Electronic Supplementary Information (ESI) for

Heavy Interstitial Hydrogen Doping into $SrTiO_3$

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Experimental details

Preparation of $SrTiO_3$ Thin Films. As ion beam irradiation modifies the near-surface region, thin films of $SrTiO_3$ were used for irradiation experiments. $SrTiO_3$ films were grown epitaxially on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) (001) substrates by pulsed laser deposition. To prepare the precursor targets, $SrTiO_3$ powder (Rare Metallic Co., Ltd. 99.9%) was pressed into pellets and then sintered at 1200 °C for 48 h in air. Deposition was conducted with a KrF excimer laser pulse with $\lambda = 248$ nm. The laser energy density was 0.7 J/cm^2, and the frequency was 1 Hz. The substrate temperature during the deposition was set to 700 °C. The target thickness was 100 nm. For electrical resistivity measurement, gold electrodes were deposited at the corners by evaporation.

Hydrogen Ion Beam Irradiation and *In Situ* Electrical Resistivity Measurements. Hydrogen ion beam irradiation and *in situ* resistivity measurements were performed using our homemade apparatus.[1] Irradiation temperatures were 300, 150, and 50 K, and an acceleration voltage was 5 kV. The ion current under irradiation was 0.3–1.5 μA, and irradiation doses were determined by integrating the incident beam current on the sample. The size of beam spot was 6–8 mm, and homogeneous hydrogen doping was achieved by raster scanning over the sample area (10 × 10 mm^2). Electrical resistivity was measured along the in-plane direction using the van der Pauw method. A digital multimeter (Keithley 2400) and a nanovoltmeter (Keithley 2182) were used for electrical resistivity and beam current measurements.

XRD Measurements. The characterization of $SrTiO_3$ films was performed by out-of-plane and in-plane φ-scan X-ray diffraction measurements with Cu $K\alpha$ radiation at room temperature by Rigaku Smart Lab 9IP.

SIMS Measurements. SIMS measurements of $SrTiO_3$ films before and after 150 K irradiation were performed at room temperature with an ULVAC-PHI, Inc PHI ADEPT1010 apparatus. A Cs^+ primary ion beam with an acceleration voltage of 3.0 kV was applied for sputtering, and the detection region was 51 × 51 μm^2. The hydrogen concentration was calibrated by using a standard sample of $SrTiO_3$, and the depth was estimated from the sputtering rate for the standard sample.

Hall Effect Measurements. The temperature dependence of carrier density and Hall mobility for the $SrTiO_3$ film was determined from the *ex situ* Hall measurements using a Quantum Design Physical Property Measurement System (PPMS) from 1.9 to 300 K.

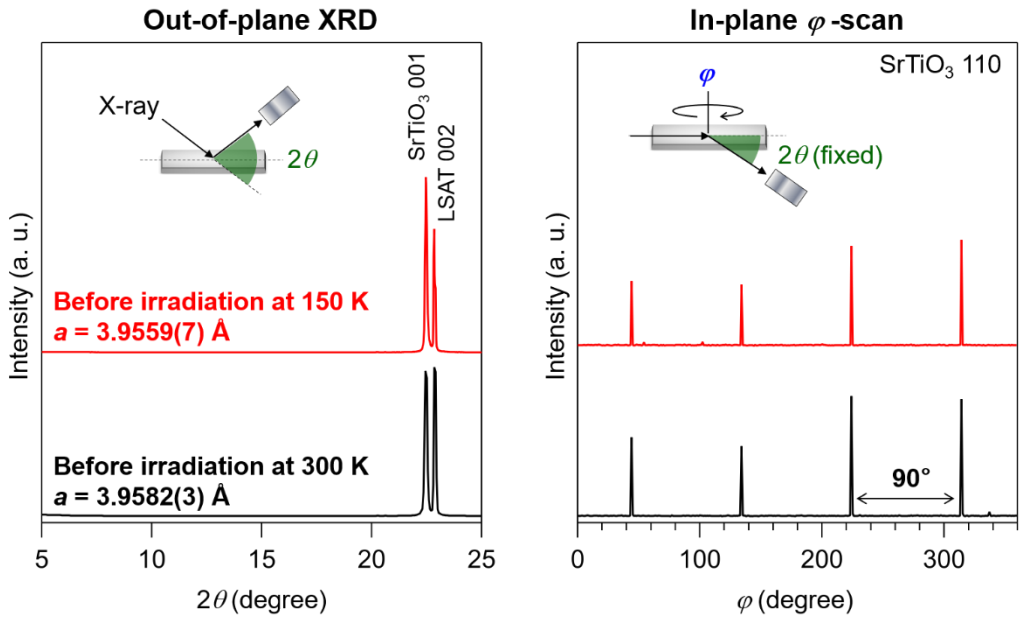

Fig. S1 Characterization of deposited $SrTiO_3$ thin films by XRD measurements. Out-of-plane XRD patterns of $SrTiO_3$/LSAT thin films (left) and XRD in-plane φ-scans of $SrTiO_3$ 110 reflection (right). The XRD patterns were measured with Cu $K\alpha$ radiation at room temperature. Red and black lines correspond to samples before irradiation at 150 K and 300 K, respectively. The inset figures denote the scattering geometries of the XRD study.

