Supplementary Information

1. Experimental set-up

Due to the high resistance of the thinnest films of pure CeO_2, the experimental set-up was modified (see Fig. S1) in order to avoid any parasitic contribution during the conductivity measurements. In particular, sample holders made of single crystal sapphire (with a resistance of 5.8 GΩ at 600 °C) were adopted for the measurements.

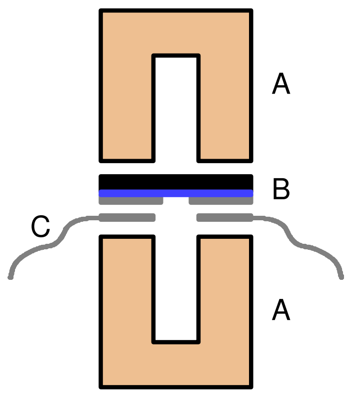

Fig. S1: Optimized measurement cell geometry
A: monocrystalline sapphire holders
B: substrate with thin film and sputtered Pt electrodes
C: Pt foil and wire

2. Substrate conductivity

The conductivity values of the bare Al_2O_3 and SiO_2 substrates (likely due to impurities) were determined. As it can be seen in

Fig. S2, in most cases this background conductance (grey area) is negligibly small compared with the conductances of the thin films. Only under certain conditions, namely nominally pure samples, high pO_2, low temperature and very small thickness, this is not the case. Interestingly, in tests performed at lower temperatures, we even observed a smaller conductance for few thin

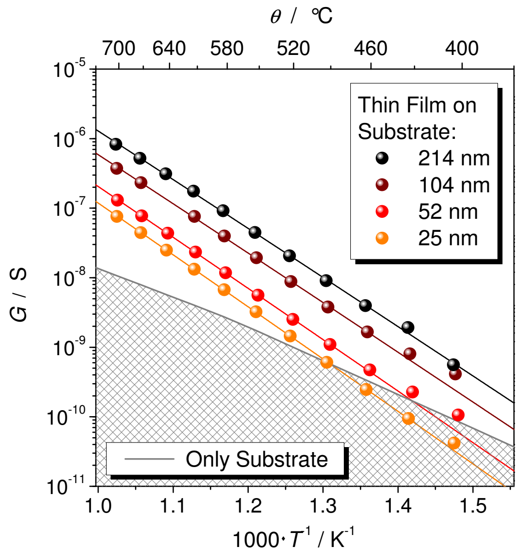

Fig. S2: Temperature dependence of the conductance of nominally pure CeO_2 on Al_2O_3 at 10^{-3} bar pO_2

films on the substrate compared with the bare substrate (up to one order of magnitude difference). A possible explanation for this effect might be that the CeO_2 films behave blocking for the impurities of the substrates while this is not the case if the platinum electrodes are sputtered directly onto the substrate. Nonetheless, the pO_2 dependence and mostly important also the thickness dependence investigations were not influenced by the conductance of the substrate as these measurements were carried out at 700°C, a temperature at which the background conductance is negligible.

3. Derivation of Equation (8) – Blocking Perpendicular Grain Boundaries

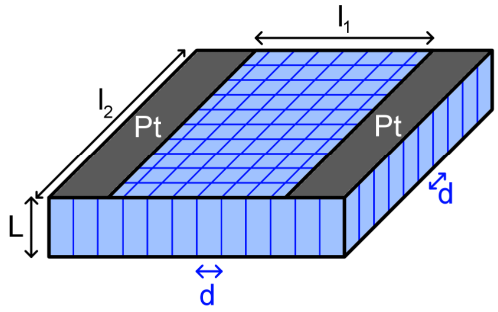

Fig. S3: Geometry of the polycrystalline CeO_2 thin films (bricklayer model)

