Supporting Information

Understanding the Phase Transition Evolution Mechanism of Partially M2 Phased VO_2 Film by Hydrogen Incorporation

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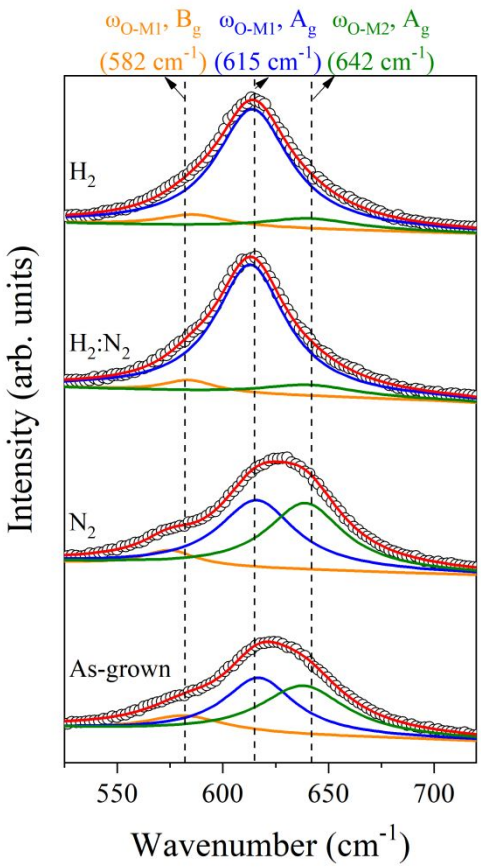

Figure S1. Deconvoluted Raman spectra in the high-frequency region of the as-grown and the post-annealed VO_2 film. Vertical dotted lines are three reference Raman peaks: $\omega_{O\text{-}M1}$, B_g (582 cm^{-1}) $\omega_{O\text{-}M1}$, A_g (615 cm^{-1}) and $\omega_{O\text{-}M2}$, A_g = 648 cm^{-1}).[27]

