

## Supplementary Information

### An *In situ* study on the depth-resolved chemical states of undoped SrTiO<sub>3</sub>(001) surface during Ar<sup>+</sup> sputtering and annealing processes with XPS

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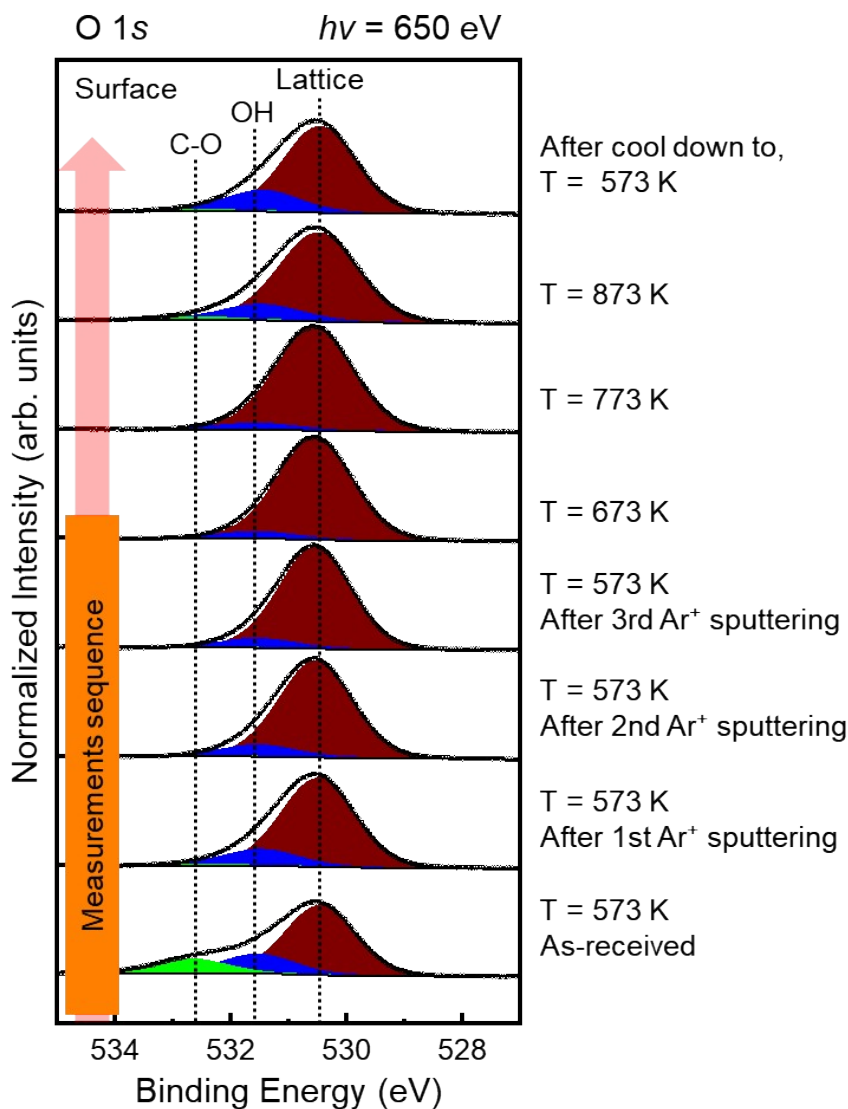


Fig. S1 O 1s spectra of undoped SrTiO<sub>3</sub>(001) during the surface preparation process, *i.e.*, Ar<sup>+</sup> sputtering and UHV annealing, in surface region (~1.6 nm). Surface contaminations such as OH<sup>-</sup> and C-O were reduced during Ar<sup>+</sup> sputtering and UHV annealing until 773 K. At 873 K, contaminations start to appear again due to the intermixing of ions in SrTiO<sub>3</sub> sample. It is to note that clear evidence of oxygen vacancies is not found due to the large amount of lattice oxygen species.

