Supporting Information

Tuning irreversible magnetoresistance in Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ film via octahedral rotation

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Outline

S1. Crystal structure
S2. Demagnetization process
S3. Transport properties of film on STO substrate
S4. Transport properties of film on LSAT and NGO substrate
S5. First principle simulation
S6. Angular dependence XMCD at different temperatures
S7. Magnetic properties of different thickness
S8. Terahertz measurement
S1. Crystal structure

Figure S1-1: L scan (a-c) around (002) and reciprocal space mapping (d-f) around (-103) for 12 nm, 20 nm and 30 nm PSMO films on (001) STO substrate, respectively.

Figure S1-1 shows the X-ray diffraction of \( L \) scan around the (002) peak and reciprocal space mapping (RSM) around the (-103) peak for PSMO films on (001) STO substrate. For \( L \) scan, thickness fringes appear due to the interference of scattering at sample surface and STO/PSMO interface, indicating the flat sample surface and STO/PSMO interface. The thickness of all these films calculated from the thickness fringe is close to nominal thickness based on the deposition rate. The RSM shows that the in-plane lattice constant of all films is clamped by the STO substrate with \( a = b = 3.905 \) Å, and no strain relaxion occurs. The out-of-plane lattice constant from the \( L \) scan is \( c = 3.803 \) Å, 3.802 Å and 3.800 Å, for 12 nm, 20 nm and 30 nm PSMO films, respectively. The error bar is ±0.002 Å. This weak change of out-of-plane lattice constant is insufficient to explain the large difference in materials properties. From the position of (002), (-103) and (013) peaks, the PSMO films on STO substrate are tetragonal with \( \alpha = \beta = \gamma = 90^\circ \) with error bar of ±0.5° for all films. Due to the cubic structure of STO substrate with equivalent in-plane \( a, b \) axis, the RSM (013) is not shown here. The relative
wide range of H comes from the twin structure of STO substrate. Datum for 12 nm PSMO are retrieved from Ref. 29.

Figure S1-2: L scan and reciprocal space mapping for 12 nm film on (110) STO (a, d, g), (001) LSAT (b, e, h), and (110 NGO) (c, f, i) substrates.

Figure S1-2 shows the X-ray diffraction for PSMO films on (110) STO, (001) LSAT, and (110) NGO, respectively. For films on (110) STO substrate, thickness fringes appear in L scan around the (002) peak, indicating flat sample surface and film/substrate interface, and was used to verify the film thickness. The RSM shows that the in-plane lattice constants along the two directions are fully clamped by the STO substrate, suggesting coherent epitaxial growth. For film on LSAT and NGO substrate, the (002) peak of PSMO film in L scan is not obvious due to the close lattice constant between film and substrate. However, thickness fringes still appear due to good film quality. Similarly, the RSM for these two films around pseudocubic (-
103) and (013) peaks also largely overlap with substrate, indicating coherent epitaxial growth. The relative wide range of H comes from the twin structure of STO substrate. Datum for PSMO film on NGO substrate are retrieved from Ref. 29.
S2. Demagnetization process

Figure S2: the magnetization signal for 12 nm film on (001) STO substrate with damping magnetic field at 10 K. This process is to verify that the film was demagnetized well during MR measurement with damping magnetic field, as shown in Fig. 1a. Please note that the Y-axis is the net moment value of the whole film, which indicates the direct signal of demagnetization process, rather than the magnetization.
S3. Transport properties of film on STO substrate

Figure S3-1: The Resistivity-temperature curve, measured during warming process without magnetic field, for (a) 20 nm film, (b) 30 nm film on (001) STO, and (c) 12 nm film on (110) STO after ZFC and 70 kOe FC from room temperature to 10 K.