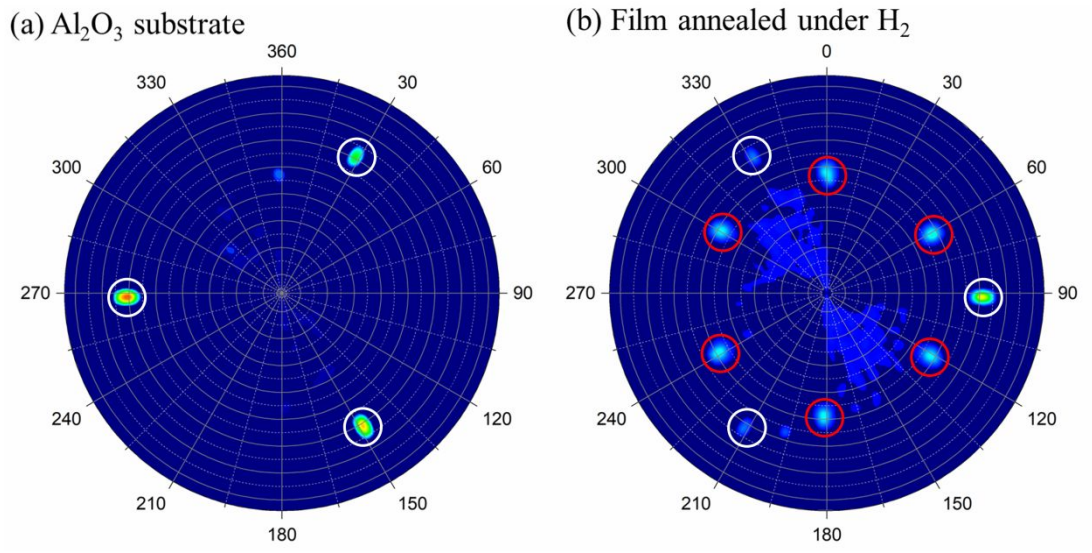

Figure S2. Pole figure of (a) $Al_2O_3\{012\}$ ($2\theta = 25.25^{o}$, $\chi = 57.6^{o}$) in Al_2O_3 substrate and (b) $Al_2O_3\{012\}$ ($2\theta = 25.25^{o}$, $\chi = 57.6^{o}$) and $VO_2\{011\}$ ($2\theta = 27.88^{o}$, $\chi = 45.27^{o}$) in VO_2 films annealed under H_2. Pole figure of Al_2O_3 shows three $Al_2O_3\{012\}$ peaks (white color). For the film annealed under H_2, it shows six $VO_2\{011\}$ peaks (red color) in addition to three $Al_2O_3\{012\}$ peaks (white color).

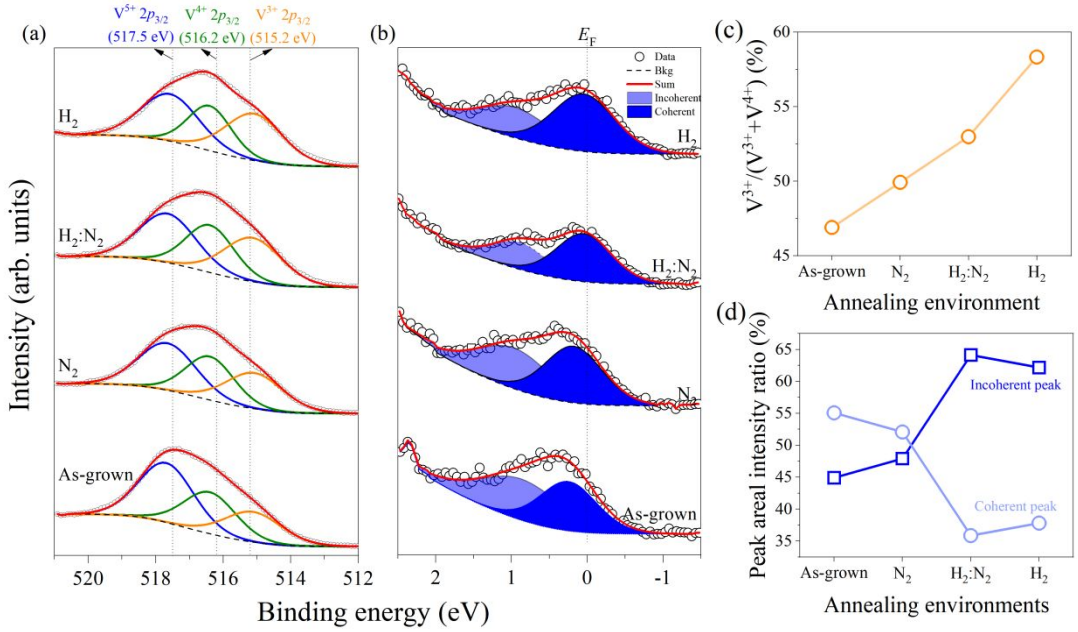

Figure S3. (a) V $2p_{3/2}$ core-level X-ray photoelectron spectra of the as-grown and the post-annealed VO_2 films measured at 100 °C. Vertical dotted lines indicate the reference binding energies of V $2p_{3/2}$ V^{5+} (517.5 eV), V $2p_{3/2}$ V^{4+} (516.2 eV), and V $2p_{3/2}$ V^{3+} (515.2 eV).[33] (b) Valence band spectra and the deconvoluted results of the as-grown and the post-annealed VO_2 films measured at 100 °C. (c) Deconvoluted V^{3+} peak areal intensity ratio to the (V^{3+} + V^{4+}) peak areal intensity ratio at 100 °C. (d) Peak area ratio of the coherent (squares) and incoherent (circles) spectra of the as-grown and the post-annealed VO_2 films measured at 100 °C.

