Supporting Information for:

Interplay between Ferroelastic and Metal-Insulator Phase Transitions in Strained quasi-2D VO₂ Nanoplatelets

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Figure S1

Examples of ferroelastic domain patterns observed in a polarizing microscope in VO₂ NPLs at room temperature. Images in panels (a)-(c) were taken in reflection (substrate is SiO₂/Si), images in (d) and (e) are in transmission (substrate is quartz). All images are bright-field. Note from the panel (b) that a critical width of the NPL is required to develop a 2D domain pattern.

Figure S2.

Monochromatic X-ray diffraction curves taken in θ - 2θ geometry from VO₂ NPLs on a Si substrate and from ground NPLs released from the substrate and imbedded into an Al holder. The curves were taken with Cu-K α radiation using a Micro Materials Analyzer MMA005 diffractometer from GBC Scientific Equipment Pty Ltd. Red and black bars show positions for diffraction peaks expected for M1 and M2 phases, respectively. No M2-phase peaks were found in the samples. Peaks marked with bullets are from the Si and Al holders, which can be verified by measuring a substrate and a holder without NPLs. A single VO₂ peak is observed on Si because the NPLs grow highly textured with $\{110\}_R \approx \{011\}_{M1}$ planes parallel to the surface.

Figure S3.

(a) An as-grown VO₂ NPl on a quartz substrate imaged with a Leica microscope of a confocal micro-Raman spectrometer (Renishaw 1000) under bright field conditions. Red arrow shows the polarization direction of the excitation radiation. (b) Typical Raman spectrum recorded from a NPl at room temperature. Only M1 phase peaks were identified (excitation laser wavelength $\lambda = 633$ nm, radiation power $W = 7$ μ W, laser spot size is about 1 μ m, spectrum integration time is 120 s). All peaks are ascribed to M1 phase according to refs s1 and s2. Nanoplatelets grown on SiO₂/Si substrate yield similar Raman spectra (not shown).

Figure S4

The result of incomplete chemical etching of the SiO₂ support layer onto the appearance of the ferroelastic domain structure in a VO₂ NPL. (a) At room temperature, the as-grown NPL is under 2D tensile strain due to a strong interaction with the SiO₂ substrate. (b) Partial etching of the SiO₂ layer leads to an increase of the domain size (width) due to partial relief of the substrate-induced tension. Complete etching of the oxide support eliminates the domain pattern. However in some experiments, metastable patterns with very wide domains were observed even after complete release of the NPL from the substrate.

Polychromatic x-ray microdiffraction

We used focused polychromatic synchrotron radiation to obtain Laue x-ray diffraction patterns from submicron areas of individual VO₂ NPLs. For these experiments, NPLs were grown on amorphous silicon nitride membranes supported by etched Si substrates to reduce background caused by substrate. The experiments were performed at beamline 34-IDE at the Advanced Photon Source (APS) at Argonne National Laboratory with a polychromatic ($\sim 8\text{--}28$ keV) X-ray beam focused to a diameter of ~ 0.5 μm .^{s3}

Figure S5 shows an example of a Laue image taken from one position on a NPL with clearly-visible domain structure at room temperature. Each Bragg peak in a Laue diffraction pattern shows the direction of the plane normal for some (hkl) planes. Thus, each pattern shows the angles between many different (hkl) planes or equivalently the directions of many $\mathbf{Q}(hkl)$ reciprocal lattice vectors. Since Laue images from VO₂ NPLs typically contain more than 100 peaks, indexation of the full pattern provides a stringent test for determining the shape of the crystal unit cell (angular resolution $\sim 0.01^\circ$). However, since the X-ray area detector (PerkinElmer amorphous Si) does not have energy resolution, we do not measure the magnitudes of the $\mathbf{Q}(hkl)$ vectors; i.e. this means we do not know the absolute lattice parameters and determine only α , β , γ and the ratios a/c , b/c , a/b . Starting with the literature values (from Inorganic Crystal Structure Database^{s4}) for the expected VO₂ structures (M1, M2, M3, and rutile), the Laue patterns

S6). It follows from the measured stereographic projections that the long in-plane axis of the NPl is the normal to the $(20\bar{1})_{M1}$ planes which is also the $a_{M1}=[100]_{M1}$ real-space direction or the $[001]_R=c_R$ rutile axis (light blue line in figure S6). This is an expected result. Then, to distinguish between twofold crystallographically equivalent orientations, we choose a notation convention where the $(20\bar{1})_{M1}$ pole is fixed to point towards the upper right side of the stereographic circle for this NPl. In this way, we fix orientation of the reference system where the structure is described. Then, the stereographic projection for each Laue pattern shows a unique domain orientation; i.e. the four different possible M1 orientations correspond to 90° rotations around the c_R axis.

The pole figures shown in figure S6 allow us to conclude that the orientation relation between the dark and light domains in the upper part of figure S6 can be described as either a 180° rotation around the c_{MI}^* axis (c_{MI}^* is the normal to the (001)_{MI} planes or the [102]_{MI} real-space direction or the [010]_R= b_{R} rutile axis) or equivalently as a 180° rotation around the long in-plane c_{R} axis of the NPI. At the same time, the domain in the lower part of the NPI is rotated 90° in respect to the two domains in the upper part of the NPI. This directly proves that the NPI is twinned at room temperature.

References

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- (s4) Inorganic Crystal Structure Database, <http://icsd.ill.eu/icsd/index.html>.