Figure S3-2: Magnetoresistance curve for 12 nm film on (001) STO measured at (a) 10 K, and (b) 200 K. The sample was cooled down to targeted temperature under zero field from room temperature. See text for more discussion.
S4. Transport properties of film on LSAT and NGO substrate

Figure S4: the Resistivity-temperature curve, measured during warming process without magnetic field, for 12 nm film on (a) (001) LSAT, (b) (110) NGO substrate after ZFC and 70 kOe FC from room temperature to 10 K. See text for more discussion.
S5. First principle simulation

Figure S5-1: The site-projected DOS of Mn $e_g$ and O 2p orbitals in the 1st MnO$_2$ layer, in case of without and with TiO$_6$ octahedral rotation in SrTiO$_3$ substrate.

The site-projected density of states (DOS) is shown in Fig. S5-1. In case of no octahedral rotation, the overlap of O2p major orbital and Mn $e_g$ major orbital is larger than that with octahedral rotation in STO substrate. The stronger hybridization between O and Mn could enhance the exchange coupling intensity, which would increase the electron mobility and the magnetic moment. In Fig. 4(d), the band width of 3$d_{z^2}$ orbital around the Fermi level for PSMO on STO with octahedral rotation $a^0a^0a^0$ is narrower than that on STO without octahedral rotation $a^0a^0a^0$. In addition, the hybridization between O 2p orbitals and Mn $e_g$ orbitals is also suppressed for the PSMO film on STO with octahedral rotation, as indicated by the less overlap between the O 2p and Mn $e_g$ major orbitals. According to the exchange coupling, the band width is directly proportional to the exchange intensity. The enhanced octahedral rotation angle at the interface weakens the ferromagnetic exchange intensity. Then the competition between the AFM superexchange interaction and the weakened FM interaction work together to align the spin moment, as suggested in recent experimental observation of modulated spin arrangement.
Figure S5-2: The simulated dependence of in-plane and out-of-plane bond angle on film thickness, with out-of-phase TiO$_6$ octahedral rotation around in-plane (a$^0a^0c^0$) and out-of-plane axis (a$^0c^0$). See text for discussion.
S6. Angular dependence XMCD at different temperatures

Figure S6-1 the Mn $L$ edge XMCD for 12 nm PSMO measured with different incident angles, at four different temperatures. Summarized in Fig. S5-3.

Figure S6-2 the Mn $L$ edge XMCD for 20 nm PSMO measured with different incident angles, at four different temperatures. Summarized in Fig. S5-3.
Figure S6-3 (a-c) the Mn $L$ edge XMCD for 12 nm PSMO measured with different incident angles, at different temperatures; the dependence of $A/B$ ratio on incident angle at different temperatures for (d) 30 nm, (e) 20 nm, and (f) 12 nm PSMO films on (001) STO substrate.

Figure S6-4 Calculated magnetic moment of three samples at 75 K according to the sum rules.

<table>
<thead>
<tr>
<th></th>
<th>12 nm</th>
<th>20 nm</th>
<th>30 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_5 (\mu_b)$</td>
<td>1.134±0.024</td>
<td>1.327±0.025</td>
<td>1.721±0.030</td>
</tr>
<tr>
<td>$\mu_4/\mu_5$</td>
<td>0.046</td>
<td>0.042</td>
<td>0.051</td>
</tr>
</tbody>
</table>

The full range Mn $L$ edge XMCD are shown in Figure S6. The magnetic moment could be calculated from the sum rules, and the calculated magnetic moment at different incident angles for the same sample at the same temperature is within the statistic error range. This
suggests that the angular dependence is not due to the magnetic anisotropy. The magnetic field is 5 T, which should be strong enough to saturate the sample in all directions. The comparison of the angular dependence on three samples, 12 nm, 20 nm, 30 nm are shown in Fig. S6-3 (d-f). For 30 nm film, the angular dependence is similar at different temperatures. However, in 12 nm film, the temperature has obvious effect on the angular dependence. At low temperature, the angular dependence behavior is enhanced in thin film. The comparison of thickness effect on angular dependence of XMCD is shown in Fig. 5(d), and discussed in the text.
S7. Magnetic properties of different thickness

Figure S7 The magnetization-temperature (MT) curves for (a) 20 nm, and (b) 30 nm film on (001) STO substrate, measured at 100 Oe after ZFC (dashed line) and 100 Oe FC (solid line) from room temperature. See text for more discussion.
S8. Terahertz measurement

