exhibits structure transition from cubic to tetragonal phase at around 105 K during cooling. The structure transition of STO leads the abundant structure domain on STO surface. Kalisky and Molet et al. used superconducting quantum interference device (SQUID) to measure the localized magnetic field, and found the domain structure strongly modified the local conductivity, which showed as the current intensity increases along the domain walls. Roy and Klein et al. also found the current-induced nonuniform enhancement of sheet resistance due to the interaction between domain walls and oxygen vacancies in STO. Erlich et al. confirmed the channel behavior of conductivity by using the polarized light microscopy technology. Ma et al. carried out SEM imaging at low temperature and found that the ferroelectric can be induced within the twin walls in STO beyond the critical electrical field. However the above works yield no results on transport properties. To understand the role of domain structure, it needs to consider the transport properties influenced by the domain structure and how the LAO layers affect the domain structure.

In this work, we focused on the electrical transport and magnetic properties during warming process after cooling to 2 K. Temperature dependent transport, magnetoresistance and magnetization properties were measured for different thicknesses of LAO films grown on STO for both cooling and warming.

**Experiment details**

The LaAlO$_3$ thin films in this work were grown on TiO$_2$ terminated (100) SrTiO$_3$ substrate in 10$^{-3}$ mbar pressure of O$_2$ and at 1073 K using pulsed laser deposition technique. To control the thickness with sub-u.c. precision, film growth was monitored in situ using reflection high energy electron diffraction (RHEED). The samples were kept in the O$_2$ atmosphere when cooling to room temperature. The Scanning Electron Microscope (SEM, Hitachi S-4800) with energy dispersive spectroscopy (EDS) was used for elemental mapping. The results of La, Al and O elemental mapping images are shown in Fig. S1† which indicates the successful formation of LAO film. The X-ray photoelectron spectroscopy (XPS) was measured using ESCALAB 250 from Thermo-VG Scientific. The XPS results are displayed in Fig. S2.† The Al 2p, O 1s and La 3d peaks can be seen in the figure. No shift of the peaks is observed, which reveal no change of chemical state.

X-ray diffraction and reciprocal space mapping (RSM) with Cu-Kz radiation (Rigaku, TTR III) was used for characterization of film growth. The STO (311) and LAO (311) planes were chosen for RSM measurement. Transport properties were tested using physical property measurement system (PPMS) from Quantum Design Company with a typical four wire electrode in the length scale of several mm which plunges into the interface. The resistance is measured through a cycle of cooling and warming between 300 K and 2 K. Magnetic properties were tested using magnetic property measurement system (MPMS) through cooling and warming between 300 K and 2 K with a field of 0.01 T.

**Results and discussion**

Fig. 1(a) is the schematic diagram for the heterostructure of LaAlO$_3$ on (TiO$_2$)$_0$ terminated SrTiO$_3$. The perovskite oxides LaAlO$_3$ and SrTiO$_3$ show similar layer structure with lattice constants 3.789 Å and 3.905 Å, respectively. The SrTiO$_3$...
consisted of two non-polar sublayers, \((\text{SrO})^0\) and \((\text{TiO}_2)^0\), while 
\(\text{LaAlO}_3\) is formed by two polar sublayers, \((\text{LaO})^+\) and \((\text{AlO}_2)^-\). 

Fig. 1(b) presents the XRD patterns for LAO/STO films with 
thickness of 7, 15 and 25 layers (also unit cells), respectively. 
The patterns around (100) of LAO indicate that LAO layers are 
epitaxially grown on the STO single crystal substrate along the 
(100) orientation. The LAO (100) diffraction peak shows a clear 
shift to lower angle with the increasing thickness, which reveals 
the lattice strain gradually releases. Fig. 1(c) shows the small 
angle X-ray reflection (XRR) for all the prepared LAO/STO thin 
films. It can be seen from XRR results that the period of finite 
size Fresnel oscillation around the diffraction peak varies with 
the thickness of LAO film. This permits us to determine the 
thickness by using the well-known Bragg equation: 
\[2d \sin \theta = n \lambda,\]

where \(d\) and \(\lambda\) stand for thickness of LAO thin film and 
wavelength of X-ray, respectively. We also calculated the thickness 
of the as-prepared LAO/STO samples remarked by the 
number of unit cells (u.c.) “\(n\)” obtained by RHEED intensity 
oscillations and the bulk lattice constant of 0.38 nm of LAO, the 
thickness was estimated to be \(n \times 0.38\) nm. Our calculated 
values are consistent with the XRR results as presented in 
Table 1.

