Supplementary information

to

Epitaxial growth of perovskite oxide films facilitated by oxygen vacancies

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S1. Epitaxy and elastic relationships.

During epitaxial growth, a thin film of a material is formed on the top of a substrate, whose crystal symmetry and lattice parameters may differ from those of the material. Here, a cube-on-cube epitaxy of a cubic material (lattice parameter a_0) on a cubic substrate (lattice parameter a_{SUB}) is considered [Fig. S1(a)]. This case is valid for STO on LSAT. Because of the material-substrate mismatch in lattice parameters, the substrate imposes biaxial in-plane compressive stress on the material, whereas there is no out-of-plane stress [Fig. S1(b)]. For a coherent film, where the in-plane lattice parameters a equals to those of the underlying substrate, the substrate-imposed stress leads to a new out-of-plane lattice parameter c, which differs from a_0 in the material [Fig. S1(c)]. The lattice parameters, tetragonality, and unit-cell volume in the mechanically stressed (strained) film differ from those in the material and can be estimated as follows.

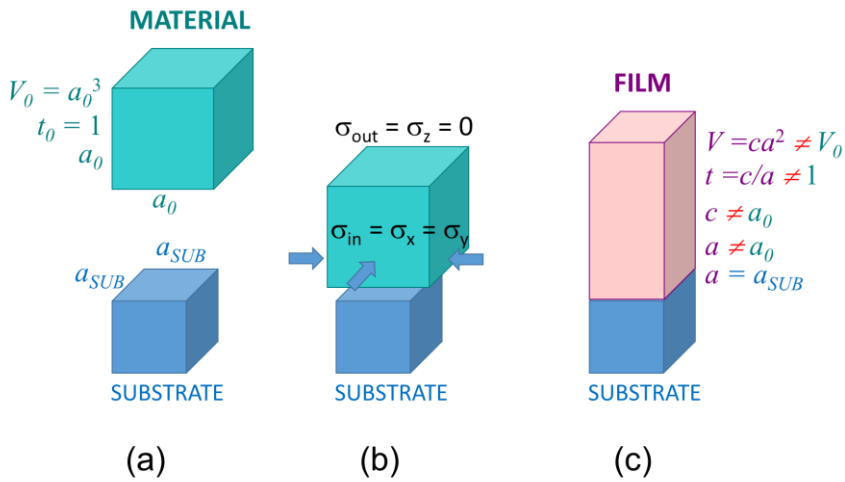

Fig. S1. Schematics of cube-on-cube epitaxy. (a) Unit cells of the material and substrate. (b) Substrate-imposed mechanical conditions. (c) Unit cell of the strained film.

The theoretical material-substrate misfit strain is

$$s_a = \frac{a_{SUB}}{a_0} - 1. \tag{1}$$

This strain is compressive, approximately -0.95 % for STO/LSAT: a_{SUB} = 3.868 Å and a_0 = 3.905 Å are the lattice parameters of LSAT and STO, respectively.

For the coherent strained cube-on-cube film [Fig. 1(c)], the in-plane lattice parameters are similar and equal to

$$a = b = a_{SUB} \tag{2}$$

The out-of-plane strain (s_c) and the out-of-plane lattice parameter (c) are elastically related to the in-plane strain (s_a):

$$s_c = -\frac{2c_{12}}{c_{11}} s_a \tag{3}$$

$$c = a_0(1 + s_c) = a_0\left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \quad . \tag{4}$$

The elastic constants of STO are $c_{11} = 3.48\times10^{11}$ N/m^2 and $c_{12} = 1.03 \times10^{11}$ N/m^2.
The unit-cell volume V and tetragonality t of the strained film are, correspondingly:

$$V = ca^2 = a_0^3(1 + s_a)^2\left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \quad , \tag{5}$$

$$t = \frac{c}{a} = \frac{\left(1-\frac{2c_{12}}{c_{11}}s_a\right)}{(1+s_a)} \quad . \tag{6}$$

The relationships (3-6) make it possible not only to calculate theoretical lattice parameters of the strained film, but also to perform reverse estimations. They allow for determining the lattice parameter a_0 of an unknown cubic material using the lattice parameters a and c, which are experimentally measured in the film made of such material. The strain s_a can be found from (6) and then the parameter a_0 can be calculated using (4) or (5).

S2. Pulsed laser deposition.

