Revealing the role of interfacial heterogeneous nucleation in metastable thin film growth of rare-earth nickelates electronic transition materials

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Section 1: The XRD pattern for SNO/STO

Fig. S1. X-ray diffraction pattern (θ-2θ scans) of as-grown SmNiO$_3$/SrTiO$_3$(001) thin film from 20°-80° under 15MPa annealing oxygen pressure. (data from the reference $^1$)

Section 2: Reciprocal Space Mappings (RSM)

Fig. S2. Reciprocal space mappings of as-grown (a) SmNiO$_3$/SrTiO$_3$(001) (data from the reference $^1$), (b) SmNiO$_3$/LaAlO$_3$(001) (data from the reference $^1$), (c)
NdNiO$_3$/LaAlO$_3$(001) and (d) EuNiO$_3$/LaAlO$_3$(001) under 15MPa annealing oxygen pressures.

Section 3: XRD patterns at a broader scanning range for SNO/LAO, NNO/LAO, ENO/LAO and GNO/LAO

Fig. S3. X-ray diffraction patterns ($\theta$-2$\theta$ scans) of as-grown (a) SmNiO$_3$/LaAlO$_3$(001) (b) NdNiO$_3$/LaAlO$_3$(001) (c) EuNiO$_3$/LaAlO$_3$(001) and (d) GdNiO$_3$/LaAlO$_3$(001) thin films from 20°-80° under various annealing oxygen pressures.

Section 4: Transmission electron microscopy (TEM)
**Fig. S4.** The transmission electron microscopy (TEM) images of the interfacial regions of (a) SNO/LAO and (b) SNO/STO

**Section 5: Calculation of lattice strain of the a-axis and b-axis**

LaAlO$_3$ has rhombohedral structure, which is defined as pseudo-cubic symmetry in order to finish the calculation. As for SrTiO$_3$, it is cubic structure. Therefore, we adopted the LaAlO$_3$ and SrTiO$_3$ as cubic structure with relaxed lattice constants of $a_0=3.82$ Å and $a_0=3.96$ Å, respectively. The orientation relationships between the rare-earth thin films and substrates follow (001)$_{\text{film}}$//(001)$_{\text{substrate}}$, [100]$_{\text{film}}$//[110]$_{\text{substrate}}$.

According to this orientation relationship we built the interface supercells and set the reference lattice constants of interface structures as $b_0=5.40$ Å (LaAlO$_3$ interface) and $b_0=5.60$ Å (SrTiO$_3$ interface), respectively. The optimized lattice constants of rare-earth nickelates are listed in the following Table S1. And we calculated the lattice strain of a-axis and b-axis between rare-earth thin films and substrates using $\varepsilon_a=(a-b_0)/b_0$, $\varepsilon_b=(b-b_0)/b_0$. The obtained results are in the manuscript Table 1.

**Table S1**

|          | a         | b         |
|----------|-----------|-----------|
| SmNiO$_3$| 5.28753   | 5.44663   |
| NdNiO$_3$| 5.32534   | 5.46882   |
| EuNiO$_3$| 5.33896   | 5.35262   |
| GdNiO$_3$| 5.24442   | 5.51225   |

**Section 6: Interfacial charge transfer for other ReNiO$_3$ grown on LAO (001) and STO (001) substrates**
Fig. S5. The interfacial charge transfer of (a) LaAlO$_3$-NdNiO$_3$ interface (b) SrTiO$_3$-NdNiO$_3$ interface (c) LaAlO$_3$-EuNiO$_3$ interface (d) SrTiO$_3$-EuNiO$_3$ interface (e) LaAlO$_3$-GdNiO$_3$ interface (f) SrTiO$_3$-GdNiO$_3$ interface.

Section 7: Details about Mott variable range hopping model fitting low temperature $R$-$T$ curves of rare-earth nickelates

In this part, the process of how to use the Mott variable range hopping (VRH) model to fit the low temperature $R$-$T$ curves of rare-earth nickelates will be illustrated, from which we can obtain electrical parameters to describe the conduction mechanism at low temperature. The correlated formula is given by

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^p$$

(S1)
where $\rho_0$ is the prefactor, $T_0$ is the characteristic temperature which represents the degree of disorder in the film\(^4\), and $p$ is the exponent depended on the conduction mechanism which is related to the density of states (DOS) near Fermi energy ($E_F$). In the light of Mott\(^5\), when the DOS is constant, $p = 1/(1+D)$ where $D$ is the dimensionality of the conduction system, which shows in three dimensions, $p = 1/4$. Localized charge carriers near the Fermi level can hop from one localized state to another due to thermal fluctuation or an electrical field provided by external factors.

