Supporting information for

Direct Probing of Oxygen Loss from the Surface Lattice of Correlated Oxides during Hydrogen Spillover

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Experimental Methods

Synthesis and hydrogen spillover of epitaxial VO₂ thin film

Epitaxial VO₂ films were grown on (0001) Al₂O₃ single-crystal substrates by pulsed laser deposition (PLD) with a base pressure of ~ 10⁻⁶ Torr in the growth chamber. A KrF excimer laser (λ = 248 nm) was focused onto a V₂O₅ rotating target at laser fluence ~ 1 J cm⁻² and repetition rate 2 Hz. The VO₂ films were grown in oxygen ambient of 14 mTorr at 300 °C to optimize the intrinsic properties of VO₂. The VO₂ films showed (020)_M peaks (i.e., (200)_R in pseudo-rutile notation), which represents (100)_R-oriented high-quality film growth.

The VO₂ epitaxial layer was hydrogenated using the hydrogen spillover method (**Fig. 1a**). Nano-sized Pt islands formed after growth on the epitaxial VO₂ layer by sputtering as catalytic for hydrogen spillover ^{10, 13}. To achieve hydrogen intercalation, the Pt/VO₂ sample was annealed at temperature below 120 °C under pure H₂ gas or under forming gas containing 5 % H₂ gas.

Time-of-flight Secondary ion mass spectrometry (ToF-SIMS)

Negative ion depth profiling of the pristine and hydrogenated VO₂ thin films was obtained using a ToF-SIMS (TOF-SIMS5 [ION-TOF, Germany]) at Korea Institute of Science and Technology (KIST). Samples were bombarded with a beam of 3 keV Cs⁺ ions with target current of 32 nA over an area of 300 μ m x 300 μ m. A pulsed 30 keV Bi⁺ primary ion source was used for analysis of SIMS data, delivering target current of 1 pA over an area of 100 μ m x 100 μ m. The VO₂⁻, Al⁻, ¹⁸O⁻ and H⁻ signals were used to characterize composition of each atom in the sample.

In situ X-ray diffraction

To characterize structural modulation during hydrogenation or dehydrogenation of the VO₂ thin film, *in situ* X-ray diffraction (XRD) scans were performed using synchrotron radiation ($\lambda = 0.15401$ nm) at the 3D XRS beamline of the Pohang Accelerator Laboratory (PAL). For *in situ* symmetrical XRD scans, the sample was mounted in an XRD chamber equipped with a thermocouple, heating system, water cooling system, and a gas flow line. During hydrogenation, forming gas containing 5 % H₂ was introduced into the chamber under 1 atm at 70 °C for 5 h. Before the dehydrogenation process, the sample was fully hydrogenated at 120 °C for 30 min. Then, dry air containing 21 % O₂ and 79 % N₂ was introduced into the chamber under 1 atm for 5 h at 70 °C.

In situ ambient pressure X-ray photoelectron spectroscopy

In situ ambient pressure XPS (APXPS) was performed using 670 eV X-ray energy at Beamline 9.3.2 at Lawrence Berkeley National Laboratory's (LBNL) Advanced Light Source (ALS). All data in the main text were collected from a single beamtime to minimize systematic errors caused by differences in beam flux and chamber cleanliness. The VO₂ thin film was placed on sample holder, with thermocouples mounted directly on the film surfaces to measure their temperatures.

Before spillover experiment in APXPS, the C 1s peak at ~283 eV was detected and the intensity of V 2p and O 1s peak was measured to be very small (**Fig. S1a**); this result indicates the

presence of an unwanted layer of carbon-related contaminates. Deconvolution of V 2p and O1s spectra revealed a large peak at high binding energy; this peak is a result of ionization associated with weakly-adsorbed species including carbon contaminants³¹ (**Fig. S1b**). To remove carbon contaminants from the film surface, the sample was heated to 250 °C under 100 mTorr O₂ (i.e., ambient pressure) as a surface treatment. After O₂ annealing, the C 1s peak completely disappeared and the peak intensity of V 2p and O 1s was significantly increased (**Fig. S1c**). Peak deconvolution of each spectrum from the surface-treated sample confirmed that the peak of O 1s mostly consisted of lattice oxygen (O-V) with negligible contribution from hydroxyl (O-H) (**Fig. S1d**).

The cleaned sample was cooled to 50 °C or 30 °C. First, the XPS spectra were collected under UHV with an incident photon energy of 670 eV to characterize the initial surface states. Subsequently, for *in situ* measurement during hydrogen spillover, XPS spectra were repeatedly measured for 850 s while injecting H₂ gas at 5 mTorr. After measurement, the sample was reheated to 250 °C under 100 mTorr O₂ to dehydrogenate the sample without removing it from the chamber.

To quantify the modulation of V valence states and O binding states, each V 2p and O 1s spectrum was deconvoluted using The XPS Peak4.1 program²⁸. The background signal was subtracted by a Shirley function, then the O 1s and V 2p XPS signals were fitted using mixed Lorentzian-Gaussian curves (**Table S1**).