For simplification it is helpful to use reduced conductances *Y*:

$$Y = \frac{l_1}{l_2} \cdot G \qquad \text{(S1)}$$

In our experimental case l_1 and l_2 have been 1 mm and 10 mm respectively. For the number of perpendicular space charge layers $N_{GB}^{\perp}$ we get:

$$N_{GB}^{\perp} = 2\frac{l_1}{d} \qquad \text{(S2)}$$

If we use the resistance R_∞ of the epitaxial layers on Al_2O_3 we can express the resistance $R^{\perp}$ of the polycrystalline films on SiO_2 as:

$$R^{\perp} = R_\infty + \Delta R_{GB} = R_\infty + N_{GB}^{\perp} \cdot \Delta R_1 = R_\infty + N_{GB}^{\perp} \cdot \frac{\Delta Z_1}{l_2 \cdot L} \qquad \text{(S3)}$$

Here ΔR_1 (ΔZ_1) is the resistance (reduced resistance) of a single blocking SCL. ΔZ_1 can be defined as follows (λ^* = length of the space charge layer, Mott-Schottky case):

$$\Delta Z_1 = \int_0^{d/2} (\rho(x) - \rho_\infty)dx \approx \int_0^{\infty} (\rho(x) - \rho_\infty)dx \qquad \text{(S4)}$$

$$\Delta Z_1 = l_2 \cdot L \cdot \Delta R_1 \qquad \text{(S5)}$$

$$\Delta Z_1 = \frac{l_2 L d}{2 l_1} \cdot \Delta R_{GB} = \frac{l_2 L d}{2 l_1} \cdot \left(R^{\perp} - R_\infty \right) \qquad \text{(S6)}$$

$$\sigma_\infty \cdot \Delta Z_1 = \frac{d}{2} \cdot \left(\frac{R^\perp}{R_\infty} - 1 \right) \tag{S7}$$

For the reduced conductance of the polycrystalline films $Y^\perp$ we then get:

$$Y^\perp = \frac{l_1}{l_2} \cdot \frac{1}{R^\perp} = Y_\infty - \frac{2 \cdot L \cdot \sigma_\infty^2 \cdot \Delta Z_1}{d + 2 \cdot \sigma_\infty \cdot \Delta Z_1} \tag{S8}$$

with $Y_\infty = \frac{l_1}{l_2} \cdot \frac{1}{R_\infty} = L \cdot \sigma_\infty$ (S9)

Here Y_∞ (σ_∞) is the reduced conductance (conductivity) of the epitaxial films. If we combine equations (6) and (S8) we obtain equation (8).

4. Derivation of Equation (19) – Conductive Parallel Grain Boundaries

The number of parallel space charge layers $N_{GB}^{\parallel}$ can be calculated using:

$$N_{GB}^{\parallel} = 2 \frac{l_2}{d} \tag{S10}$$

In this case the conductance (reduced conductance) of polycrystalline films $G^{//}$ ($Y^{//}$) is given as the sum of the epitaxial conductance G_∞ (Y_∞) and the grain boundary contribution:

$$G^{\parallel} = G_\infty + \Delta G_{GB} = G_\infty + N_{GB}^{\parallel} \cdot \Delta G_1 = G_\infty + N_{GB}^{\parallel} \cdot \frac{L}{l_1} \cdot \Delta Y_1 \tag{S11}$$

$$Y^{\parallel} = \frac{l_1}{l_2} \cdot G^{\parallel} = Y_\infty + \frac{2L \cdot \Delta Y_1}{d} \tag{S12}$$

Y_∞ is defined according to (S9). ΔG_1 (ΔY_1) is the conductance (reduced conductance) of a single parallel SCL which is here defined as follows:

$$\Delta Y_1 = \int_0^{d/2} (\sigma(x) - \sigma_\infty) dx \approx \int_0^{\infty} (\sigma(x) - \sigma_\infty) dx \tag{S13}$$

$$\Delta Y_1 = \frac{l_1}{L} \Delta G_1 \tag{S14}$$

If equation (6) is inserted in (S12) we obtain (19).