Fig. S6 shows the plots of $\ln \rho(T)$ versus $T^{0.25}$ from 100K to a certain temperature decided by two temperature values, metal-insulator transition temperature and 300K for $ReNiO_3$ ($Re$=Sm, Eu, Gd) thin films grown on LaAlO$_3$ (001) substrates annealing at various oxygen pressures.
Fig. S6. Plots of \( \ln(\rho_T) - T^{-0.25} \) for (a) SmNiO\(_3\) 0.1 MPa (b) SmNiO\(_3\) 4 MPa (c) SmNiO\(_3\) 15 MPa (d) EuNiO\(_3\) 0.1 MPa (e) EuNiO\(_3\) 4 MPa (f) EuNiO\(_3\) 8 MPa (g) EuNiO\(_3\) 15 MPa (h) GdNiO\(_3\) 0.1 MPa (i) GdNiO\(_3\) 4 MPa (j) GdNiO\(_3\) 8 MPa (k) GdNiO\(_3\) 15 MPa (data from reference 6) grown on LaAlO\(_3\)(001) substrates. Black lines are the linear
fitting curves.

According to eqn (S1), when $p=1/4$, the corresponding $T_0$ ($T_{\text{Mott}}$) for each condition can be obtained from the slope of the fitting curve in Fig.S6, which is listed in the Table S2. And according to the reference $^4$, the localization length can be further calculated by

$$T_0 \equiv T_{\text{Mott}} = \frac{18}{k_B N(E_F) a^3}$$  \hspace{1cm} (S2)

Where $N(E_F)$ is the DOS near the $E_F$ and $a$ is the localization length. We take $N(E_F) = 1.5 \times 10^{18}$ eV$^{-1}$cm$^{-3}$ $^5$. The calculated results of localization length $a$ are also tabulated in the Table S2. The room temperature ($T=300$ K) optimum average hopping energy ($W_h$) and hopping distance ($R_h$) for Mott-VRH model are estimated using the following expressions:

$$R_h = \left(\frac{9a}{8\pi k_B T N(E_F)}\right)^{1/4}$$ \hspace{1cm} (S3)

$$W_h = \frac{3}{4\pi R_h^3 N(E_F)}$$ \hspace{1cm} (S4)

In order to verify the validity of the fittings for Mott VRH in ReNiO$_3$ thin films, it is necessary to calculate the values of $R_h/a$ and $W_h/k_BT$ listed in the Table S2 as well. Clearly, the two criteria (1) $R_h/a>1$ and (2) $W_h/k_BT>1$ are satisfied, which proves the correctness of the fitting. As shown in Table S2, $T_{\text{Mott}}$ and localization length $a$ are found to be different for various annealing oxygen pressure, which means the annealing oxygen pressure has an influence on the film formation process. Nevertheless, it is worth noticing that the value of $W_h/k_BT$ is not obviously larger than 1 especially for the as-grown thin films at the low oxygen pressure. This phenomenon suggests the possible violation of VRH model. More details are in the corresponding manuscript.

### Table S2

Parameters of Mott-VRH hopping mechanism in the ReNiO$_3$ ($Re=$Sm, Eu, Gd) thins films at various oxygen pressures.