The reciprocal space mapping (RSM) technique is employed 
to study the interfacial strain dynamics with increasing thick-
ness of LAO/STO film. The (311) planes of both LAO and STO 
were chosen for the observation of both in-plane (0LL) and out-
of-plane (H00) information. Fig. 1(d–f) display the RSM images 
for the prepared LAO/STO epitaxial films. These results allow us 
to calibrate the LAO lattice constants comparing with standard 
single-crystal STO substrate, the outcomes are shown in Table 1. 

As for the 7 u.c. layers of LAO film, the (0LL) in-plane direction 
shows no obvious difference from the substrate, suggesting the 
growth is in the plan lattice parameters similar to the substrate 
and can be considered as fully strained. Furthermore, the LAO 
(H00) out-of-plane direction shows a broad diffraction profile 
for this ultrathin film, which confirms the formation of highly 
strained interface between substrate and epitaxial film. When 
the number of LAO layers increases, the diffraction profiles of 
LAO and STO gradually separate each other. This indicates the 
formation of a gradually relaxed interface. Quantitative calcula-
tion results also exhibit such changeover in Table 1. So the 
RSM results clearly reveal that the LAO/STO interface strain 
varies from fully strained state to a partial strained state with 
the increasing layers of LAO film.

Fig. 2 is the transport properties of the interfaces between 
different LAO layers and STO substrate. The resistance is tested 
against temperature for both cooling and warming. During 
warming up, two anomalies in \(R-T\) curves are found for 15 u.c. 
and 25 u.c. samples. The resistance temporally deviates the 
rising trend at 80 K and 176 K. Within a little temperature 
region about 5 K, the conductivity is enhanced and then 
decreased. The two inflection points indicate that the sample 
undergoes a conductivity accelerating recovering (CAR) process.

Table 1  \(\text{LaAlO}_3\) thickness and lattice constants derived from XRR and 
RSM measurement results

<table>
<thead>
<tr>
<th>Theoretical thickness</th>
<th>XRR results</th>
<th>RSM: out-of-plane</th>
<th>RSM: in-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 u.c.</td>
<td>2.66 nm</td>
<td>2.94 nm</td>
<td>3.734 Å</td>
</tr>
<tr>
<td>15 u.c.</td>
<td>5.70 nm</td>
<td>6.61 nm</td>
<td>3.745 Å</td>
</tr>
<tr>
<td>25 u.c.</td>
<td>9.50 nm</td>
<td>10.13 nm</td>
<td>3.746 Å</td>
</tr>
</tbody>
</table>
As observed in Fig. 2(a), the two deviations are more obvious for more layers of LAO/STO. The derivative curves of resistance are shown in Fig. 2(b). It can be seen that the two derivative valleys always appear at the same temperatures for different samples, which shows high stability. Similar anomalies have also been observed in the patterned LAO/STO and STO samples with the length scale of several μm.\textsuperscript{28,32,33} The anomalies presenting in these references significantly enhance when the sample length decreases to nm scale, the previous works considered that the anomalies could only occur in several u.c. layers LAO/STO samples with length scale of micron.\textsuperscript{34} The small scale limited the wide application from the anomaly property. Contrary to the previous conclusion, in our current work the anomalies can also appear in large length scale of several mm with increasing the number of LAO layers. Because this two novel points are of the precise temperature interval it provides a potential temperature standard reference in the region of low temperature based on its resistance measurement and can be widely applied due to its larger scale.

