Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

In Situ Probing of Doping- and Stress-Mediated Phase Transitions in a Single-Crystalline VO_2 Nanobeam by Spatially Resolved Raman Spectroscopy

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1. A schematic illustration of a PDMS transfer method

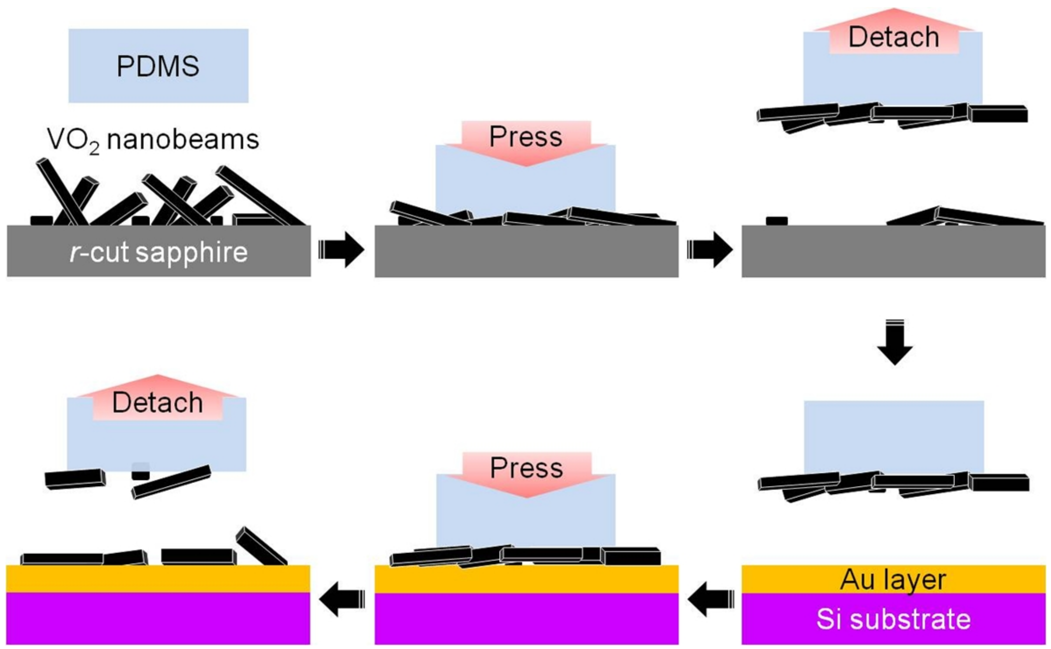

Fig. S1. A schematic illustration of PDMS transfer method: the procedures for the mechanical transfer of VO_2 nanobeams into a Au-coated substrate from VO_2 nanobeams grown on *r*-cut sapphire substrates using a PDMS slab.