| Sample | $T_{\text{Mott}}$(K) | $a$(nm) | $T_{\text{max}}$(K) | $R_{\text{min}}$(nm) | $R_h/a$ | $W_h$(eV) | $W_h/k_BT$ |
|--------|-----------------|--------|-----------------|-----------------|--------|-----------|-------------|
| SNO 0.1 MPa | 2.35E+06 | 3.90  | 300  | 17.77 | 3.53  | 0.0609 | 2.36 |
| SNO 4 MPa | 2.44E+06 | 3.85  | 300  | 13.73 | 3.57  | 0.0615 | 2.38 |
| SNO 15 MPa | 1.65E+07 | 2.04  | 300  | 11.71 | 5.75  | 0.0991 | 3.83 |
| ENO 0.1 MPa | 5.60E+05 | 6.29  | 300  | 15.52 | 2.47  | 0.0425 | 1.64 |
| ENO 4 MPa | 1.09E+07 | 2.34  | 300  | 12.12 | 5.19  | 0.0894 | 3.46 |
| ENO 8 MPa | 3.63E+06 | 3.37  | 300  | 13.28 | 3.94  | 0.0679 | 2.63 |
| ENO 15 MPa | 1.58E+07 | 2.07  | 300  | 11.75 | 5.69  | 0.0981 | 3.79 |
| GNO 0.1 MPa | 1.47E+07 | 2.12  | 300  | 11.82 | 5.59  | 0.0963 | 3.73 |
| GNO 4 MPa | 1.22E+06 | 4.85  | 300  | 14.55 | 3.00  | 0.0517 | 2.00 |
| GNO 8 MPa | 8.08E+06 | 2.58  | 300  | 12.43 | 4.81  | 0.0829 | 3.21 |
GNO 15 MPa 1.20E+07 2.26 300 12.0 5.31 0.0915 3.54
Fig. S7. Plots of $\ln (\rho T^{-1/3})$ for (a) SmNiO$_3$ 0.1 MPa (b) SmNiO$_3$ 4 MPa (c) SmNiO$_3$ 15 MPa (d) EuNiO$_3$ 0.1 MPa (e) EuNiO$_3$ 4 MPa (f) EuNiO$_3$ 8 MPa (g) EuNiO$_3$ 15 MPa (h) GdNiO$_3$ 0.1 MPa (i) GdNiO$_3$ 4 MPa (j) GdNiO$_3$ 8 MPa (k) GdNiO$_3$ 15 MPa (data from reference 6) grown on LaAlO$_3$(001) substrates. Black lines are the linear
fitting curves.

Considering the thickness of as-grown ReNiO$_3$ thin films (about 10 nm), we also fit the \( \ln(\rho_T) \)-\( T \) tendencies via two-dimensional carrier transport model. For the situation of two dimensions, \( p=1/3 \). Using the similar method, the fitting plots of \( \ln(\rho_T) \)-\( T^{-1/3} \) for various ReNiO$_3$ can be obtained in Fig.S7. According to the reference 4, the localization can be obtained by

\[
T_0 \equiv T_{\text{Mott}} = \frac{13}{k_B N(E_F)a^2}
\]

(S5)

where \( N(E_F) \) is the DOS near the \( E_F \) and \( a \) is the localization length. The calculated results are listed in the Table S3.

In order to verify the correctness of the fits with the Mott VRH for ReNiO$_3$, we calculated the hopping distance \( R_h \) by formula (S6) and the average hopping energy \( W_h \) by formula (S7) to testify whether the two conditions \( R_h/a > 1 \) and \( W_h/(k_B T) > 1 \) are satisfied. The results are listed in the Table S3 as well.

\[
R_h = \left( \frac{9a}{8\pi k_B T N(E_F)} \right)^{1/3}
\]

(S6)

\[
W_h = \frac{3}{4\pi R_h^2 N(E_F)}
\]

(S7)

Table S3
Parameters of Mott-VRH hopping mechanism in the ReNiO$_3$(Re=Sm, Eu, Gd) thins films at various oxygen pressure.