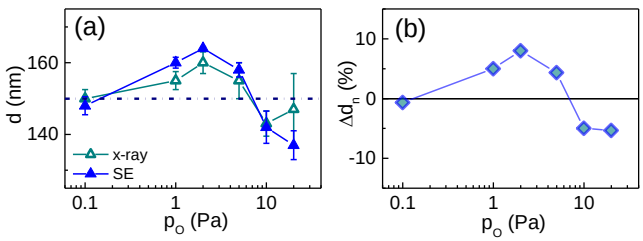

Fig. S2. Growth kinetics in pulsed laser deposition of STO. (a) Thickness and (b) thickness variation as a function of oxygen pressure. Data were obtained by x-ray reflectivity and/or by x-ray diffraction (from Laue satellites) and by spectroscopic ellipsometry (a). Data are averaged in (b).

S3. Crystal structure.

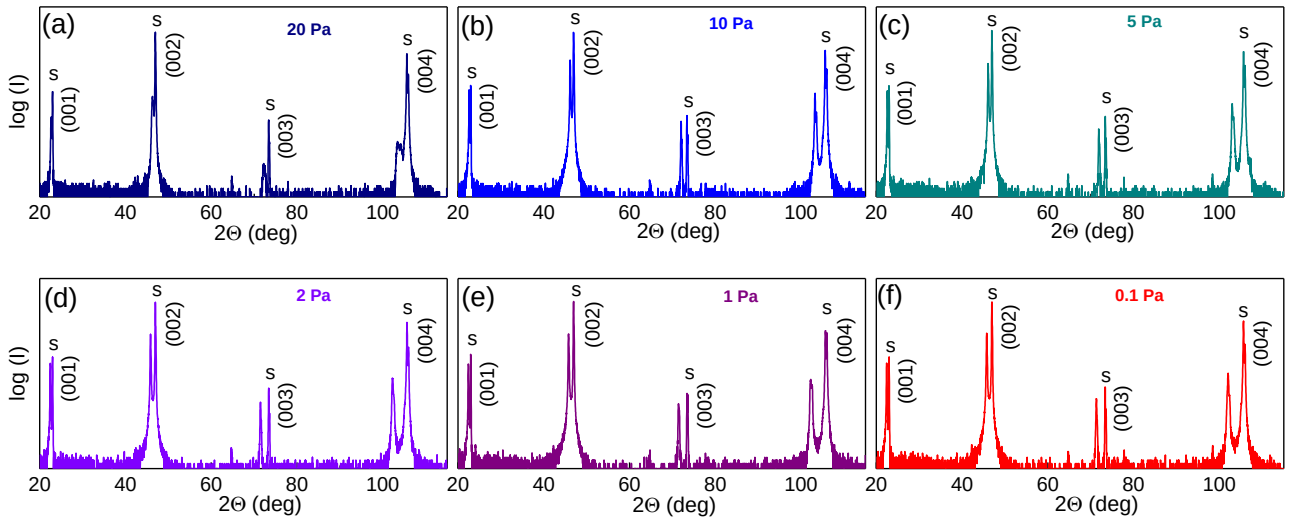

Fig. S3. XRD Θ-2Θ scans in the 150-nm-thick STO films on LSAT. Deposition pressure is marked on the plots.

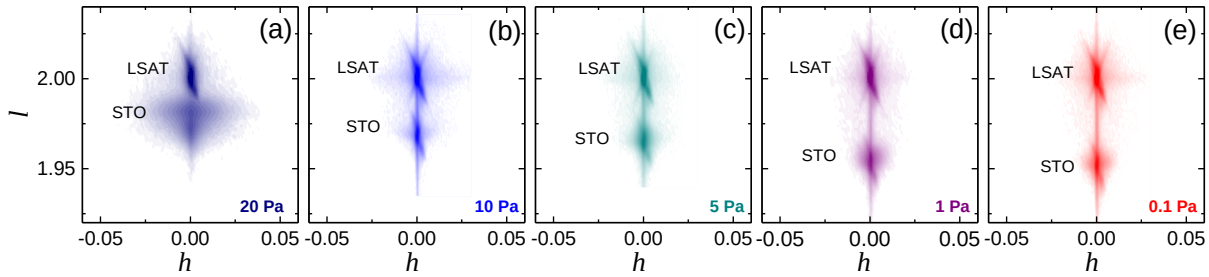

Fig. S4. Reciprocal space maps around (002) lattice points in the 150-nm-thick STO/LSAT films deposited at different pressures of oxygen. Coordinates are expressed in reciprocal lattice units of LSAT.

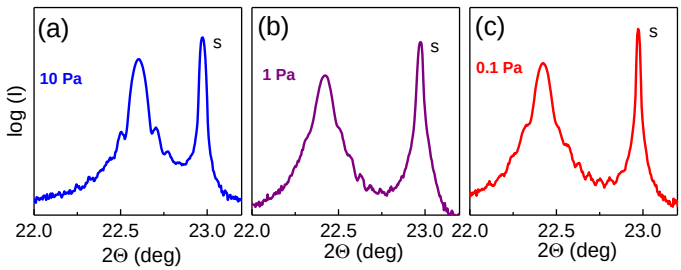

Fig. S5. Details of XRD Θ-2Θ scans around (001) perovskite peaks in the 150-nm-thick STO films on LSAT. Deposition pressure is marked on the plots. Laue satellites evidence smooth films of high crystal quality.