The out-of-plane lattice parameters of the $SrTiO_3$ films before irradiation at 300 K and 150 K were a = 3.9582(3) and 3.9559(7) Å, respectively, i.e., slightly larger than the lattice parameter of the bulk (3.905 Å) because of in-plane compression resulting from the smaller lattice parameter of the LSAT substrate (3.868 Å), and in agreement with values previously reported.[2]

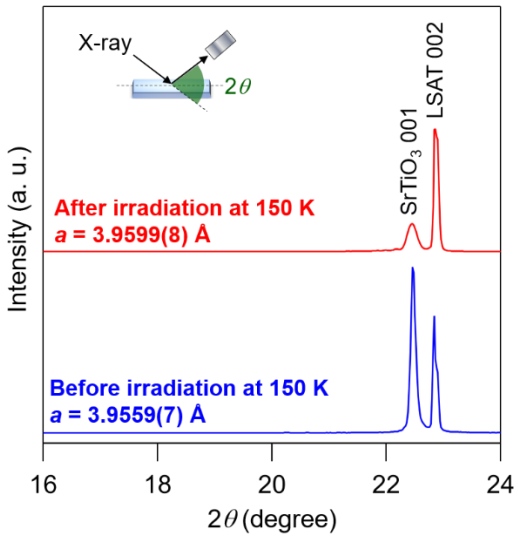

Fig. S2 *Ex situ* out-of-plane XRD patterns of the $SrTiO_3$/LSAT thin film before (blue) and after (red) 150 K irradiation. The XRD patterns were measured with Cu *K*α radiation at room temperature. The inset figure denotes the scattering geometries of the XRD study.

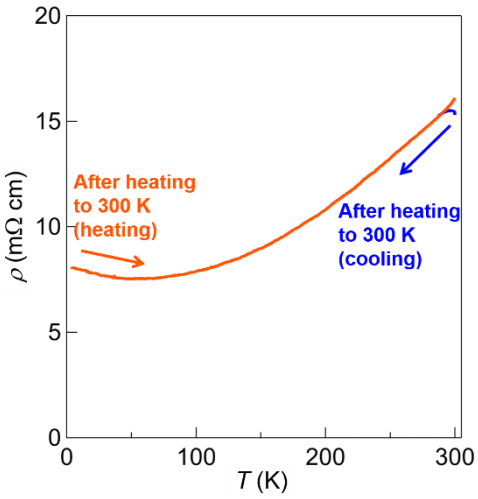

Fig. S3 Temperature dependence of the resistivity after heating to 300 K. Blue and orange lines correspond to the cooling and heating processes, respectively. When the film was heated again to 300 K, the temperature dependence of the resistivity was almost identical to that during the cooling process.

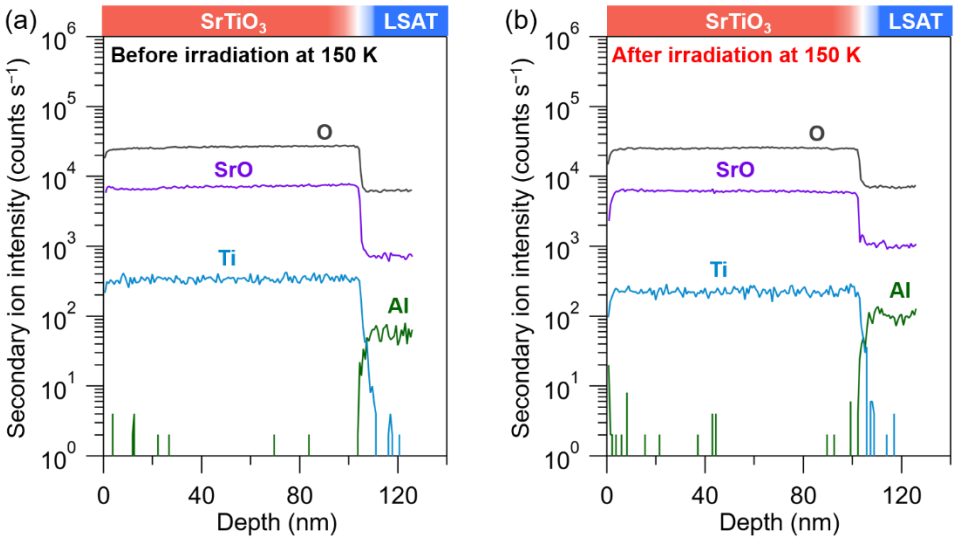

Fig. S4 Dynamic SIMS depth profiles of SrO, Ti, O, and Al secondary ions in $SrTiO_3$/LSAT film (a) before and (b) after irradiation at 150 K. The SIMS profiles were measured at room temperature.

