Measurement of a solid–state triple point at the metal–insulator transition in VO₂

Jae Hyung Park1, Jim M. Coy1, T. Serkan Kasirga1, Chunming Huang2, Zaiyao Fei1, Scott Hunter1 & David H. Cobden1

First-order phase transitions in solids are notoriously challenging to study. The combination of change in unit cell shape, long range of elastic distortion and flow of latent heat leads to large energy barriers resulting in domain structure, hysteresis and cracking. The situation is worse near a triple point, where more than two phases are involved. The well-known metal–insulator transition in vanadium dioxide1, a popular candidate for ultrafast optical and electrical switching applications, is a case in point. Even though VO₂ is one of the simplest strongly correlated materials, experimental difficulties posed by the first-order nature of the metal–insulator transition as well as the involvement of at least two competing insulating phases have led to persistent controversy about its nature2–4. Here we show that studying single-crystal VO₂ nanobeams5–16 in a purpose-built nanomechanical apparatus allows investigation of this prototypical phase transition with unprecedented control and precision. Our results include the striking finding that the triple point of the metallic phase and two insulating phases is at the transition temperature, Tₘᵢₜ, which we determine to be 65.0 ± 0.1 °C. The findings have profound implications for the mechanism of the metal–insulator transition in VO₂, but they also demonstrate the importance of this approach for mastering phase transitions in many other strongly correlated materials, such as manganites17 and iron-based superconductors18.

The metal–insulator transition (MIT) in VO₂ is accompanied by a large and rapid change in the conductivity and optical properties, with potential uses in switching and sensing. VO₂ has recently received renewed attention as a convenient strongly correlated material for the application of new ultrafast19–24 and microscopy19–23 techniques, ionic gating24 and improved computational approaches24. However, the problems associated with bulk or film samples that consist of a complex of multiple solid phases and domains under highly non-uniform strain, as well as compositional variations such as oxygen vacancies25 and hydrogen doping26, make it almost impossible to disentangle the underlying parameters on which rigorous understanding can be built. The experiments described here eliminate these problems, allowing unprecedented control of the MIT and accurate determination of the underlying phase stability diagram of pure VO₂.

Figure 1a illustrates the structures of the phases involved in the MIT. In every phase there are two interpenetrating sets of parallel chains of vanadium atoms each surrounded by six oxygen atoms forming a distorted octahedron (the oxygen atoms are not shown). In the high-temperature metallic (rutile, R) phase all the chains are straight and periodic, whereas in the low-temperature insulating (monoclinic M1) phase every chain is dimerized. There are also two other known insulating phases: monoclinic M2, in which only one set of chains is dimerized, and triclinic T, which is intermediate between M1 and M2. The existence of both M1 and M2, with similar dielectric properties yet different magnetic properties, provides constraints on the theory of the MIT; for example, it rules out a purely Peierls-type mechanism2. In the older literature the MIT is taken to occur between R and M1, although recent studies9–10,25 have shown that M2 domains occur in most VO₂ samples near the MIT, raising the question of its role in the transition.

The largest difference in unit cell shape between R, M1 and M2 is along the pseudo-rutile c axis (the vanadium chain axis), with cₐ = 5,700 Å, cₐ₁ = 5,755 Å and cₐ₂ = 5,797 Å, as indicated in Fig. 1a. Compressive strain along this axis in an epitaxial film can lower the transition to room temperature15,22; thus, applying uniaxial tensile stress Pₓ along it can be used to control the transition13,15. A stability diagram in the Pₓ–T plane (with all other stress components zero) is expected to have the layout indicated in Fig. 1b. A shaded region indicates where the T phase occurs27. The effect of Pₓ on the phase stability (Fig. 1b) resembles that of stress along the [110] axis27 and of doping28 by chromium. Rough ideas of the locations of the three phase boundaries have been obtained by modelling bent nanobeams16. The triple point (Tₘᵢₜ, Pₓ) has not been located, although M1 and M2 are known to be very close in free energy near the transition27. The stress Pₓ is normally taken to be positive, implying that a perfect unstrained crystal...
shows a direct transition from M1 to R at $T_C$. We find that this is not in fact true, and $T_C$ is identical to $T_y$, to within $\pm 0.05 \, ^\circ$C, or one part in 10$^4$ absolute temperature. We further determine $T_y$ to be 65.0 $\pm 0.1 \, ^\circ$C. In addition we present evidence that in the neighbourhood of $T_y$, the M1 phase can distort continuously under tension into the metastable T phase. These discoveries have deep implications for the physics of the MIT, for the interpretation of many measurements on VO$_2$ crystals and films, and for mastering the transition with a view to applications.