| Sample | \( T_{\text{Mott}} \)(K) | \( a \)(nm) | \( T_{\text{max}} \)(K) | \( R_{\text{min}} \)(nm) | \( R_h/a \) | \( W_h \)(eV) | \( W_h/(k_B T) \) |
|--------|-----------------|---------|-----------------|-----------------|-------|-----------------|-----------------|
| SNO 0.1 MPa | 9.21E+04 | 0.010 | 300 | 0.021 | 2.04 | 0.0351 | 1.36 |
| SNO 4 MPa | 9.46E+04 | 0.010 | 300 | 0.021 | 2.06 | 0.0355 | 1.37 |
| SNO 15 MPa | 3.97E+05 | 0.005 | 300 | 0.017 | 3.32 | 0.0572 | 2.21 |
| ENO 0.1 MPa | 3.77E+04 | 0.016 | 300 | 0.025 | 1.51 | 0.0261 | 1.01 |
| ENO 4 MPa | 2.91E+05 | 0.006 | 300 | 0.018 | 2.99 | 0.0515 | 1.99 |
| ENO 8 MPa | 1.28E+05 | 0.009 | 300 | 0.020 | 2.27 | 0.0392 | 1.52 |
| ENO 15 MPa | 3.86E+05 | 0.005 | 300 | 0.017 | 3.28 | 0.0567 | 2.19 |
| GNO 0.1 MPa | 3.66E+05 | 0.013 | 300 | 0.017 | 3.22 | 0.0556 | 2.15 |
| GNO 4 MPa | 5.62E+04 | 0.007 | 300 | 0.023 | 1.72 | 0.0298 | 1.15 |
| GNO 8 MPa | 2.33E+05 | 0.006 | 300 | 0.018 | 2.78 | 0.0479 | 1.85 |
| GNO 15 MPa | 3.12E+05 | 2.26 | 300 | 0.017 | 3.06 | 0.0528 | 2.14 |

We can notice that although two conditions are satisfied, the values of \( W_h/(k_B T) \) for the as-grown thin films at low oxygen pressure are close to 1. This result suggests Mott VRH model is expected to be violated in such situation since oxygen vacancy donating electrons leads to the variation of the density of states around Fermi energy.
Section 8: XRD pattern and RSM for Nd$_{0.3}$Sm$_{0.4}$Gd$_{0.3}$NiO$_3$/LaAlO$_3$ (001)

![X-ray diffraction pattern](image)

Fig. S8. (a) X-ray diffraction pattern ($\theta$-2$\theta$ scans) and (b) Reciprocal space mapping of as-grown Nd$_{0.3}$Sm$_{0.4}$Gd$_{0.3}$NiO$_3$/LaAlO$_3$ (001)

Section 9: Estimation of parameters of $h$ and $s$ in molar Gibbs free energy of formation of bulk ReNiO$_3$

According to the reference 7, the molar Gibbs free energy of formation of bulk ReNiO$_3$ can be estimated from the following:

$$
\Delta G = \Delta H_{LNO,1000K} - T\Delta S_{LNO,1000K} + (h - sT)(r(Re^{3+}) - r(La^{3+})) - \frac{1}{4}RT\ln(P/p)
$$

where LNO stands for LaNiO$_3$, $T$ is the absolute temperature, $R$ is the ideal gas constant, the $P$ represents oxygen pressure with MPa unit, $p$ represents the standard atmospheric pressure (0.1MPa) and $r(Re^{3+})$ and $r(La^{3+})$ are the radii of $Re^{3+}$ and $La^{3+}$, respectively. According to the reference 8, the enthalpy and entropy changes for the formation of LaNiO$_3$ from oxides and O$_2$ at 1000K are $\Delta H_{LNO,1000K} = -46.07$kJmol$^{-1}$ and $\Delta S_{LNO,1000K} = -26.4 \times 10^3$kJK$^{-1}$mol$^{-1}$. $h$ and $s$ represent the trend in enthalpy and entropy with variation of ionic radii. They can be estimated from the following process. As mentioned in the reference 7, the value of $h$ is calculated using a statistically weighted averaged of linear slope from $\Delta G$ vs. $r(Re^{3+})$ for ReMnO$_3$, ReFeO$_3$ and ReCoO$_3$, which has been obtained that $h = -207$ kJmol$^{-1}$Å$^{-1}$. As a typical rare-earth nickelate perovskite, the synthesis conditions of SmNiO$_3$ have been widely investigated. And it is accepted that the molar Gibbs free energy of formation of bulk SmNiO$_3$ is zero at the lowest pressure for high temperature synthesis of SmNiO$_3$. And the lowest pressure for successful high temperature synthesis of SmNiO$_3$ is reported by Escote et al. (1273K, 70 bar) 9. This condition was further used to estimate the value of $s$. In addition, the radii of rare-earth elements are obtained from the reference 10. Based on these conditions, the value of $s$ is estimated as -0.00744 kJK$^{-1}$mol$^{-1}$Å$^{-1}$. It is clear that the value of $s$ is much smaller than the value of $h$, indicating our
assumption is effective.

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