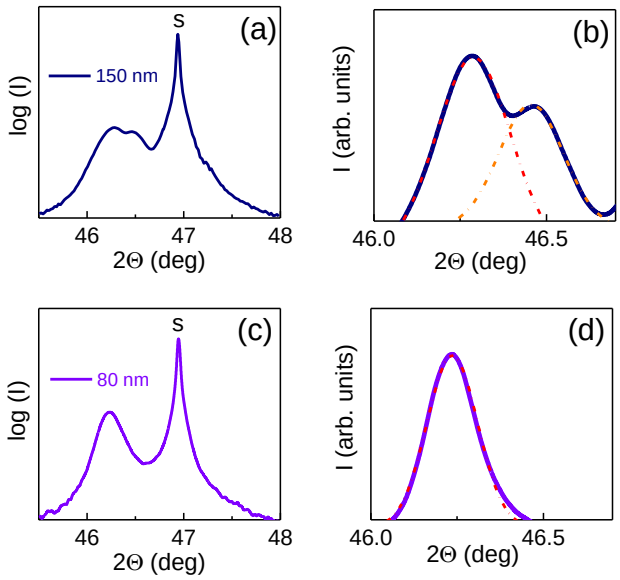

Fig. S6. XRD Θ-2Θ scans around (002) perovskite peaks in the (a, b) 150-nm-thick and (c, d) 80-nm-thick STO films on LSAT. Deposition pressure is 20 Pa. Strain relaxation is evidences by the two phases – strained and relaxed – in the 150-nm-thick film.

S4. Optical losses

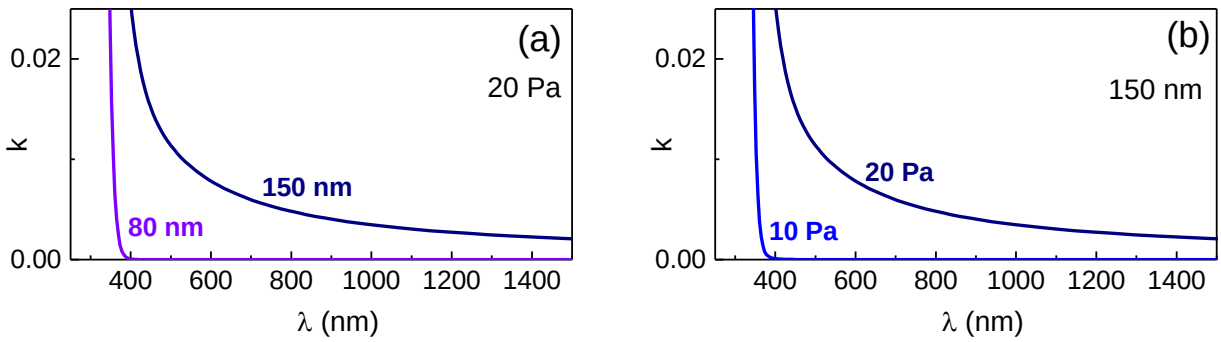

Fig. S7. Extinction coefficient as a function of wavelength in the (a) films of different thicknesses deposited at 20 Pa and (b) films of 150 nm in thickness deposited at different pressures.

S5. Anisotropic chemical expansion.

The unit cell of a material, from which the film is made, is assumed to be tetragonal with the lattice parameters (a_0, c_0), tetragonality (t_0), and unit-cell volume (V_0):

$$c_0 = t_0 a_0 \tag{7}$$

$$V_0 = t_0 a_0^3 = V_{STO} = (3.905\text{Å})^3 \tag{8}$$

The unit-cell volume in the film is V:

$$V = ca^2 = t_0 a_0^3 (1 + s_a)^2 \left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \tag{9}$$

$$\frac{V}{V_0} = (1 + s_a)^2 \left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \tag{10}$$

Or in another form:

$$\left(\frac{V}{V_{STO}} - 1\right) = \left(2 - \frac{2c_{12}}{c_{11}}\right) s_a + \left(1 - \frac{4c_{12}}{c_{11}}\right) s_a^2 - \frac{2c_{12}}{c_{11}} s_a^3 \tag{11}$$

Here, equation (11) was solved graphically for the strain s_a using the measured unit-cell volume of the films (V). Then the tetragonality of the material was calculated for each film:

$$t_0 = \frac{c(1+s_a)}{a\left(1 - \frac{2c_{12}}{c_{11}} s_a\right)} \tag{12}$$

S6. Tetragonal material.

