SUPPLEMENTARY MATERIAL

Oxygen defect engineering by current effect assisted with temperature cycling in perovskite-type $La_{0.7}Sr_{0.3}CoO_3$ Film

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I. Sr distribution on surface

To check the influence of the substrate and temperature cycling on the surface Sr content, we performed the scanning electron microscopy (SEM) and energy-dispersive X-ray spectra (EDS) experiments (S4800, from HITACHI) in the film before and after repeated transport measurements, respectively. The surface topography scanning and corresponding element mapping show that no anomalous Sr cluster area appears in the surface of the film after repeated transport measurements (see Fig.S1). Meanwhile, the Sr distribution is nearly consistent with that of La and Co elements both before and after the repeated measurements (Fig.S1 (b)-(d)&f)-h)). These results indicate that the observed increase in the overall resistivity is unlikely to be the result of the possible reduction of Sr doping or segregation of Sr in the surface of the film.

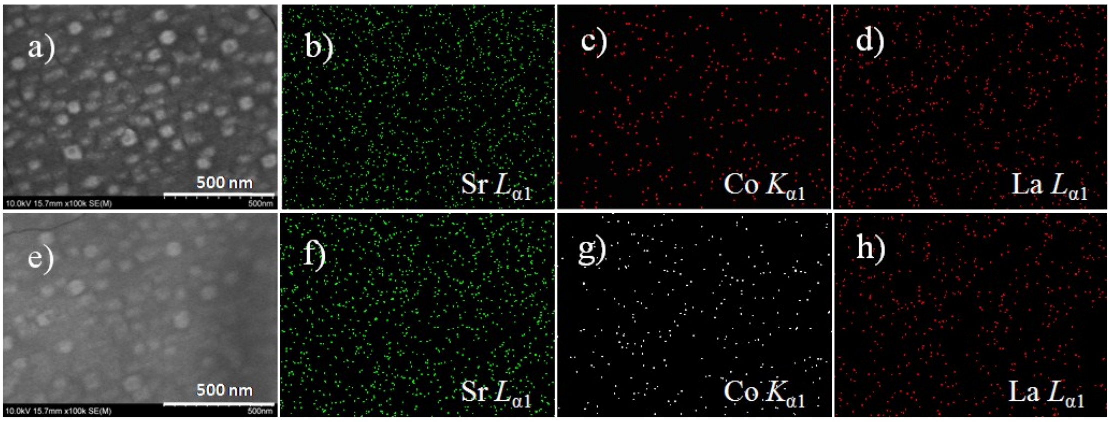

Fig.S1 Typical morphology and elemental mappings of the LSCO film before ((a)-(d)) and after ((e)-(h)) repeated transport measurements: (a)&(e) SEM image, (b)&(f) Sr mapping, (c)&(g) Co mapping and (d)&(h) La mapping.

II. High-resolution TEM characterization

To check the possible structural change due to the repeated temperature-dependent transport measurements, we performed careful X-ray diffraction (XRD) experiments before and after the repeated measurements. However, no obvious change in the diffraction patterns are observed, which indicates that the possible structural change related to the variation in conductivity, if any, may locate in very small areas. By using a high-resolution transmission electron microscope (HRTEM) (JEM-F200, from JEOL), operated at 200kV, we did observe a local change in the microstructure of the film after repeated transport measurements. Figure S2 shows a typical image for the film after repeated transport measurements. The image shows a good heteroepitaxial growth of the film onto the PMN-PT substrate despite of the large lattice mismatch. Meanwhile, it was found that periodic dark stripes emerge in some small areas (with a size level of ~10nm) after repeated measurements (see area marked by LSCO-B in Fig.S2). Previous researches [ref.S1] have shown that such dark stripes in cobaltite films are oxygen deficient, demonstrating an oxygen vacancy ordering modulation in the structure. Thus one can speculate that oxygen vacancies are accumulated in the film by repeated transport measurements, resulting in a conductivity transformation. Note that such periodic modulations only locate within very small regions and most area of the film retains a perovskite lattice structure (area marked with LSCO-A in Fig.S2). It suggests that the lattice modulation induced by oxygen vacancy in our film is very local, which is consistent with the fact that XRD patterns show no obvious change after repeated measurements.

