Strain engineering and one-dimensional organization of metal–insulator domains in single-crystal vanadium dioxide beams

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Correlated electron materials can undergo a variety of phase transitions, including superconductivity, the metal–insulator transition and colossal magnetoresistance. Moreover, multiple physical phases or domains with dimensions of nanometres to micrometres can coexist in these materials at temperatures where a pure phase is expected. Making use of the properties of correlated electron materials in device applications will require the ability to control domain structures and phase transitions in these materials. Lattice strain has been shown to cause the coexistence of metallic and insulating phases in the Mott insulator VO2. Here, we show that we can nucleate and manipulate ordered arrays of metallic and insulating domains along single-crystal beams of VO2 by continuously tuning the strain over a wide range of values. The Mott transition between a low-temperature insulating phase and a high-temperature metallic phase usually occurs at 341 K in VO2, but the active control of strain allows us to reduce this transition temperature to room temperature. In addition to device applications, the ability to control the phase structure of VO2 with strain could lead to a deeper understanding of the correlated electron materials in general. Lattice strain, if tuned continuously, would be a sensitive means to shed light on the origin of phase inhomogeneity. In contrast to conventional materials, where elastic deformation causes continuous, minor variations in material properties, lattice strain has a profound influence on the electrical, optical and magnetic properties of correlated electron materials (CEMs) through coupling between the charge, spin and orbital degrees of freedom of electrons. If phase correlations are dislocation-free, and can be subjected to coherent and continuously tunable external stress. CEM phase transitions and domain dynamics can then be explored through in situ microscopic experiments varying strain and temperature independently. Such an approach would enable, for the first time, probing of CEMs at the single domain level under continuous tuning of their lattice degree of freedom.

VO2 is a CEM that, in the strain-free state, undergoes a first-order metal–insulator phase transition (MIT) at \( T_C^0 = 341 \text{ K} \) with a change in conductivity of several orders of magnitude. The MIT is accompanied by a structural phase transition from the high-temperature tetragonal phase (metallic, M) to the low-temperature monoclinic phase (insulating, I). On cooling through the MIT, the vanadium ions dimerize and these pairs tilt with respect to the tetragonal c-axis, causing the specimen to expand by \( \epsilon_c \approx 1\% \) along the c-axis. Along the tetragonal a- and b-axes, on the other hand, the lattice shrinks by 0.6 and 0.1%, respectively, causing a volume expansion of 0.3% (refs 8–10). The relationship between the MIT and the accompanying structural transition in VO2 has been a topic of debate for decades.

As expected from the abrupt change in lattice constant with the phase transition, a uniaxial compressive (tensile) stress along the tetragonal c-axis direction would drive the system towards the M (I) phase. In the stress–temperature phase diagram, the rate at which the transition temperature \( T_C \) is modified by the uniaxial stress \( \sigma \) is given by the Clausius–Clapeyron equation,

\[
\frac{dT_C}{d\sigma} = \frac{(k_B T_C^0)}{\Delta H}
\]

where \( \Delta H \) is the latent heat of the transition. \( dT_C/d\sigma \) was measured to be \(~1.2 \text{ K kbar}^{-1}\) for c-axis uniaxial stress. As the volume change at the MIT is much weaker than the c-axis expansion, it is expected from the Clausius–Clapeyron equation that \( T_C \) is much more sensitive to uniaxial stress than to hydrostatic pressure. This offers an efficient way to organize M–I domains in single-crystal VO2 by imposing a uniaxial strain distribution. It has been shown that single-crystal VO2 nanobeams fully clamped on a SiO2 surface spontaneously exhibit periodic M–I domains near \( T_C^0 \) owing to uniaxial strain imposed by elastic mismatch with the substrate. The work was recently advanced by etching the fully clamped system into an end-clamped configuration, and interesting phase coexisting phenomena were observed. In the present work, instead of passively observing the strain effect, we fully eliminate the substrate-imposed strain and then induce and continuously modulate the MIT by artificially stressing the VO2. Single-crystal VO2 micro- and nanobeams were prepared with the length direction along the tetragonal c-axis (see Methods). We established coherent strain fields in the VO2 beams by bending or applying uniaxial stress. The small width and the single-crystal nature of these beams...
VO2. We generated a strain–temperature phase diagram for VO2, that allows them to withstand an extraordinarily high uniaxial strain (>2.5%, as compared to <1% in bulk) without plastic deformation or fracture. The system responded to the strain field by self-organizing one-dimensionally micro- to nanoscale M–I domains along the beam length. Such an active and continuous control of the phase inhomogeneity opens possibilities for device applications of the MIT in VO2.