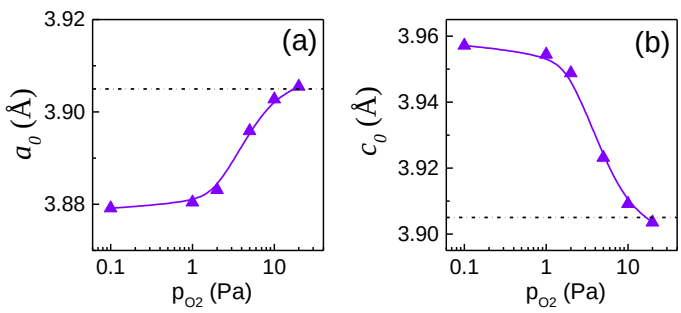

Fig. S8. Lattice parameters of unstressed tetragonal material estimated from the measured parameters of each of the films.

S7. First-principles analysis of elastic properties.

To demonstrate high accuracy of *ab initio* calculations, the lattice parameters of misfit-strained stoichiometric STO and the elastic constants of STO were calculated. The in-plane strain $\underline{s_a}$ = -0.95%, corresponding to the STO/LSAT misfit strain, was considered. The in-plane lattice parameters of the model cubic STO were reduced, respectively, and the out-of-plane parameter was optimized. The optimization gave the out-of-plane strain s_c = 0.0057, tetragonality t = 1.015, and relative change of the unit-cell volume ΔV = -1.33 %. These *ab initio* values are in excellent agreement with the theoretical macroscopic ones [see elastic relationships (1-6) above]. The calculated elastic constants $c_{11} = 3.83\times10^{11}$ N/m^2 and $c_{12} = 1.13\times10^{11}$ N/m^2 and the ratio c_{12}/c_{11} = 0.295 practically coincide with the tabulated data. Here, minor overestimation of elastic constants occurs because the calculations are performed for the temperature T = 0 K and the thermal expansion is consequently neglected.

S8. Interaction of oxygen vacancy stress with misfit strain.

For an oxygen vacancy in the (001)[SrO] plane, the interaction energy of the vacancy stress (described by elastic dipole tensor)[33] with the STO/LSAT misfit strain is

$$E^{int}(eV) = -\begin{bmatrix} 4.53 & 0 & 0 \\ 0 & -2.1 & 0 \\ 0 & 0 & -2.1 \end{bmatrix} \times \begin{bmatrix} 0.0056 \\ -0.0095 \\ -0.0095 \end{bmatrix} \approx -0.065 \quad . \tag{13}$$

For an oxygen vacancy in the (001)[TiO] plane, the interaction energy with the STO/LSAT misfit strain is

$$E^{int}(eV) = -\begin{bmatrix} 4.53 & 0 & 0 \\ 0 & -2.1 & 0 \\ 0 & 0 & -2.1 \end{bmatrix} \times \begin{bmatrix} -0.0095 \\ -0.0095 \\ 0.0056 \end{bmatrix} \approx 0.035 \quad . \tag{14}$$

The density of elastic energy (energy per unit volume) W_s, which is associated with misfit strain s_a, can be calculated as

$$W_s = \frac{Ys_a^2}{(1-\nu)}, \tag{15}$$

where Y and ν are the Young's modulus and the Poisson's ratio, correspondingly.

We assume that the misfit elastic energy is fully compensated by the formation of non-interacting elastic dipoles caused by oxygen vacancies in the (001)[SrO] planes. Then the maximum concentration N of oxygen vacancy stress dipoles can be estimated as

$$N = \frac{Y s_a^2}{E^{int}(1-\nu)}. \tag{16}$$

For Y = 236 GPa, ν = 0.23, s_a = -0.0095, and E^{int} = 0.065 eV, we obtain $N \approx 2\times10^{27}$ m^{-3}, which is nearly two orders of magnitude smaller than the concentration of atoms in STO. This estimation suggests that oxygen deficiency of less than 1 at % is sufficient for stabilizing epitaxial growth and raising the critical thickness in the STO/LSAT films.

S9. Residual strain.

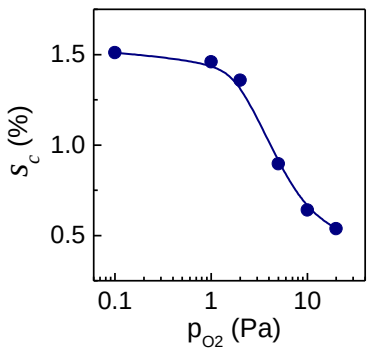

Fig. S9. Out-of-plane strain as a function of oxygen pressure in the 150-nm-thick STO/LSAT films.