Our investigations of the MIT rest on the ability to precisely control the length of a suspended single-domain nanobeam and thereby to apply pure uniaxial stress along it, a situation that cannot be achieved in larger crystals because of domain structure. The elements of the experiment are illustrated in Fig. 1c (see Methods). A VO$_2$ nanobeam is fixed, in some cases with electrical contacts, across a micromachined slot in a silicon chip whose width $L$ can be varied with nanometre precision. We perform measurements only when the nanobeams are straight, so the maximum compressive stress is limited by buckling. By varying $L$ and $T$, the three phases R, M1 and M2 can be induced and can be differentiated by reflection contrast with linearly polarized light,$^a$ as illustrated in Fig. 1d, as well as by Raman spectroscopy$^{14}$ and measurements of electrical resistance. Linearly polarized light also reveals twinning,$^{11}$ allowing us to select devices in which twinning is absent.

According to the phase diagram in Fig. 1b the state of the nanobeam as a function of $L$ and $T$ should include regions of two-phase coexistence as sketched in Fig. 2a. We find that the suspended part of the nanobeam can indeed be brought into coexistence between any pair of the three phases. The position of the interface moves smoothly and reproducibly with both $L$ and $T$ in between sudden reconfigurations. For the case of M2 + R coexistence we define the interface position $y_{M2R}$ as the shift relative to an initial position such that it increases as R converts to M2. We define $y_{M2M1}$ and $y_{M1R}$ similarly.

The MIT in VO$_2$ is usually studied as a function of $T$, without paying close attention to strain or to interconversion between M1 and M2. In undoped samples it is seen in the range 65–68 $^\circ$C, with a hysteresis of several degrees Celsius, and the value of $T_y$ is now known more precisely than this. In our experiments on nanobeams, as $T$ is varied at fixed $L$ we see the behaviour shown in Fig. 2b, which can be understood with reference to the colour-coded lines in the inset phase diagrams. If we start in M2 + M1 coexistence (Fig. 2b, upper panel, green) and increase $T$, the interface position $y_{M2M1}$ first moves smoothly as the stress required for phase equilibrium changes$^{13}$. Then at a temperature $T_{M1 \rightarrow R}$ there is a sudden reconfiguration to M2 + R coexistence (Fig. 2b, upper panel, red) after which the interface position $y_{M2R}$ moves smoothly again. On cooling, the reverse reconfiguration occurs at temperature $T_{R \rightarrow M1}$. Starting instead at a smaller length, in M1 + R coexistence (Fig. 2b, lower panel, blue), a jump to M2 + R coexistence (again red) occurs at $T_{M1 \rightarrow M2}$, whereas the reverse occurs at $T_{M2 \rightarrow M1}$. Histograms of the reconfiguration temperatures on repeated cycling at 0.1 $^\circ$C min$^{-1}$ are shown in Fig. 2c. For this device $T_{M1 \rightarrow R}$ and $T_{M2 \rightarrow M1}$ are narrowly peaked at 66.4 and 65.3 $^\circ$C, respectively; for other devices different values are found. This can be explained by superheating of M1, which varies between devices because the ease of nucleation of the high-temperature phase (R or M2) depends on microscopic details.

In contrast, $T_{R \rightarrow M1}$ and $T_{M2 \rightarrow M1}$ are both peaked at the same temperature, 65.0 $^\circ$C, indicated by the dotted line in Fig. 2c. In several nanobeams of different sizes, grown on different occasions, these two temperatures always lay in the narrow range between 64.9 and 65.2 $^\circ$C, moreover, neither storage in air for 6 months nor heating to 200 $^\circ$C for 1 h changed them, indicating that effects of oxygen vacancies$^{23}$ and hydrogen doping$^{26}$ were minimal. This observation can be explained as follows. A small amount of M1 is often visible at the interface in M2 + R coexistence, probably because it reduces the elastic energy. On cooling there is therefore no need for nucleation of M1, and reconfiguration occurs as soon as the triple point is reached. In fact, the dynamics of this process can sometimes be observed.