2. An experimental set-up equipment for *in situ* Raman measurements combined with confocal laser scanning microscopy

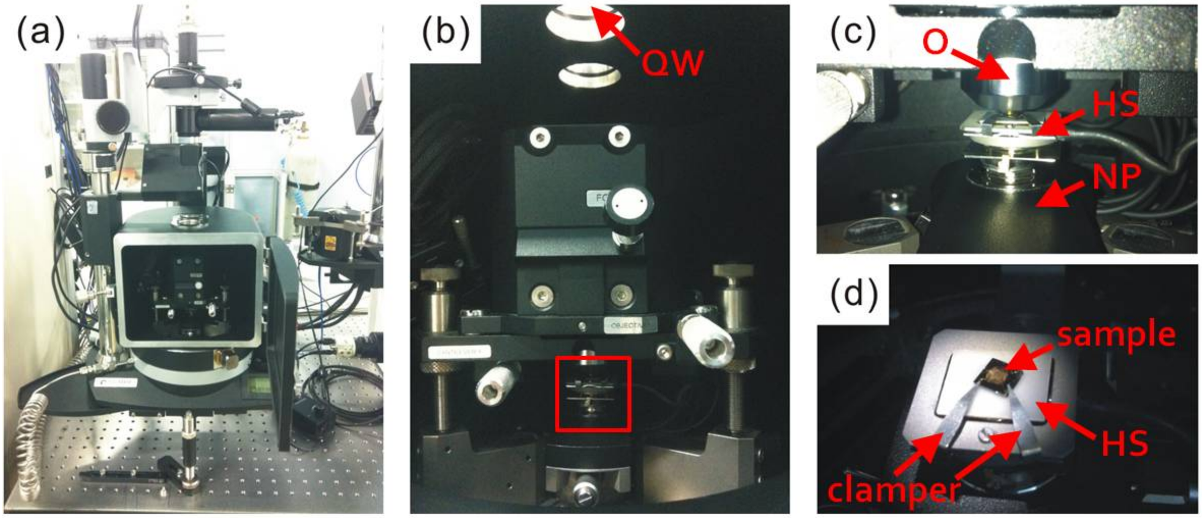

Fig. S2. An experimental set-up equipment for *in situ* Raman measurements: (a) an airtight chamber, (b) header with an objective lens (O) inside the chamber with the quartz window (QW) in (a), (c) the magnified view of red box in (b), the objective lens (O), the heating stage (HS), and the nano-positioner (NP), and (d) the sample clamped on the heating stage (HS).

3. A schematic illustration of a chronological sequence of experiments

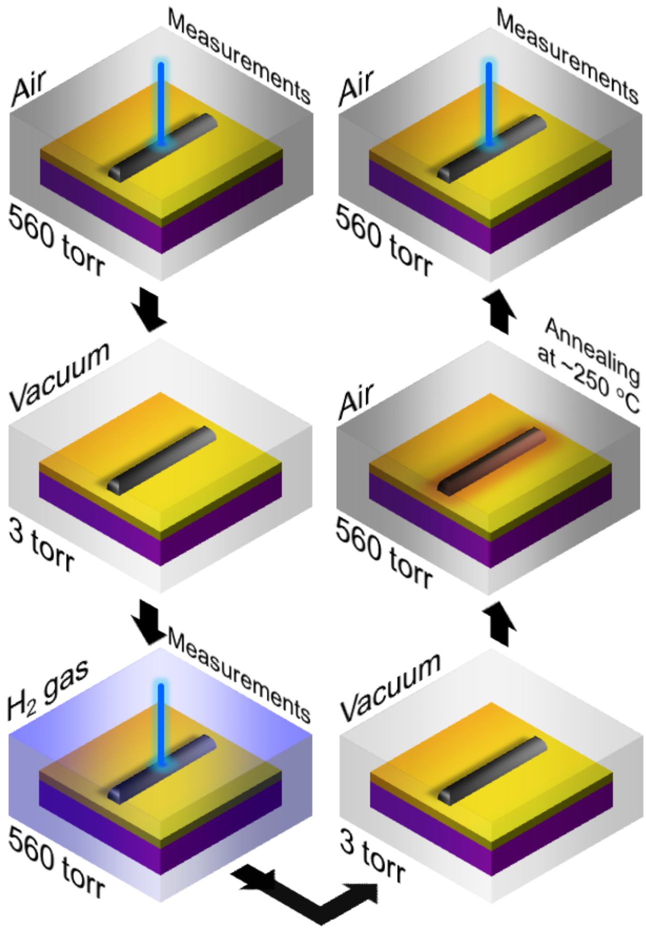

Fig. S3. A schematic illustration of a chronological sequence of *in situ* Raman measurements.

