Supporting Information

Tensile Lattice Distortion Does Not Significantly Affect Oxygen Transport in Yttria-stabilized Zirconia (YSZ)–CeO\textsubscript{2} Hetero-Interfaces

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1) HR-TEM analysis of isolated crystalline defects and local morphological inhomogenities

In agreement with the XRD analysis, no evidence of misoriented grains was observed, with the exception of few and isolated small grains in the region close to the STO buffer layer, as shown in Figure S1a and S1b.

**Figure S1.** Misoriented grains (marked with dashed contours) observed close to the STO seed layer (a). HRTEM image of one of such a grain (b). The deviation from a cubic structure of such grains showed an in-plane misorientation of 45° with respect to the hetero-structure, as revealed by the comparison between the Fast Fourier Transform (FFT) patterns of the misoriented grain (c) and that of the heterostructure (d).

These grains showed epitaxial out-of-plane orientation but an in-plane rotation of 45° with respect to the hetero-structure, as was revealed by the analysis of the FFT patterns shown in Figure S1c and S1d. Careful inspection of such patterns showed that the structure of the grains is
slightly distorted with respect to the cubic 8YSZ. Most of the misoriented grains comprised only the first 8YSZ layer and only some of them extended for more than one layer crossing few interfaces. Local roughness of the STO seed layer or instabilities in the growth process can be responsible for the nucleation of these grains.

**Figure S2.** Local defects observed along the cross section of the samples: flatness deviation in sample E (a), thickness inhomogeneity in sample D (b).

Only a few isolated defects induced by the local inhomogeneity of the STO seed layer were observed (Fig. S2). The average density of such defects was very small and resulted in local flatness deviations (Fig. S2a) and local thickness variations (Fig. S2b) without affecting the crystallographic orientation. The effect of smoothing of local irregularities with increasing thickness of the layers was clearly observed.
2) Reciprocal Space Map analysis of CeO$_2$-YSZ hetero-structures.

Reciprocal Space Maps of the CeO$_2$-8YSZ hetero-structures were measured using the (113) asymmetric reflections of the two materials with the intent of quantifying the degree of strain relaxation by measuring the in-plane lattice parameters.

For thicknesses larger than about 20 nm the (113) asymmetric reflection peaks of CeO$_2$ and of 8YSZ were measured at the angular positions relative approximately to the fully relaxed structures of the two materials. For thicknesses between approximately 15 and 5 nm the presence of several satellite peaks of low intensity and in close proximity resulted in RSMs which were difficult to interpret. When the thickness of each individual layer was below 5 nm only the first order satellite peaks were visible and the identification of the average structure peak became clear.

Figure S3 shows the XRD analysis of a superlattice fabricated by growing 50 CeO$_2$-8YSZ bilayers on a STO-buffered MgO substrate. For this superlattice the average structure peak is approximately in the center of the angular region confined between the (002) reflection lines of the two fully relaxed materials (Fig. S3a). The angular position of the first order satellite peaks allows calculating the thickness of all bilayers which is approximately 6 nm.

In the RSM plot reported in Fig. S3b, the two white squares indicate the positions of the reciprocal vectors of CeO$_2$ and 8YSZ relative to the fully relaxed crystalline structures of the two materials. The value of the in-plane reciprocal vector (Qx) associated with the average structure peak (the region of maximum intensity in Fig. S3b) ranges from that of fully relaxed CeO$_2$ up to that of fully relaxed 8YSZ. The average value was found for an in-plane reciprocal vector corresponding to an in-plane lattice parameter of about 5.29 Å. This is the average value of the in-plane lattice parameter of the supercell comprising the two materials and would imply an
average tensile strain of about 2.8% for YSZ and a corresponding compressive strain of about 2.3% for CeO$_2$.

**Figure S3.** XRD (a) and RSM (b) of a CeO$_2$-8YSZ superlattice fabricate on STO-buffered MgO by stacking up 50 bilayers (3+3) nm.

This analysis can be considered a further prove of the significant distortion of the lattice but does not allow a reliable quantification of the degree of strain relaxation. Actually, the conclusion is the same as that provided by Geometric Phase Analysis, i.e. the strain field is not uniform and the crystalline structure consists on regions almost fully relaxed and regions in which the strain is very close to the theoretical lattice misfit.

**3) Compositional analyses using SIMS**

The depth profile achieved through sample C, analysing positive secondary ions, is shown in Figure S4 along with ion images projected on the x-z plane. For clarity the strongest signal is
plotted from each component matrix cation, either the molecular or atomic species, although the lower intensity signals showed the same trends and depth resolution.
**Figure S4.** (a) ToF-SIMS compositional depth profile through sample C and (b) ion images projected on the x-z plane for the species represented in (a).

Using post-analysis data reconstruction no significant level of contamination from unexpected sources was detected in any sample. Leading edges on all peaks showed depth resolutions of 1.5-4 nm (using the conventional measure of 16-84% intensity) with very little loss in resolution with crater depth. This is consistent with the expected level of ion beam mixing from the 2 keV Cs+ beam. The trailing edge slope was seen to be between 4-7 nm/decade (the distance to drop one decade in signal intensity) in all layers. This is at the limits of what can be measured due to effects such as ion beam mixing and roughening of the sputtered area, and indicates compositionally sharp layer interfaces. As the ion images, shown in Figure S4b, have an aspect ratio of approximately 250:1 (width:depth), the uniformity of the layers is highlighted over a long range. While this may appear to contradict the defects in the film flatness and thickness seen by TEM in Figure S2 it must be noted that there is a difference in lateral scale between the two analyses and any local effect would be averaged over the large (submicron) ion beam spot size while sputtering would occur evenly through the films making them appear flatter than in reality.

All signals show a small rise before the trailing edge of each peak which can be attributed to a surface charging effect, a complementary rise is seen in the total ion counts in the same position. The only interdiffusion evident is from the yttrium signal in the STO buffer layer. Samples A and B also showed zirconium in the STO layer. While $^{108}\text{ZrO}^+$ and $^{105}\text{YO}^+$ are plotted in the figure, the atomic species showed the same features, further indicating that this is not a case of mass interference.