Figure 2d shows a sequence of images taken in less than a second during the reconfiguration of a nanobeam after bringing it slowly down to 65.0 $^\circ$C in M2 + R coexistence. A small pre-existing wedge of M1 at the M2 + R interface rapidly expands to replace the R part of the nanobeam completely. All the above observations thus suggest that the triple point is between 64.9 and 65.2 $^\circ$C.

We now consider varying $L$ at fixed $T$. First, in coexistence between any pair of phases the interface position is linear in $L$, as shown in Fig. 2e. This follows from the fact that the interface moves so as to maintain $P_i$ at the phase equilibrium value. A length increase $\delta L$ causes an interface shift $\delta y_{M1R}$ which changes the natural length by $\delta L$ to keep the strain constant. This implies that $\delta L = \frac{\delta y_{M1R}}{\frac{\partial y_{M1R}}{\partial L}}$, and similarly $\delta y_{M2M1} = \frac{\partial y_{M2M1}}{\partial L} = 1$. Hence $y_{M1R}$ should vary according to $\frac{\partial y_{M1R}}{\partial L} = \frac{\partial y_{M2M1}}{\partial L} = 1$. Best linear fits to the data given $y_{M2M1} = 0.0074$, $y_{M1R} = 0.0100$ and $y_{M2R} = 0.0174$, close to the values of 0.0073, 0.0098 and 0.0172 calculated from the known lattice constants.$^{28,29}$

The ability to control $L$ allows us to confirm the temperature of the triple point and to determine the behaviour very close to it. We exploit the fact that the electrical resistance of the nanobeam, $R_y$, is sensitive to the phase composition because each phase has a different resistivity.$^{12,13}$ The measurements in Fig. 3 are for a device (P10) with indium contacts. Figure 3a shows that at 65.3 $^\circ$C $R_y$ changes smoothly with $L$, as a result of a smoothly changing M2 + R interface position for $T > T_y$ (see inset, red line). In contrast, at 63.9 $^\circ$C it changes in a more complicated way, reflecting the sequence M1 + R→M1→M2 + M1

![Figure 2](image-url)
Figure 3 | Resistance–length measurements. a, At 65.3 °C, above the triple point (red line in inset), the resistance varies steadily in M2 + R coexistence. At 63.9 °C, below the triple point (blue line in inset), it reflects a sequence of transitions (device P10: L is varied at 8 nm s⁻¹). b, Starting in the R state, M2 nucleates if \( T \approx 65.10 \) °C (red), whereas M1 nucleates if \( T \approx 64.95 \) °C (blue), implying that these lie on either side of \( T_{tr} \) (see inset). c, The variation of the resistance with \( L \) is due to a strain-dependent activation energy in the M1 phase (dotted lines, offset by \(-0.15 \) M2 for clarity) and to conversion of M1 to M2 in coexistence (dashed line). Grey lines indicate an additional transition rise attributed to the T phase.

expected for \( T < T_{tr} \) (see Fig. 3a inset, blue line). Jumps and hysteresis here show that M1 and M2 both require nucleation, which is consistent with the transitions being first order. To establish \( T_{tr} \) we measured \( R_{tr} \) at a series of closely spaced temperatures, each time preparing the nanobeam in a fully metallic R state by cooling at sufficiently small \( L \) for R to be stabilized by compression, and then increasing \( L \) until an insulating domain nucleated. At 64.95 °C and below, the domain that appeared was always M1, whereas at 65.10 °C and above it was always M2, implying that \( T_{tr} \) was between these two values (see Fig. 3b). This is perfectly consistent with the range of \( T_{tr} \) deduced above from the T-sweeping measurements. Including uncertainties from variation between samples, temperature fluctuations and calibration, we conclude that \( T_{tr} = 65.0 \pm 0.1 \) °C.