Figure 1a–c shows low- and high-resolution images of typical VO2 beams. By adjusting the synthesis conditions, the beams can be grown with either a weakly coupled beam–substrate interface that slips to relieve stress, or a strongly coupled, clamped interface that pins the beam to the substrate. In the latter case thermal stress is imposed on the beams after cooling from the growth temperature to room temperature. Both types of beams were incorporated into four-probe devices using lithography. With increasing temperature, devices made from the unstressed beams displayed a sharp drop of resistance at $T_c = 341$ K (Fig. 1d, single-domain device). When heated through the transition temperature, the beam shows an abrupt change in brightness in white-light optical microscope images, from bright reflection in the low-temperature I phase to dark reflection in the high-temperature M phase. A direct correlation between optical contrast and the electronic phases is therefore established, where bright and dark reflection indicates the I and M phase, respectively.

Clamped VO2 beams of various widths (300 nm to 5 μm) displayed periodic M–I domains in high-resolution optical microscopy within the transition range (see Supplementary Information). Such a periodic domain pattern forms spontaneously as a result of the competition between strain energy in the elastically mismatched VO2/substrate system and domain wall energy in the VO2 (ref. 16). The period of the pattern is determined by the balance between the strain-energy minimization that favours small, alternating M–I domains and domain-wall energy minimization that opposes them. The domain structure could not be resolved by optical microscopy on beams narrower than 300 nm, and beams wider than 5 μm displayed an irregular, two-dimensional domain texture, possibly due to biaxial or non-uniform strain (as in the case of thin films). We focused our optical study on beams with widths between 1 and 2 μm, in which the micro-domains could be readily imaged and the local strain was easily controlled. In these beams a chain of M–I domains self-organize along the beam axis with a characteristic domain size comparable to the beam width.

To establish a wider range of coherent strain in the VO2 beam, we bent non-clamped beams on the substrate by pushing part of the beam with a microprobe. A large compressive (tensile) strain results near the inner (outer) edge of the high-curvature regions of the bent beam. Figure 2a shows the development of an array of triangular domains along a bent VO2 beam imaged at different temperatures. The bent beam was in I phase at room temperature.
At elevated temperatures, sub-micrometre, periodic triangular M domains started to nucleate at the inner edge of the bent region where the strain was the most compressive. These domains continued to grow and expand with increasing temperature, while the triangular geometry and periodic arrangement were maintained. At $T \approx T_{0} = 341$ K, the straight, strain-free part of the beam switched abruptly to the M phase as expected, while the bent part of the beam showed a nearly 50%–50% coexistence of M and I domains. These domains were highly periodic and triangular, with each triangle running through the entire width of the beam. As temperature further increased, the M phase expanded toward the outer edge and finally completely eliminated the I phase at $T \approx 383$ K. Upon cooling (not shown), the domain evolution was reversed, with a $\sim 10$ K hysteresis from the heating process. Therefore, the domain organization at the microscale evolves from a periodic, nanoscale phase nucleation.