Fig. S4 shows the nearly identical SIMS profiles of SrO, Ti, and O before and after irradiation, which indicates that the composition is uniform with depth and no decomposition occurs upon irradiation.

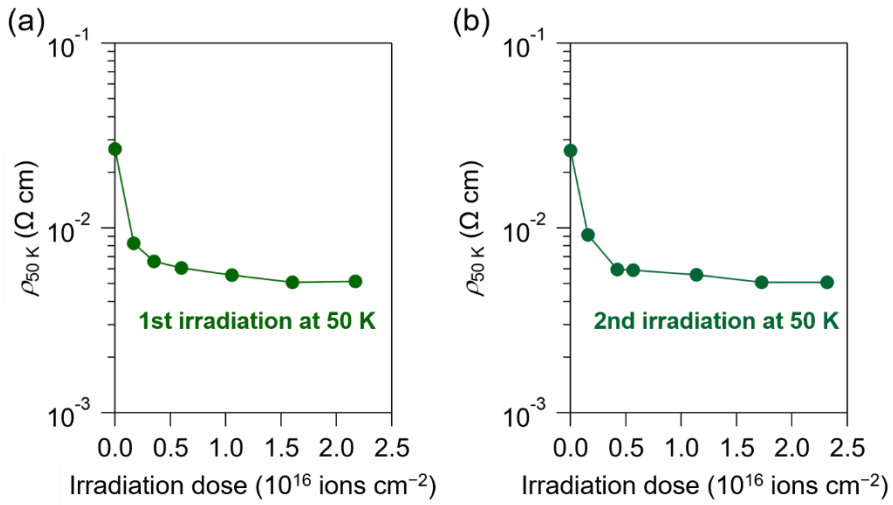

Fig. S5 Dose dependence of the resistivity of the $SrTiO_3$ under (a) first and (b) second irradiation at 50 K.

After irradiation at 300 K, we cooled the sample (blue open circles in Fig. 4(a)) and further irradiated hydrogen at 50 K (green arrow in Fig. 4(a) and S5(a)). The additional low-temperature irradiation induced a further decrease in the resistivity and then saturation behavior was observed as shown in Fig. S5(a). On subsequent heating up to 300 K, the resistivity decreased above 70 K and started to increase rapidly above 180 K, and returned to nearly the initial value at 300 K (red open circles in Fig. 4(a)). It was well reproduced by a second irradiation at 50 K (closed circles in Fig. 4(a) and S5(b)).

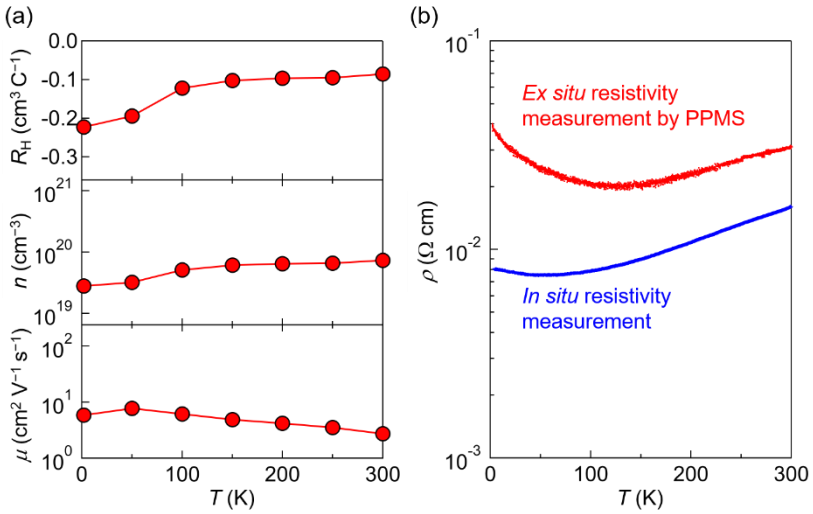

Fig. S6 *Ex situ* Hall effect measurements. (a) Temperature dependence of the Hall coefficient (R_H), carrier density (n), and mobility (μ) for the $SrTiO_3$ film after 150 K irradiation determined from the Hall measurements. (b) Temperature dependence of the resistivity evaluated by *in situ* (red) and *ex situ* (blue) resistivity measurements. *Ex situ* resistivity measurements were performed one week later by Quantum Design PPMS.

The H_2^+ irradiation of $SrTiO_3$ film successfully introduced a substantial amount of carriers (nearly 10^{20} cm^{-3}) even after partial hydrogen desorption. Although the carrier density is not greatly inferior to other n-doped $SrTiO_3$ systems such as $SrTiO_{3-\delta}$ and Nb-doped $SrTiO_3$,[3] the Hall mobility of our sample is lower than that of the other n-doped systems, which might be attributable to the grain boundaries in the pristine film and/or some lattice strains induced by the doped hydrogen atoms and possible irradiation damage.

Although the resistivity of the film was slightly increased, it remained relatively low (10^{-2} Ω cm), and metallic behavior was observed above 130 K (Fig. S6(b)).

References

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