Measurements of resistance versus length also yield other useful information, as illustrated in Fig. 3c (see Supplementary Information for details). First, the variation of the resistance of the M1 state with \( L \) and \( T \) is explained by a linear increase in the activation energy of the resistance with tensile strain \( \eta = (L - L_0)/L_0 \) being the effective natural length. The dotted lines are plots of \( R_n \propto \exp \left[ -(D_0 + \gamma \eta)/k_B T \right] \) using coefficient values \( D_0 = 0.31 \) eV and \( \gamma = 0.77 \) eV (the uncertainty in \( \gamma \) is 10%), where \( k_B \) is Boltzmann’s constant. Second, from the variation of \( R_n \) in M1 + M2 coexistence (such as that indicated by the dashed line) we can deduce that \( \rho_{M2}/\rho_{M1} \approx 2.3 \pm 0.2 \) and that the activation energies of M1 and M2 are the same to within a few per cent. Third, a distinct additional increase in \( R_n \) indicated by the solid grey lines, precedes the nucleation of M2 from M1. This can be explained by a continuous distortion of M1 into the T phase, which we immediately infer has a higher resistivity than M1 and is unstable relative to M2 at all temperatures from \( T_{tr} \) to below 26 °C.

Although we cannot measure the axial stress \( P_c \) directly, we can realize the condition \( P_c = 0 \) simply by breaking a nanobeam with a micromanipulator after other measurements have been completed. This produces opposing cantilevers, as illustrated in Fig. 4a. If the cantilevers are prepared in the fully M1 state by warming from lower temperature to around \( T_{tr} \) and are then brought together, the compression produces a domain of R phase in one of them. After retraction, this domain persists only above a certain temperature, and shrinks and disappears below it. We identify this temperature with \( T_c \), the transition temperature at zero stress. By performing the procedure on several devices we obtained the striking result that in every nanobeam \( T_c \) was equal to \( T_{tr} \) to within an uncertainty of \( \sigma T \approx 0.05^\circ \)C governed by temperature fluctuations. We thus conclude that \( T_c = T_{tr} = 65.0 \pm 0.1 \) °C.

Figure 4b shows the phase diagram of VO₂ inferred from measurements on ten nanobeams (see Supplementary Information for details). In brief, the \( P_c(T) \) were deduced from measurements of \( y_{ij} \) (i, j = M1, M2, R) versus \( T \) as follows. Because the stress in coexistence must take the phase equilibrium value, consideration of the variation of the

Figure 4 | Phase diagram of VO₂. a, The transition temperature \( T_c \) at zero stress is measured by finding the temperature above which the metallic phase (darker) becomes stable in a cantilever, as illustrated here (device P8). It is found to be equal to the triple point temperature: \( T_c = T_{tr} = 65.0 \pm 0.1 \) °C.

b, Deduced stress–temperature phase diagram. The small black filled circles are for the superheated M1 phase. The grey shaded strip is where a metastable T phase can occur. c, The results imply that the free energies of all the phases are degenerate at \( T_c \) in unstrained pure VO₂.
strain $\eta = P/E$ with $T$ (E is Young’s modulus, taken to be 140 GPa for every phase) yields$^3$

$$\frac{1}{E} \frac{\partial P_i}{\partial T} = \frac{d\eta}{dT} = -\frac{\partial S_{ij}}{L_0 \partial T} - \Delta K$$

(1)

The first term on the right is the change due to movement of the interface. The second, $\Delta K$, is the thermal expansion mismatch between nanobeam and silicon substrate, which produces a correction of 5–10%. Given that $\eta = (\partial S_{ij}) = 0$, equation (1) can be used to derive, with $\eta(T)$ for each boundary. The deduced phase boundaries are in their slopes with uncertainties in their slopes of 5–10%, and obey the constraint at the triple point

$$\frac{d\eta}{dT} = \frac{\partial P_i}{\partial T}$$

(2)

which is imposed by the Clausius–Clapeyron relations

$$\frac{d\eta}{dT} = \frac{S_j - S_i}{\mathbf{b}^T (a_j - a_i)} = \frac{S_j - S_i}{\alpha V}$$