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\tilde{c}$</th>
<th>$\omega_p/2\pi$ (THz)</th>
<th>$\tau$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-0.41</td>
<td>104</td>
<td>4.713</td>
</tr>
<tr>
<td>25</td>
<td>-0.45</td>
<td>150</td>
<td>4.731</td>
</tr>
<tr>
<td>50</td>
<td>-0.79</td>
<td>270</td>
<td>4.575</td>
</tr>
<tr>
<td>75</td>
<td>-0.99</td>
<td>241</td>
<td>4.539</td>
</tr>
<tr>
<td>90</td>
<td>-0.46</td>
<td>221</td>
<td>5.818</td>
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<tr>
<td>125</td>
<td>-0.39</td>
<td>153</td>
<td>6.617</td>
</tr>
<tr>
<td>175</td>
<td>-0.99</td>
<td>156</td>
<td>6.339</td>
</tr>
<tr>
<td>300</td>
<td>-0.98</td>
<td>78</td>
<td>5.759</td>
</tr>
</tbody>
</table>

Figure S8: The detailed parameters from THz data analysis.

In this study, low energy (4 meV) charge dynamics of PSMO thin film with 12 nm thickness under increasing temperature from 15 K to 300 K by Terahertz time-domain spectroscopy (THz-TDS). The frequency-dependent complex sheet conductivity $\sigma(\omega)$ can be obtained from the measured transmission spectra by the following equations:

\[
n(\omega) = \frac{c\phi(\omega)}{\omega d} + 1
\]

\[
\alpha(\omega) = \frac{2}{d} \ln \left( \frac{4n(\omega)}{E(\omega)\cdot[1+n(\omega)]^2} \right)
\]

\[
k = \frac{c\alpha}{2\omega d}
\]

\[
\epsilon(\omega) = \epsilon_r + i\epsilon_i, \quad \epsilon_r = n^2 - k^2, \quad \epsilon_i = 2nk
\]

\[
\tilde{\sigma}(\omega) = \sigma_r + i\sigma_i, \quad \sigma_r = \epsilon_0 \omega \epsilon_r, \quad \sigma_i = \epsilon_0 \omega (1 - \epsilon_r)
\]

where $\phi$ and $E$ are, respectively, the phase and amplitude of the THz signal, $\omega$ is its frequency, $c$ is the speed of light in vacuum, $d$ is the samples thickness and $k$ is the extinction coefficient. $\epsilon_r$ is real part of the dielectric, $\epsilon_i$ is imaginary part of the dielectric constant, $\epsilon_0 \approx 8.85 \times 10^{-12}$ F/m, $\sigma_r$ is the real part of the conductivity and $\sigma_i$ is the imaginary part of the conductivity. The refractive indices ($n$) and absorption coefficients ($\alpha$) of PSMO/STO samples can be obtained from equation (1) and (2). Equation (5) allows us to determine the frequency-dependent real and imaginary parts of the complex film conductivity $\sigma(\omega)$ from our transmission measurements. In the strongly correlated systems, Drude-Smith model was utilized to describe the carriers undergoing the restricted motion, possibly resulting from the spin fluctuations and
phonons in the strained manganite.\textsuperscript{61-62} As a phenomenological extension of the Drude mode, the Drude-Smith model, incorporating the effect of incomplete randomization of carrier momentum after scattering events, was used to describe our results.\textsuperscript{61} Only accounting the first scattering term,\textsuperscript{63} the complex conductivity is given by

\[
\tilde{\sigma}(\omega) = \frac{\varepsilon \omega_p^2 \tau}{1 - i\omega \tau} \left[ 1 + \frac{\tau}{(1 - i\omega \tau)} \right]
\]

where \( \omega_p \) is the plasma frequency, \( \tau \) is the scattering relaxation time, \( c \) describes the persistence of the carrier’s initial velocity after one scattering event. The fitted results are shown in Figure S8, and see text for discussion.