Minhas et al.\textsuperscript{34} made nano-patterned 6 u.c. layers LAO/STO samples and observed giant resistance anomaly. The anomaly is explained as the current, which flows along the domain wall, is interrupted near the structure transition region of STO. However the theory comes to a conclusion that the anomalies cannot appear for large scale sample, which suggests more mechanisms need to be introduced. The domain wall can be generated by the structure transition from cubic to tetragonal at 105 K for STO during cooling. It is clear that the carriers such oxygen vacancies were firstly trapped in the vicinity of the domain wall with the further cooling. The two recoveries correspond to two times of release for the carriers. Seri et al.\textsuperscript{35} determined the two trapping energy barriers $E_{b1}$ and $E_{b2}$ from less than 10 μm patterned 4 u.c. LAO/STO sample. Roy et al.\textsuperscript{28} also found two accelerated conductivity recoveries in Ar$^+$-irradiated SrTiO$_3$. They considered that the two trapping energy barriers perfectly match the migrating energies of oxygen single vacancies and divacancies. At low temperature, comparing to the current of 40 μA in Seri group’s work, the larger current of 8 mA in this work strongly polarized the domain walls, which attract the vacancies around the domain walls. The trapped single-vacancies and divacancies become mobile above 80 K and 176 K, which yields the conductivity recovery, separately. The reported cases\textsuperscript{28,32-34} are the patterned few layers LAO/STO in the length scale less than 10 μm, which means the interface is fully strained. When the number of LAO layers increases, the sample changes from fully strained state to partial strained state. The vertical strain gradient of the sample increases and leads to the longitudinal diffusion of the domain and furtherly expands the network of the domain in plane and enlarges the domain formation area. The larger domain area and deep diffusion of the domain makes the accelerated recoveries of conductivity more obviously observed in the current case. It is worth emphasizing that preparation condition also plays the key role in observing the CAR. Ariando et al.\textsuperscript{7} also made the 10 u.c. LAO/STO sample in length scale of several mm, however they did not observe the CAR in the resistance curves. The electronic phase formation of 2-dimension electron gas in the interface is greatly affected by the oxygen pressure, the annealing temperature and other detail factors in the preparing process.

In the cryogenic region, the resistance shows the abnormal rising behavior with decreasing temperature as seen in Fig. 2(a). This behavior is attributed to the spin scattering of the conducting electrons interacting with localized magnetic moments at the interface.\textsuperscript{4-6} The temperature dependence of resistance is helpful to understand the nature of the scattering. The $R$-$T$ curves for 7 u.c. and 15 u.c. samples are in logarithmic relationship and can be described well by:

$$R_s = a \ln \left( \frac{T}{T_{C18}} \right) + bT^2 + cT^5,$$

where first term of right side stands for the contribution of Kondo effect, $T^2$ and $T^5$ terms are response to electron-electron and electron-phonon scatterings, respectively.\textsuperscript{4} The fitting for 15 u.c. sample is shown in Fig. 2(c). The logarithmic curve is dominated by Kondo effect from the interaction between conducting carriers and localized magnetic moment. The experimental curve is found to be saturation at around 5 K as seen in inset of Fig. 2(c). We consider that this is the contribution of weak anti-localization induced by spin-orbital scattering, which is discussed in the following part. This is worth mentioning that the Kondo temperature ($T_{C18}$) is shifting towards lower values as the thickness of the LAO thin film increases, in the current work they are 26 K for 15 u.c. LAO and 20 K for 7 u.c. LAO as pointed out in Fig. 2(a), separately. As for sample with 25 u.c. layers, its resistance shows a reverse trend and decreases with the further cooling below 25 K. Its temperature derivative of resistance reveals the conducting fluctuation below 40 K.