(3)

in combination with equation (1). Here $S_j$ is the entropy per vanadium

phase in phase $b$, $b = 4.55 \text{Å}$ is the base length of the rutile unit cell, and $V = 59.1^3$ is the rutile unit cell volume. The value of $\partial P_i/\partial T = 71 \text{MPa} \cdot \text{C}^{-1}$ corresponds to the known latent heat of 1,020 cal per mole formula unit; $\partial P_i/\partial T = 29 \text{MPa} \cdot \text{C}^{-1}$ corresponds to 710 cal mol$^{-1}$; and $\partial P_i/\partial T = 29 \text{MPa} \cdot \text{C}^{-1}$ from the results we deduce entropy differences $S_R - S_M = (3.0 \pm 0.3) k_B$ and $S_R - S_M = (2.1 \pm 0.1) k_B$. The equality of $T_C$ and $T_R$ to within $\delta T = 0.05 \text{°C}$ implies that the strain $\eta_i$ at the triple point is smaller than $\delta T d\eta_j/\partial T = 1 \times 10^{-3}$, where $d\eta_j/\partial T = 2.0 \times 10^{-3} \text{°C}^{-1}$, and this is also indicated on the phase diagram. Finally, the finding that the T phase is metastable with respect to M2 is indicated by a grey shaded strip within the M2 stability region.

To stress the implication of these results we sketch in Fig. 4c the $T$ dependence of the Gibbs free energies $G_i$ of the phases of unstrained VO$_2$, setting $G_R = 0$. The slopes are the entropies $S_j = -\mathbf{d} G_i/\mathbf{d} T$ at zero stress. Precisely at the MIT the insulating M1 and M2 phases are simultaneously degenerate with the metallic R phase. This and other facts revealed by our measurements are not explained by current models of the transition, but will be crucial ingredients of the correct theory.

METHODS SUMMARY

VO$_2$ nanobeam grown by physical vapour transport were transferred onto slots on the micromachined silicon chips by using a micromanipulator and bonded with ultraviolet-curable epoxy (see Supplementary Information). Measurements from ten chips were used, and the temperature was calibrated with the known melting points of gallium and potassium (Supplementary Information). The slot width $L$ (20 or 40 μm) was varied piezoelectrically on a temperature stage under an optical microscope (Supplementary Information).

Online Content  Any additional Methods, Extended Data display items and Source Data are available in the online version of the paper; references unique to these sections appear only in the online paper.

Received 12 April; accepted 24 June 2013.