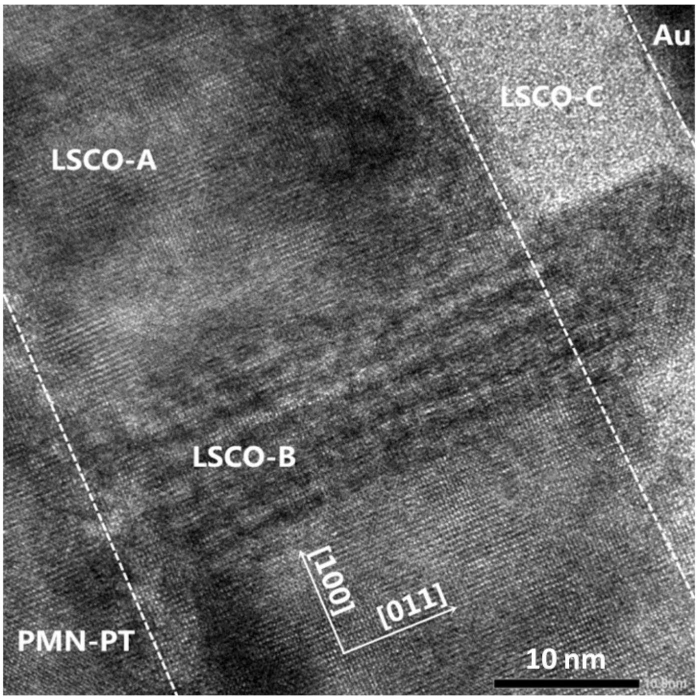

Fig.S2 HRTEM image of the LSCO film after repeated transport measurements, obtained in a high-resolution transmission electron microscope (JEM-F200, from JOEL). The zone axis is along the [01-1] direction of the PMN-PT substrate. The investigated cross-section specimen with a dimension of 3μm×5μm×50nm was cut from the film by using focused ion beam (FIB). The marked areas in the image represent regions of substrate PMN-PT, the perovskite LSCO (LSCO-A), the LSCO with oxygen vacancy ordering (LSCO-B), the amorphous layer (LSCO-C) produced during etching process of FIB and the Au layer used for FIB, respectively.

III. Conductivity variation for bulk sample

We have also performed the repeated transport measurements on the bulk sample of $La_{0.7}Sr_{0.3}CoO_3$, which was cut from the target. No obvious change of transport properties was observed after repeated measurements, as shown in Fig.S3, demonstrating that no conductivity transformation caused by current effect assisted with temperature cycling occurs in the bulk sample. Obviously, such distinct conductivity response to the temperature cycling assisted current effect in bulk and thin film of LSCO should arise from the tensile strain in the thin film, suggesting that the lattice strain plays an important role in the oxygen vacancy formation.

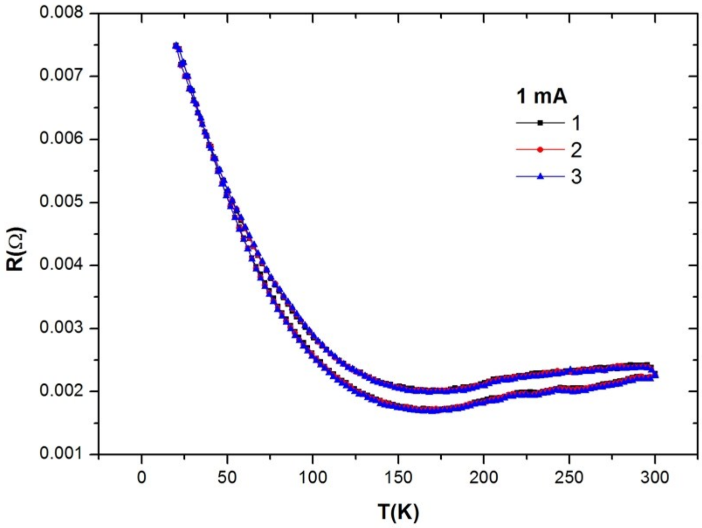

Fig.S3 Repeated temperature-dependent resistance measurements of bulk LSCO with current of 1mA. The numbers in the image represent the cycle index of measurements. No obvious change of transport properties was observed after repeated measurements for the bulk.

Reference:

[S1] Neven Biškup, Juan Salafranca, Virat Mehta, Mark P. Oxley, Yuri Suzuki, Stephen J. Pennycook, Sokrates T. Pantelides, and Maria Varela, *Phys. Rev. Lett.* **2014**, 112, 087202.