To test the magnetic behavior of the LAO/STO heterostructure, the magnetization measurement was carried out in the temperature range between room temperature and 2 K under the magnetic field of 0.01 T, as shown in Fig. 3. As the LAO and STO are both diamagnetic perovskites, the fascinating feature of this measurement is the low temperature diamagnetic to paramagnetic transition for 7 u.c. and 15 u.c. samples. The magnetization is almost a straight platform and with the negative value at high temperature, shows the diamagnetic property. Below a critical temperature, the magnetization value start to increase and then with a sharp increase, which shows an upturn and becomes positive. The similar trend is also observed for the 25 u.c. sample, but negative magnetization exists for whole temperature. This conclusion is different with Ariando’s work.\textsuperscript{7} Ariando et al. found the ferromagnetic phase exists in LAO/STO for whole temperature range. This distinction reveals the important pole of preparing conditions again. To analysis the measured magnetization curves, we divide the contribution of the magnetization into two terms, the paramagnetic term and diamagnetic term.

The results are fitted using the following formula:

$$M = \frac{C}{T} + M_d,$$

the first term is the contribution of paramagnetic while the second one is response to the diamagnetic term. The fitting results are shown in Fig. 3(a). The fitting curves are in good agreement with the experiment results, which demonstrate that the samples are coexistence of paramagnetic and diamagnetic in whole temperature region.
cooling and warming magnetization curves shows no obvious
difference. The relative content of paramagnetic and diamag-
netic is shown in Fig. 3(b). With the increasing of LAO layers,
the paramagnetic ratio increase and the diamagnetic ratio
decrease. The corresponding fitting parameters are shown as
insets of (b-1) and (b-2) in Fig. 3. The value of diamagnetic term
and the paramagnetic coefficient both decrease with increasing
the layers of LAO. The larger paramagnetic contribution
induces the higher Kondo temperature as seen in Fig. 2(a) and
description in the paragraph above.

The resistances below CAR point of 80 K obviously separate
during warming up for 15 u.c. LAO/STO sample with applied
magnetic field of 0 T and 9 T as seen in Fig. 4(a). Below 80 K, the
trapped single oxygen vacancies and oxygen divacancies along
the polarized domain walls are localized and carriers are
dominated by a few of electrons. Under applied magnetic field
the cyclotron precession lengthens the electron path and lifts
the resistance. Above 80 K, the trapped vacancies are gradually
released, dominate the carriers and recombine with the con-
ducting electrons at low temperature. Because the larger effec-
tive mass and smaller mobile velocities of vacancies only induce
the tiny cyclotron precessional path, the difference of resistance
between non-applied field and applied field can be ignored
above 80 K, as seen in Fig. 4(a). Fig. 4(b) presents the magne-

toresistance at different temperature during warming for 15 u.c.
LAO/STO sample. The result is clear that the magnetoresistance
shows ordinary positive value, and decreases with temperature
increasing from 20 K. It is worth mention that the magnetore-
sistance at 2 K shows clearly two segment distribution, which is
known as the weak anti-localization phenomenon. At the
condition of low temperature and low
field, there exists the
relation of \( \tau_\phi > \tau_B > \tau_{SO} \) (the terms are the relaxation time of
electron–phonon scattering, magnetic field and spin-orbital
scattering, respectively), therefore the main contribution is
spin-orbital scattering. When the field increases and leads to \( \tau_\phi \approx \tau_{SO} \) or the temperature increase and makes \( \tau_\phi \approx \tau_{SO} \), the
spin-orbital contribution for resistance could disappear, and
electron–phonon scattering take places. This also contributes to
the saturation of logarithmic term of transport result as
mention above.

**Conclusion**

The temperature dependent transport and magnetization of
LAO/STO with 7, 15 and 25 u.c. layers of LAO were investigated
during cooling and warming. The conductivity accelerated
recoveries were observed at 80 K and 176 K for the large electrode area of several mm, which are induced by the oxygen single vacancy and divacancy trapped by the polarized domain walls become mobile at these temperatures. The recoveries are found to be more obvious for more layers LAO sample, which is attributed that the domain walls diffuse along longitudinal direction and expand larger network with increasing vertical strain gradient. The strain modified domain provides a novel method tuning the CAR effect and related transport properties. Due to the stable and precise temperature interval and large scale device, the CAR may provide a potential widely applied application devices of LAO/STO.

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Conflict of interest

There are no conflicts to declare.

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References