1. Zybertzejin, A. & Mott, N. F. Metal–insulator transition in vanadium dioxide. Phys. Rev. B 13, 4383–4395 (1975).
2. Rice, T. M., Launois, H. & Pougnet, J. P. Comment on ‘VO$_2$ Peiers or Mott–Hubbard? A view from band theory’. Phys. Rev. Lett. 73, 3042 (1994).
3. Biermann, S., Poteryaev, A., Lichtenstein, A. I. & Georges, A. Dynamical singlets and correlation-assisted Peiers transition in VO$_2$. Phys. Rev. Lett. 94, 026404 (2005).
4. Eyert, V. VO$_2$: a novel view from band theory. Phys. Rev. Lett. 107, 016401 (2011).
5. Wu, J. Q. et al. Strain-induced self organization of metal–insulator domains in single-crystalline VO$_2$ nanobeam. Nano Lett. 6, 2313–2317 (2006).
6. Guo, H. et al. Mechanics and dynamics of the strain-induced M1–M2 structural transition in individual VO$_2$ nanowires. Nano Lett. 11, 3207–3213 (2011).
7. Adkin, J. M. et al. Strain and temperature dependence of the insulating phases of VO$_2$ near the metal–insulator transition. Phys. Rev. B 85, 020101(R) (2012).
8. S Koh, J. et al. Surface-stress-induced Mott transition and nature of associated spatial phase transition in single-crystalline VO$_2$ nanowires. Nano Lett. 9, 3392–3397 (2009).
9. Zhang, S. X., Chou, J. Y. & Launon, L. J. Direct correlation of structural domain formation with the metal insulator transition in a VO$_2$ nanobeam. Nano Lett. 9, 4527–4532 (2009).
10. Tsiev, A. et al. Symmetry relationship and strain-induced transitions between insulating M1 and M2 and metallic R phases of vanadium dioxide. Nano Lett. 10, 4409–4416 (2010).
11. Tsiev, A. et al. Interplay between ferroelastic and metal–insulator phase transitions in strained quasi-two-dimensional VO$_2$ nanoplatelets. Nano Lett. 10, 2003–2011 (2010).
12. Cao, J. et al. Constant threshold resistivity in the metal-insulator transition of VO$_2$. Phys. Rev. B 82, 241101(R) (2010).
13. Wei, J. et al. Strain engineering and one-dimensional organization of metal–insulator domains in single-crystal vanadium dioxide beams. Nature Nanotechnol. 4, 420–424 (2009).
14. Kasirga, T. et al. Photoresponse of a strongly correlated material determined by scanning photocurrent microscopy. Nature Nanotechnol. 7, 723–727 (2012).
15. Wu, J. Q. et al. Strain engineering and one-dimensional organization of metal–insulator domains in single-crystal vanadium dioxide beams. Nature Nanotechnol. 4, 732–737 (2009).
16. Cao, J. et al. Extended mapping and exploration of the vanadium dioxide stress–temperature phase diagram. Nano Lett. 10, 2667–2673 (2010).
17. Podzorov, V., Kim, B. G., Kryukhin, V., Goehring, A. & Cheong, S. W. Martensitic accommodation strain and the metal–insulator transition in manganites. Phys. Rev. B 64, 140406(R) (2001).
18. Chu, J.-H., Kuo, H.-H., Anis, J. G. & Fisher, R. Divergent nematic susceptibility in an iron arsenide superconductor. Science 337, 710–712 (2012).
19. Becker, M. F., Buckman, A. B. & Walser, R. M. Femtosecond laser excitation of the semiconductor–metal phase transition in VO$_2$. Appl. Phys. Lett. 65, 1507–1509 (1994).
20. Hilton, D. J. et al. Enhanced photosusceptibility near $T_c$ for the light-induced insulator-to-metal phase transition in vanadium dioxide. Phys. Rev. Lett. 99, 226401 (2007).
21. Kubler, C. et al. Coherent structural dynamics and electronic correlations during an ultrafast insulator-to-metal phase transition in VO$_2$. Phys. Rev. Lett. 99, 116401 (2007).
22. Qazilbash, M. M. et al. Mott transition in VO$_2$ revealed by infrared spectroscopy and nano-imaging. Science 318, 1750–1753 (2007).
23. Jones, A. C., Berweger, S., Wei, J., Cobden, D. & Raschke, M. B. Nano-optical investigations of the metal–insulator phase behavior of individual VO$_2$ microcrystals. Nano Lett. 10, 1574–1581 (2010).
24. Nakano, M. et al. Collective bulk carrier delocalization driven by electrostatic surface charge accumulation. Nature 487, 449–462 (2012).
25. Jeong, J. et al. Suppression of metal–insulator transition in VO$_2$ by electric field–induced oxygen vacancy formation. Science 339, 1402–1405 (2013).
26. Wei, J., Ji, H., Guo, W. H., Nevidomskyy, A. H. & Nafis, J. Hydrogen stabilization of metallic vanadium dioxide in single-crystal nanobeam. Nature Nanotechnol. 7, 357–362 (2012).
27. Pouget, J. P., Launois, H., Dhahenens, J. P., Merenda, P. & Rice, T. M. Electron localization induced by uniaxial stress in pure VO$_2$. Phys. Rev. Lett. 35, 873–875 (1975).
28. Marezio, M., McWhan, B., Dernier, P. D. & Remeika, J. P. Structural aspects of metal–insulator transitions in Cr-doped VO$_2$. Phys. Rev. B 5, 2541–2551 (1972).
29. Kucharczyk, D. & Nikielski, T. Accurate X-ray determination of the lattice parameters and the thermal expansion coefficients of VO$_2$ near the transition temperature. J. Appl. Crystallogr. 12, 370–373 (1979).
30. Berglund, C. N. & Guggenheim, H. J. Electronic properties of VO$_2$ near the semiconductor–metal transition. Phys. Rev. 185, 1022–1033 (1969).