4. Raman spectra of the M1, T, M2, and R phases

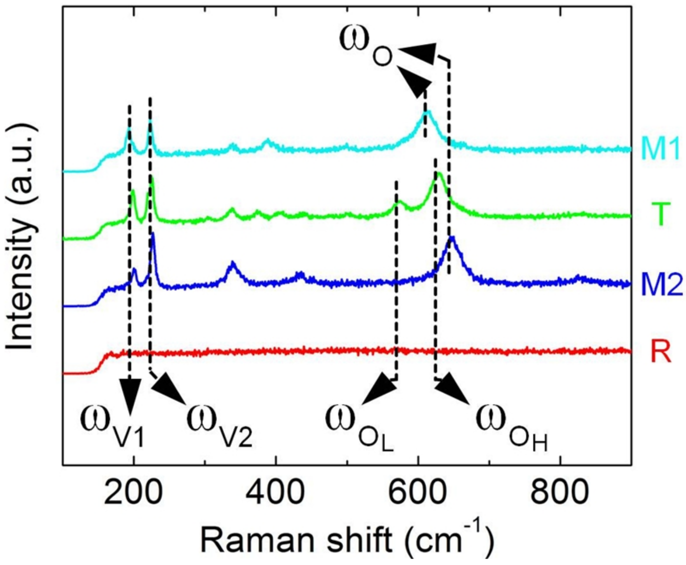

Fig. S4. Raman spectra of the M1 (cyan), T (green), M2 (blue), and R (red) phases for individual single-crystalline VO_2 nanobeams.

5. Energy dispersive X-ray spectroscopy (EDS) data of a VO_2 nanobeam synthesized on an *r*-cut sapphire substrate

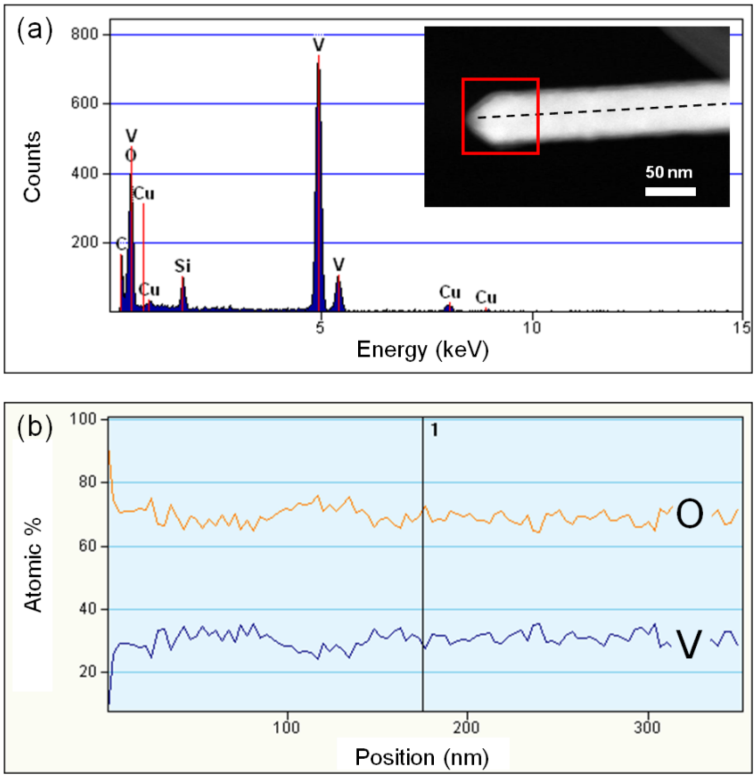

Fig. S5. (a) The EDS spectrum obtained from the region marked by square on the inset image of a VO_2 nanobeam that grown on an r-cut sapphire substrate. The inset of (a) shows high-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) image of the VO_2 nanobeam. (b) The STEM EDS elemental line profile obtained the VO_2 nanobeam along the dotted line in the inset of (a).