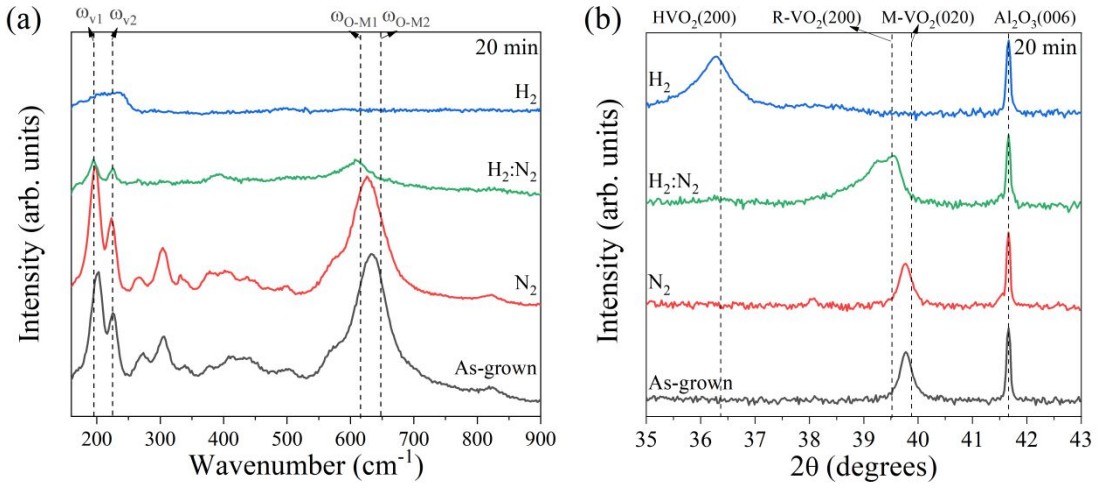

Figure S4. (a) Room-temperature Raman spectroscopy of the as-grown and the VO_2 films annealed for 20 min. Vertical dotted lines are the four dominant reference Raman peaks: V-V vibration (ω_{V1} = 195 cm^{-1}, ω_{V2} = 224 cm^{-1}) and V-O vibration ($\omega_{O\text{-}M1}$ = 615 cm^{-1}, $\omega_{O\text{-}M2}$ = 648 cm^{-1}).[27] (b) Symmetric ω/2θ XRD scan of the as-grown and VO_2 films annealed for 20 min. Vertical dotted lines represent the M-VO_2(020) (2θ = 39.88°), R-VO_2(200) (2θ = 39.51°), H-VO_2(200) (2θ = 36.37°), and the reference Al_2O_3(006) (2θ = 41.66°) peak position.