To quantitatively understand the strain-stabilized M–I phase coexistence, the bent part of the beam is approximated with a constant curvature geometry in which the strain varies linearly from the outer to the inner edge along the radial direction. The optically determined M-phase fraction $\eta$, at each radius, was measured from Fig. 2a and plotted in $\sigma$–$T_{c}$ phase space in Fig. 2b. As expected, the system was in pure M phase ($\eta = 1$) at high temperatures and high compressive stresses, and in pure I phase ($\eta = 0$) at low temperatures and high tensile stresses. At intermediate temperatures and stresses, M and I phases coexisted with the spatial arrangement and relative fraction determined by energy minimization. According to equation (1), the boundary separating the M and I phases in the $\sigma$–$T_{c}$ phase diagram in Fig. 2b is directly related to the latent heat of the MIT. Fitting the experimental data using the upper and lower boundaries, we obtain a latent heat of $\Delta H$ between 1,200 and 950 cal mol$^{-1}$. This value is consistent with a $\Delta H$ of 1,025 cal mol$^{-1}$ reported for bulk VO$_2$ (refs 20,21). Note that these values are nearly four times higher than the latent heat calculated from the $\sigma$–$T_{c}$ data reported recently$^{17}$. This difference might be because the phase transition in ref. 17 is between another monoclinic phase (M$_{2}$) and the rutile M phase.

Assuming a linear M–I phase boundary, the $\sigma$–$T_{c}$ phase diagram predicts that a compressive strain of $\sim 2.2\%$ would be sufficient to drive VO$_2$ from I to M phase at room temperature. To test this prediction, we applied compressive stress directly along the length of a VO$_2$ beam clamped onto a soft substrate$^{22}$ and investigated how $\eta$ changed with external stress (see Methods). With increasing compressive

**Figure 2 | Strain-induced metal–insulator transitions along VO$_2$ beams.** a, Optical images of an array of triangular metallic (M, dark regions) and insulating (I, bright regions) domains nucleated and co-stabilized by tensile and compressive strain during heating. A colour-inverted image with better contrast between the I and M phases is included in the Supplementary Information. b, Phase diagram showing the fraction of the M phase (red is 100% M and blue is 100% I; see colour bar) as a function of temperature ($x$-axis) and uniaxial stress ($y$-axis, left) or strain ($y$-axis, right). Data were extracted by optical measurements from the bent beam shown in a, c, Uniaxial compression reversibly induces a metal–insulator transition (MIT) at room temperature in clamped VO$_2$ beams. The inset shows representative optical images of M–I domains along a stressed beam. d, Room-temperature $I$–$V$ characteristic of a VO$_2$ beam under different axial compressions, showing a MIT induced by Joule heating, with the threshold voltage and current both being significantly reduced by external compression. The experiment was carried out under ambient conditions. Scale bars in a and c, 10 $\mu$m.
stress along the beam axis, periodic M phase (dark domains) emerged out of the I phase (bright part) and gradually expanded, eventually merging to form a pure M phase beam. The VO2 beam was monitored optically and $\eta$ was measured as a function of the total strain. As shown in Fig. 2c, the beam remained entirely insulating ($\eta = 0$) until stressed to a total strain of $\varepsilon \approx -1.9\%$, then entered a strain regime where periodic M and I domains coexisted, ultimately reaching a full M state ($\eta = 1$) at $\varepsilon \approx -2.1\%$. Upon releasing the strain from the M state, the $\eta$-$\varepsilon$ curve showed a hysteretic behaviour and the beam returned to a full I state at $\varepsilon \approx -1.8\%$.

As the resistance of the VO2 beams changes by several orders of magnitude across the MIT, this actively controlled, room-temperature phase transition can be used as a 'strain-Mott' transistor. Very recently, Joule heating-induced MIT in single VO2 nanowires was used to achieve a novel type of gas sensor23. The nanowire was self-heated optically and $V_{th}$ was typically needed to achieve such device function23. The strain sensitivity of the MIT provides a strategy to drastically reduce the operation power and hence potentially increase the sensitivity and lifetime of these devices. In Fig. 2d we show such an effect observed from a self-heated VO2 device under uniaxial compression at room temperature. Over the range of compression, $V_{th}$ and threshold current were reduced by a factor of 5 to 6; consequently, the operation power was reduced by a factor of 30. Further compression directly drove the device to the M state without the need for Joule heating, which can be seen from the trend of decreasing resistance of the I phase at $V < V_{th}$. Active and extensive control of strain in these nano/microbeams thus offers a new ‘knob’ to tune the MIT for novel or improved device applications.