6. Raman spectra of a free-standing VO_2 nanobeam (as-grown sample) under air unpon heating

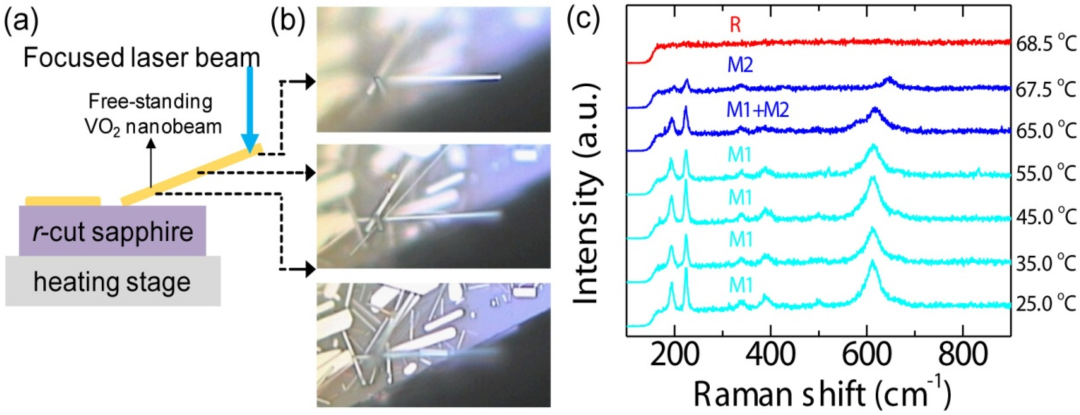

Fig. S6. (a) Schematic illustration, (b) optical microscopy images, and (c) temperature dependence of Raman spectra during a heating cycle for a free-standing VO_2 nanobeam grown on an r-cut sapphire substrate.

7. Mapping images of the Raman spectra intensity of a VO_2 nanobeam under air

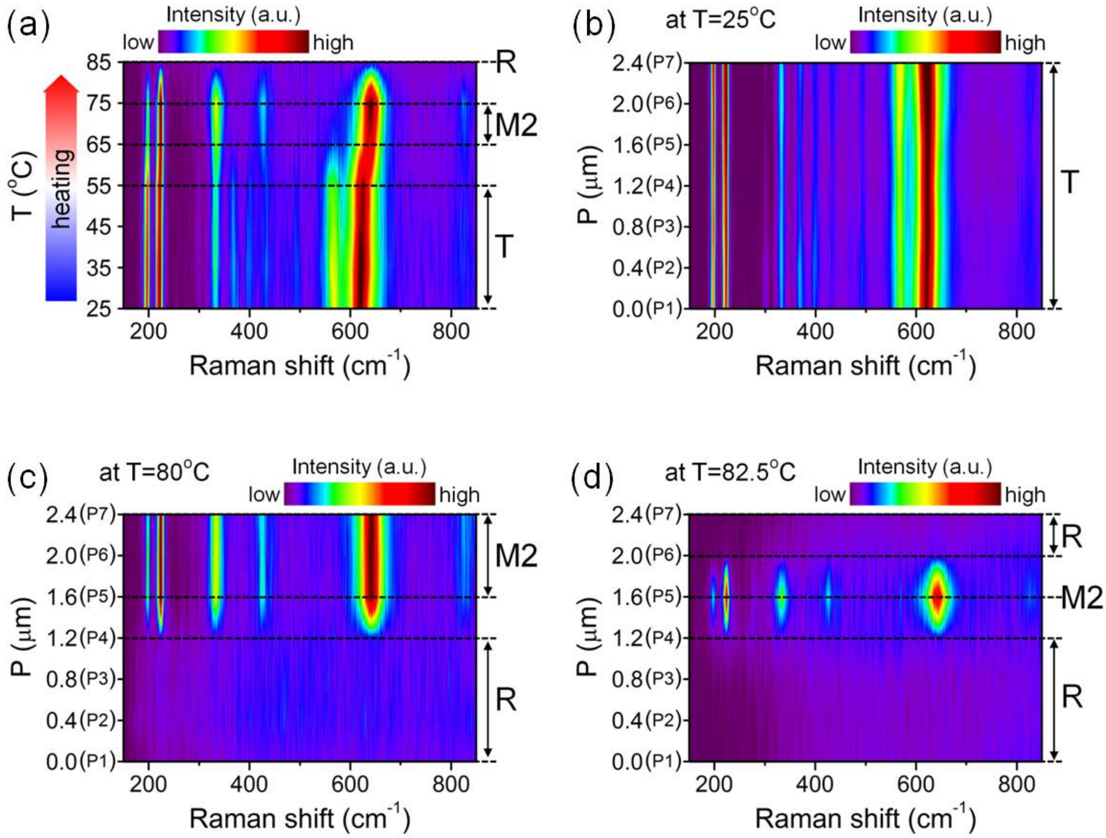

Fig. S7. Mapping images of the Raman spectra intensity of an individual VO_2 nanobeam under air (at the pressure of ~560 torr). (a) A mapping image of the Raman intensity at the position of P2 on the nanobeam (Figure 3a) as a function of temperature upon heating. (b-d) Mapping images of the Raman intensity as a function of position along the length of the nanobeam (from P1 to P7 in Figure 3a) at (b) 25 °C, (c) 80 °C, and (d) 82.5 °C upon heating, respectively.