First-principles calculations

First-principles density functional theory (DFT) calculations were performed using the Projector Augmented Wave method³⁴ and the generalized gradient approximation of Perdew,

Burke, and Ernzerhof⁴¹ for the exchange-correlation potential as implemented in Vienna Ab-initio Simulation Package (VASP) code.⁴² Periodic boundary condition and Monkhorst-Pack k-point sampling⁴³ with a Γ -centred k-point grid of 2x2x1 was used for the Brillouin zone integration. An energy cutoff of 500 eV was used for the plane-wave representation of the wavefunctions and the 3s electrons of V ion were considered as valence electrons. Atomic structures were relaxed until all Hellman-Feynman forces were < 0.01 eV/Å. For surface calculations, the (110) plane of rutile VO₂ with fully-oxidized surface termination was chosen. A 4x2x3 supercell with > 15 Å of vacuum space along the *c* axis was provided to prevent spurious interaction between periodic images.



Fig. S1 | Wide scan and detailed scan near V 2p and O 1s of ambient-pressure X-ray photoelectron spectroscopy (APXPS) using 670 eV X-ray energy of VO₂ thin film on (0001) Al₂O₃ (**a**, **b**) before and (**c**, **d**) after 100 mTorr O₂ annealing at 250 °C as a surface treatment. Before O₂ annealing, deconvolution of V 2p and O1s spectra revealed a large peak at high binding energy; this peak is a result of ionization associated with weakly-adsorbed species including carbon contaminants (**b**). On the other hands, the C 1s peak completely disappeared and the peak intensity of V 2p and O 1s was significantly increased after O₂ annealing. Peak deconvolution of each spectrum from surfacetreated sample revealed that the peak of O 1s consisted mostly of lattice oxygen (O-V) with negligible contribution from hydroxyl (O-H) (**d**)



Fig. S2 | *In-situ* APXPS spectra of VO₂ epitaxial films on (0001) Al₂O₃ during hydrogen spillover (H₂ pressure of 5 mTorr) at 30 °C using 670 eV X-ray energy. Intensity map of (**a**) V 2p_{3/2} and (**b**) O 1s core-level as a function of time. (**c**) *In-situ* APXPS evolution of V 2p and O 1s photoelectron peak with peak deconvolution. V 2p peaks were deconvoluted to V³⁺, V⁴⁺ and V⁵⁺; O 1s peaks were deconvolutied to lattice oxygen (O-V), hydroxyl (O-H), and adsorbed water (H₂O).



Fig. S3 | The comparison of in-situ APXPS spectra of Pt 4f in our Pt/VO₂ samples using 670 eV synchrotron X-ray energy before and after hydrogen spillover. The black line and red line indicate the Pt 4f spectra measured before and after hydrogen spillover, respectively. Although the change of Pt 4f is relatively negligible compared to the change of V 2p and O 1s during hydrogen spillover, the spectra show the slight shift to the higher binding energy after hydrogen spillover, which might be attributed to the formation of Pt-H_{ads} or Pt^{δ}-OH_{ads} with higher binding energy than Pt⁰ due to adsorbed hydrogen on the Pt catalyst during hydrogen spillover.



Fig. S4 | Sequential change of V 2p and O 1s spectra using 670 eV photon energy during repeated hydrogenation and dehydrogenation process (i.e., after oxygen treatment for carbon removal (red line) \rightarrow after the 1st hydrogenation (orange line) \rightarrow after dehydrogenation (blue line) \rightarrow after the 2nd hydrogenation (sky blue line)). Obviously, perfect match between the red and blue lines indicates that the hydrogenation and dehydrogenation of VO₂ occurs reversibly. Moreover, the sky-blue line (after the 2nd hydrogenation) perfectly matches the orange line measured after the first hydrogenation, indicating that the valance state of V and O atom was changed only by hydrogenation; this observation excludes the effect of beam damage by x-ray exposure on VO₂ film.

	B.E. (eV)	Δ (eV)
O1s	530.0	-
$V^{5+}2p_{3/2}$	517.2	12.8
$V^{4+}2p_{3/2}$	515.84	14.16
$V^{3+}2p_{3/2}$	515.29	14.71
$V^{5+}2p_{1/2}$	$V^{5+}2p_{3/2} + 7.33$	
$V^{4+}2p_{1/2}$	$V^{4+}2p_{3/2} + 7.33$	
$V^{3+}2p_{1/2}$	$V^{3+}2p_{3/2} + 7.33$	
О-Н	531.5	-1.5
H ₂ O	532.6	-2.6

Table S1 | The binding energy of each deconvoluted peak of XPS spectra (G. Silversmit et al, *Journal of Electron Spectroscopy and Related Phenomena* **135**, 2004). The symbol Δ represents the difference in binding energy between O1s peak at 530 eV and other peaks.