Table S1 Percentage ratio of Si and Al impurities on the surface of SrTiO<sub>3</sub> during surface preparation procedures, *i.e.*, Ar<sup>+</sup> sputtering and UHV annealing processes. Impurities are effectively removed after Ar<sup>+</sup> sputtering, and their quantities remain stable during UHV annealing until 873 K. As temperature reaches 873 K, both Si and Al impurities segregate to the surface and then diffuse back into the bulk after cooling down to 573 K. The amount of Si impurity in the bulk is higher than on the surface, indicating that the Si impurity originates from the deep bulk region. On the other hand, the amount of Al impurity shows little change during UHV annealing process, implying that the Al impurity originates from the surface region.

	Si concentration (%)			Al concentration (%)		
	Surface	Subsurface	Bulk	Surface	Subsurface	Bulk
T = 573 K, As-received	14.22	9.03	6.72	5.25	2.90	1.25
T = 573 K, After 3 cycles of Ar <sup>+</sup> sputtering	2.12	1.93	3.13	1.45	1.01	0.57
T = 773 K	2.26	1.62	2.56	1.65	0.93	0.56
T = 873 K	13.77	9.24	6.68	2.21	1.25	0.53
After cooling to 573 K	2.94	2.35	5.00	1.03	0.78	0.82

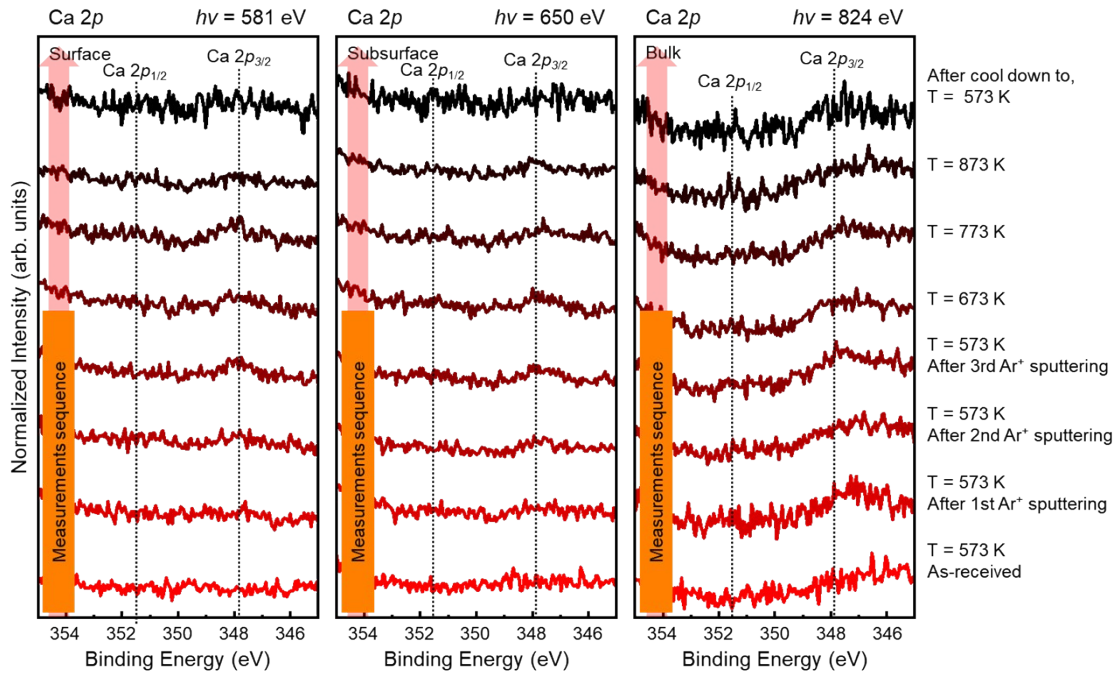


Fig. S2 Ca 2p spectra of undoped SrTiO<sub>3</sub>(001) during the surface preparation process, *i.e.*, Ar<sup>+</sup> sputtering and UHV annealing, with various probing depth regions: (a) surface region (~2.6 nm), (b) subsurface region (~3.1 nm), and (c) bulk region (~4.3 nm), respectively. On the as-received SrTiO<sub>3</sub> surface, no Ca impurities are found. However, during Ar<sup>+</sup> sputtering and UHV annealing, Ca impurities are segregated to the surface. As temperature increases to 873 K, segregated Ca impurities are migrated to the bulk region, and they do not appear on the surface again even temperature is decreased to 573 K.