8. Mapping images of the Raman spectra intensity of a VO_2 nanobeam under hydrogen gas

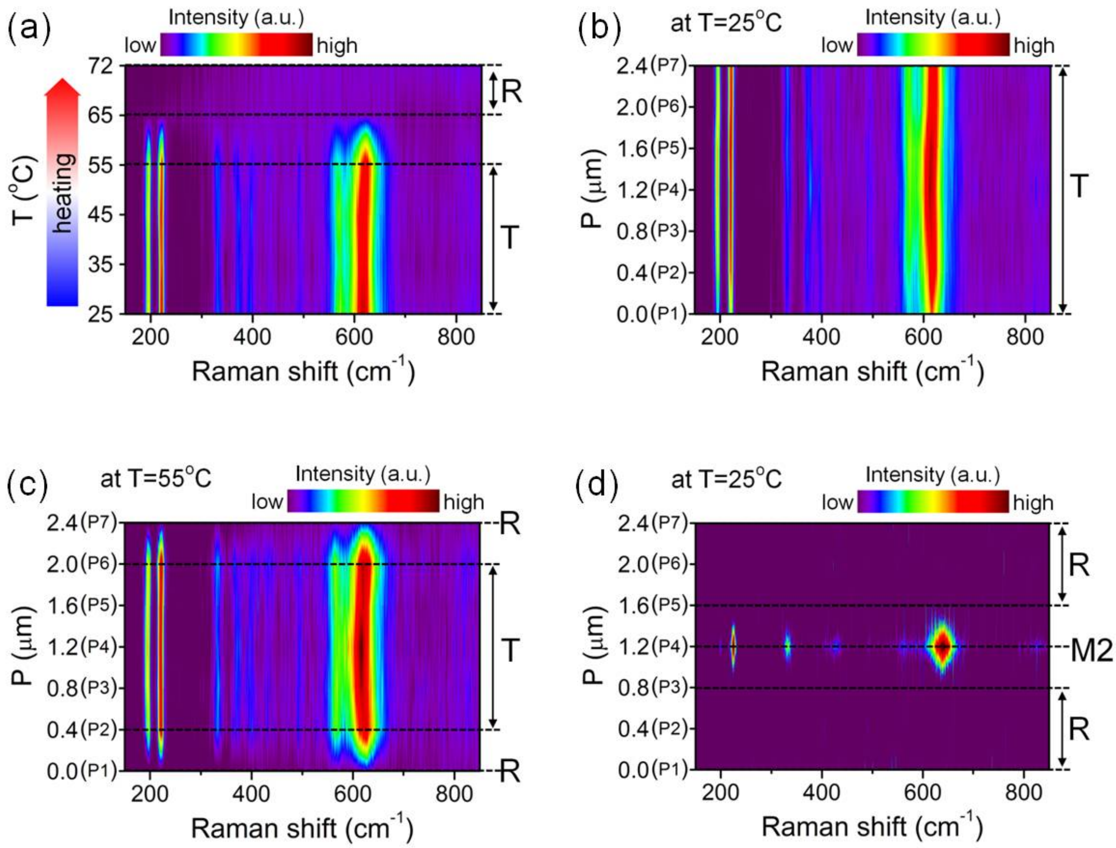

Fig. S8. Mapping images of the Raman spectra intensity of an individual VO_2 nanobeam under hydrogen gas (at the pressure of ~560 torr). (a) A mapping image of the Raman intensity at the position of P2 on the nanobeam (Figure 4a) as a function of temperature upon heating. (b-d) Mapping images of the Raman intensity as a function of position along the length of the nanobeam (from P1 to P7 in Figure 4a) at (b) 25 °C and (c) 55 °C upon heating, and (d) 25 °C upon cooling, respectively.