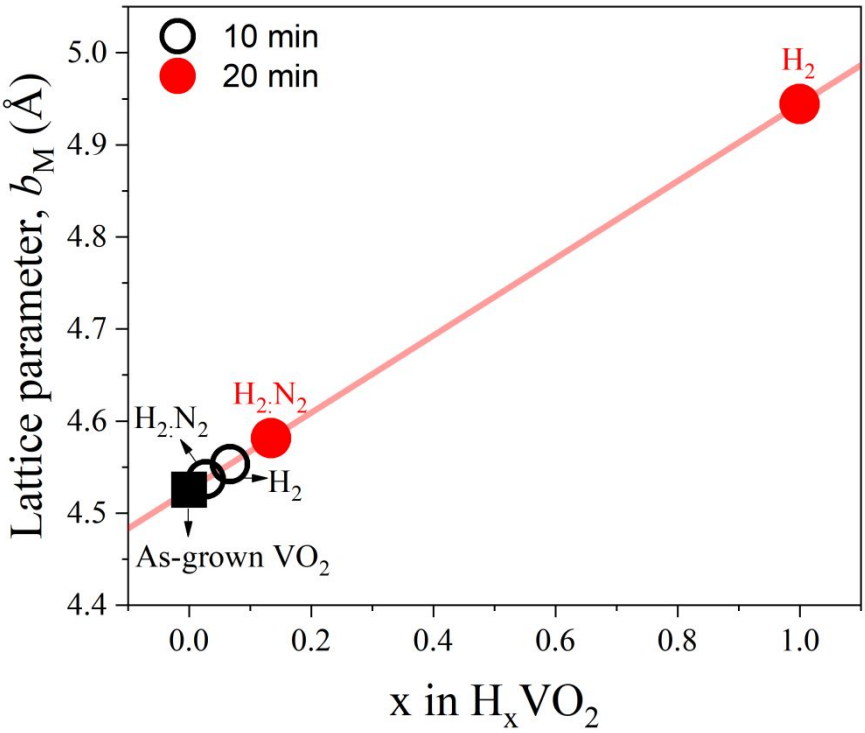

Figure S5. Linear relationship between the lattice parameter of VO_2 annealed hydrogen environments for 10 min and 20 min and the amount of hydrogen atom in VO_2.

Table S1. *d*-spacing, lattice parameters (a_M and b_M), and strains of the as-grown and the post-annealed VO_2 films.

Sample & Annealing environments	*d*-spacing (Å)		Lattice parameter (Å)		Strain (%)	
	(110)	(020)	a_M	b_M	[100]	[010]
As-grown	3.2113	2.2625	5.2154	4.5251	-2.97	0.18
N_2	3.2084	2.2639	5.2105	4.5278	-3.06	0.24
H_2:N_2	3.2119	2.2683	5.2246	4.5366	-2.80	0.43
H_2	3.2186	2.2766	5.2315	4.5531	-2.67	0.80
Bulk	3.3093	2.2585	5.6142	4.5170	-	-

Table S2. Binding energy, FWHM, and the relative peak areal intensity ratio of the deconvoluted V $2p_{3/2}$ core-level X-ray photoelectron spectra of the as-grown and the post-annealed VO_2 films at 100 °C.

Sample & Annealing environments	Binding energy (eV)			FWHM (eV)			Relative peak areal intensity ratio (%)		
	V^{3+}	V^{4+}	V^{5+}	V^{3+}	V^{4+}	V^{5+}	V^{3+}	V^{4+}	V^{5+}
As-grown	514.53	515.81	517.10	2.00	1.83	1.91	24.16	30.40	45.44
N_2	514.58	515.89	517.15	1.99	1.70	2.00	29.90	30.74	39.36
H_2:N_2	514.50	515.76	517.02	1.98	1.68	1.68	33.09	30.10	36.81
H_2	514.48	515.83	517.00	2.00	1.52	2.01	36.51	26.45	37.04

Table S3. Calculated lattice parameters, V-V bond lengths, and V-V angles of M1 and M2 phases.

	M1	M2
a (Å)	5.30	9.04
b (Å)	4.55	5.69
c (Å)	5.34	4.50
β (°)	117.8	91.0
V-V bond (Å)	2.48 (zigzag-short) 3.05 (zigzag-long)	3.19 (linear-long) 2.50 (linear-short) 2.87 (zigzag)
V-V angle (°)	168	164
Magnetic ground states	Non-magnetic	A-type Antiferromagnetic

Table S4. Binding energy, FWHM, and the relative peak areal intensity ratio of deconvoluted valence band spectra of the as-grown and the post-annealed VO_2 films at 100 ^oC.

Sample & Annealing environments	Binding energy (eV)		FWHM (eV)		Relative peak areal intensity ratio (%)	
	Coherent	Incoherent	Coherent	Incoherent	Coherent	Incoherent
As-grown	0.25	0.88	0.88	1.30	44.92	55.08
N_2	0.18	0.98	0.90	1.14	47.92	52.08
H_2:N_2	0.05	0.90	0.86	0.86	64.13	35.87
H_2	0.05	0.96	0.70	1.11	62.18	37.82