To understand if the domain patterns self-organized along the beams are to be expected given the material parameters of VO2 and the geometric dimensions of the beams, we implemented a two-dimensional phase field model, where the total energy $F(\phi)$ is equal to the sum of bulk thermodynamic energy, interfacial (domain wall) energy and strain energy,

$$F(\phi) = \int \left[ f(\phi) + \frac{\beta^2}{2} |\nabla \phi|^2 + \frac{1}{2} C_{ijkl}(\varepsilon_{ij} - \varepsilon_0^i)(\varepsilon_{kl} - \varepsilon_0^k) \right] dA$$

(2)

The parameter $\phi$ denotes the phase, where $\phi = 0$ corresponds to M and $\phi = 1$ corresponds to I. A double well potential $f(\phi)$ describes the relative thermodynamic energy of the M and I phases and is temperature dependent. The second term reflects the interfacial energy. The last term is the elastic energy, where $C$ is the elastic modulus tensor, $\varepsilon$ the strain, and $\varepsilon^T$ the lattice mismatch between the two phases: $\varepsilon^T_{ij}$ varies smoothly from $\varepsilon_0 = 0$ to 1% as the phase varies from $\phi = 0$ to 1, and $\varepsilon_{0}^{ij}$ and $\varepsilon_{0}^{kl}$ are 0. The parameters used in the modelling are typical for bulk VO2 (refs 16,19). In the simulations, the phase distribution evolves from an initial random phase distribution (Fig. 3a) according to Cahn–Allen dynamics under boundary conditions corresponding to a uniform beam bending. Videos showing the evolution of the phases and the accompanying relaxation of the strain field are available in the Supplementary Information.

At $T = T_C^0$, the equilibrium phase distribution shows a periodic, triangular domain pattern as shown in Fig. 3b, demonstrating quantitatively that realistic geometric, elastic and interfacial energy parameters give rise to the patterns observed in the experiment. This pattern nearly completely relieves the strain energy in the bent beam, with some remnant strain at the triangular tips (Fig. 3c). Between the upper and lower edges, the ratio of metal and insulator phases varies linearly for optimal strain energy relief, corresponding exactly to the initial linear variation of strain. The period varies for different interfacial energy density and

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Figure 3 | Phase field modelling of domain formation in a bent VO2 beam. a, At first, the metallic (M, dark green) and insulating (I, yellow) phases are randomly distributed at the natural MIT temperature, $T_C^0$. b, Equilibrium phase distribution showing a self-organized array of M and I phases at $T_C^0$. c, Equilibrium strain ($\varepsilon_{ij}$) distribution at $T_C^0$ yellow and dark green denote the maximum tensile and maximum compressive strain, respectively. d, Equilibrium strain energy density distribution: yellow denotes the highest strain energy density; dark green denotes the lowest. e, f, Equilibrium phase distribution showing more of the I phase (yellow) at a temperature below $T_C^0$ (e), and more of the M phase (dark green) above $T_C^0$ (f).

Figure 4 | Strain engineering domains in a VO2 beam. Before bending, the beam was purely insulating (bright, top image) at 298 K and purely metallic (dark, second image) at 343 K. A tungsten needle (denoted by the arrows) was used to push-bend the beam, which created I domain arrays in the strained regions. Scale bar, 10 µm.
elastic constants. Specifically, the period is determined by competing effects of strain energy relaxation and interfacial energy minimization: a smaller period results in more effective strain energy relaxation and interfacial energy minimization. The system considered corresponds to a beam of length 5 μm and width 1 μm, which is bent so that the strain on the upper and lower edge is 0.5% and ~0.5%, respectively.

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Author contributions

J.W. and J.C. conceived and planned the experiments. J.C. performed the experiments with assistance from W.F. E.E., V.S. and J.C.G. carried out the modelling. H.Z. performed the TEM. S.H., J.W.L.Y., D.R.K. and D.F.O. contributed to materials synthesis and analysis. J.C. and J.W. analysed the data and wrote the paper.

Additional information

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