9. Mapping images of the Raman spectra intensity of a VO_2 nanobeam after 250 °C annealing process in air

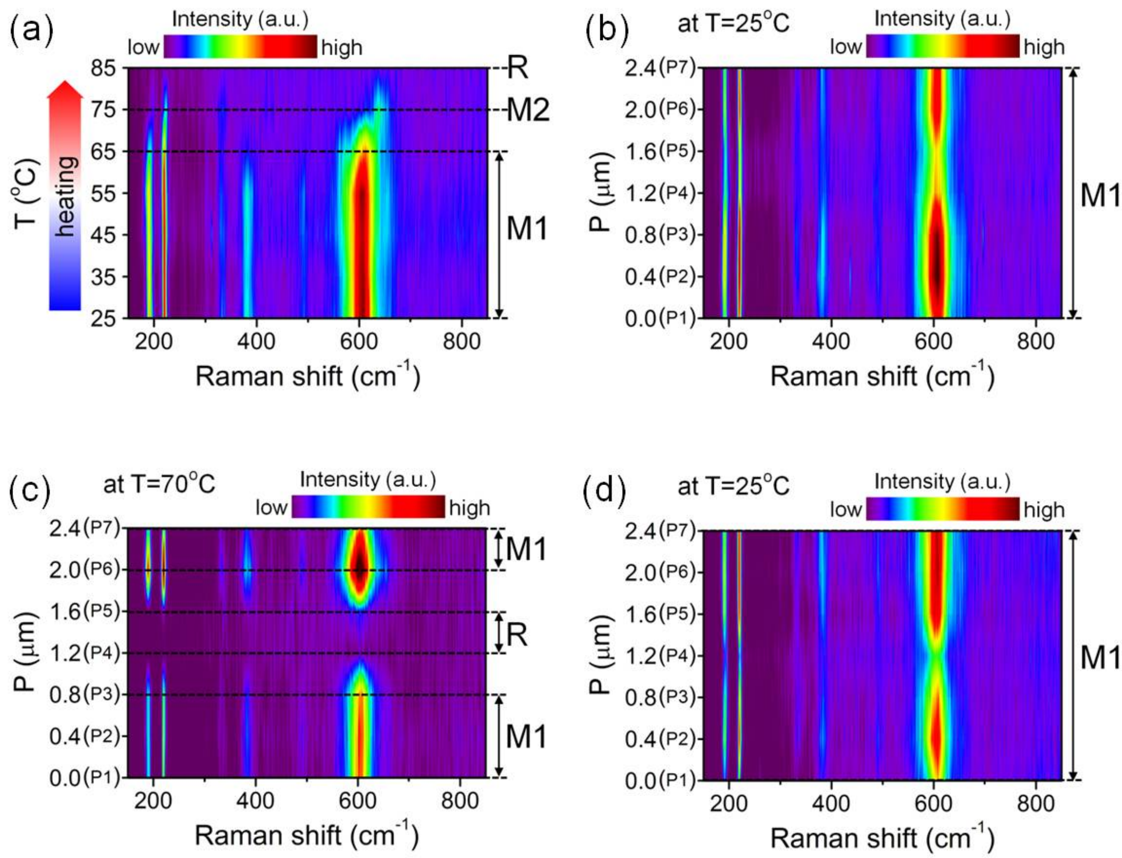

Fig. S9. Mapping images of the Raman spectra intensity of an individual VO_2 nanobeam under air (at the pressure of ~560 torr) after annealing at 250 °C in air. (a) A mapping image of the Raman intensity at the position of P2 on the nanobeam (Figure 5a) as a function of temperature upon heating. (b-d) Mapping images of the Raman intensity as a function of position along the length of the nanobeam (from P1 to P7 in Figure 5a) at (b) 25 °C and (c) 70 °C upon heating, and (d) 25 °C upon cooling, respectively.

10. *In Situ* Raman measurement conditions and corresponding phase evolutions in a VO_2 nanobeam

Table S1 Summary of *in situ* Raman probing of phase evolution in a VO_2 nanobeam.

Measurement conditions	Phase evolution at position P2 (Figs. 3-5)		Remarks
	Heating	Cooling	
~560 torr in air	T → M2 at 65 °C M2 → R at 85 °C	R → T at 35 °C	Transferred VO_2
~560 torr in hydrogen gas	T → R at 65 °C	R → R	Hydrogen-doped VO_2
~560 torr in air	M1 → M2 at 75 °C M2 → R at 85 °C	R → M1 at 55 °C	After annealing at ~250°C of hydrogen-doped VO_2