New aspects of the metal-insulator transition in single-domain vanadium dioxide nanobeams

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Many strongly correlated electronic materials have a domain structure that greatly influences the bulk properties and obscures the fundamental properties of the homogeneous material. Nanoscale samples, on the other hand, can be smaller than the characteristic domain size, thus making it possible to explore these fundamental properties in detail. Here, we report new aspects of the metal-insulator transition\(^n\)\(^{13}\), studied in single-domain vanadium dioxide nanobeams\(^n\)\(^{3-6}\). We have observed supercooling of the metallic phase by \(50\) \(^\circ\)C, an activation energy in the insulating phase that is consistent with the optical gap, and a connection between the metal-insulator transition and the equilibrium carrier density in the insulating phase. Our devices also provide a nanomechanical method for determining the transition temperature, enable measurements on individual metal-insulator interphase walls to be made, and allow general investigations of phase transitions in quasi-one-dimensional geometries.

Bulk vanadium dioxide, VO\(_2\), is a poor metal above a critical temperature \(T_c\) of \(68\) \(^\circ\)C, and below this temperature it is a semiconductor with an optical gap \(E_g\) of 0.6 eV. The transition to the metal can be induced very rapidly and has recently been studied intensively using ultrafast techniques\(^n\)\(^{8-14}\). The lattice in the metallic phase has the rutile structure, with the vanadium ions arranged in periodic chains parallel to the c-axis. In the insulating phase these are distorted into dimerized zigzag chains, resulting in a monoclinic structure known as M1. Many factors indicate that the transition involves strong electron–electron correlations, as in a Mott transition. These include the anomalously low conductivity and other properties of the metal\(^n\)\(^{15-17}\), the fact that band structure calculations fail to yield the insulator bandgap\(^n\)\(^{13-18}\), the fact that an intermediate M2 structure, which can be stabilized by stress\(^n\)\(^{19}\) or doping\(^n\)\(^{20}\), is insulating in spite of having undimerized vanadium chains\(^n\)\(^{21}\), and the dependence on excitation power in optical experiments, which indicates sensitivity to excited carrier density\(^n\)\(^{10,13,12}\). However, the nature of the transition is still quite unclear even half a century after its discovery\(^1\), and potential applications in electrical\(^n\)\(^{23}\) and optical\(^n\)\(^{24}\) switching or detection, for example, remain unrealized. The blame for this falls largely on the domain structure produced on passing through the metal–insulator transition (MIT)\(^n\)\(^{25}\), which leads to irreproducibility between samples (properties such as resistivity are very sensitive to the arrangement of domains), broadening and hysteresis of the characteristics, and non-uniform stresses producing mechanical degradation\(^n\)\(^{15}\). All these problems are absent in our nanobeam devices, which are smaller than the characteristic domain size.

The nanobeams were grown directly on oxidized silicon wafers by a physical vapour transport technique based on that introduced by Park’s group\(^n\)\(^{15}\). The substrate was placed in 20 mbar argon carrier gas downstream from a granular VO\(_2\) source in a tube furnace at 1,000 \(^\circ\)C for 30 min. Each nanobeam is a single crystal elongated along the rutile c-axis. The length can be hundreds of micrometres and the cross-section is roughly rectangular, the width \(W\) ranging down to 50 nm and thickness \(H\) down to 15 nm, as determined by atomic force microscopy. As reported by others\(^5\), on warming, quasiperiodic thin stripes of darker metallic phase can be seen to appear around \(65\) \(^\circ\)C in an optical microscope (Fig. 1a). These stripes then widen and eventually merge, and the insulating phase disappears by \(\sim 105\) \(^\circ\)C. This behaviour results from strain caused by firm attachment to the SiO\(_2\) substrate. A fully insulating nanobeam is under compressive axial strain, whereas a fully metallic one, having a smaller equilibrium c-axis lattice constant, is under tension. Alternation of metallic and insulating regions reduces the average strain at the cost of creating interphase walls. Park’s group\(^5\) has also found that if the nanobeams are released from the substrate, completely relieving the strain, the transition becomes sudden with no stable domain pattern formation.

Here, rather than eliminating the axial strain, we take advantage of it. Using electron-beam or optical lithography we patterned a series of electron-beam evaporated metal contacts (typically 10 nm vanadium under 400 nm gold) onto each nanobeam, and then immersed it in buffered oxide etch to remove the 1-\(\mu\)m-thick SiO\(_2\) beneath it where it was not covered by metal, thereby suspending the nanobeam sections between the contacts. The behaviour of many of the resulting devices, under repeated cycling in air between room temperature \(T_{\text{room}}\) and 120 \(^\circ\)C, is reproducible over a period of months. Unlike bulk crystals, these nanobeams do not degrade or fracture. At \(T_{\text{room}}\) shorter sections are straight and longer ones are buckled (see Fig. 1b). This is consistent with the behaviour of clamped beams, in which Euler buckling occurs when the compressive axial stress \(P\) exceeds a critical value \(P_c\), which is smaller for longer beams. Firm adhesion to the substrate under the contacts provides the clamping. After buckling, the compressive strain \(\eta\) is much smaller and the nanobeam adopts approximately its natural length \(L_o\). By taking \(L_o\) to be the length along the curved profile of a buckled section measured in an atomic force microscope, and calling the contact separation \(L\), we find that the substrate-induced strain in most nanobeams at \(T_{\text{room}}\) is \(\eta_o = (L_o - L)/L = 0.4 \pm 0.1\%\). This is consistent with an 0.7% thermal contraction of the rutile VO\(_2\) relative to the substrate followed by a 1.1% expansion on conversion to the M1 form during cooling from the growth temperature\(^n\)\(^{26,27}\).

Seen in an optical microscope, between \(\sim 68\) and 105 \(^\circ\)C every segment of each nanobeam is unbuckled, and in nearly all cases each consists of one metallic and one insulating region coexisting and separated by a single interphase wall (see Fig. 1c). As \(T\) increases, the fraction \(x\) of the insulating phase, plotted in Fig. 1d, decreases steadily until at a temperature \(T_{\text{in}}\) in the vicinity of 105 \(^\circ\)C the nanobeam becomes fully metallic. This behaviour can be understood by noting that given fixed \(L\), once the nanobeam begins to convert from insulator to metal its equilibrium length \(L_o\) decreases because of the shorter c-axis of the metal, and therefore so do both \(\eta\) and \(P\). At any particular \(T\) the fraction \(x\) of insulator adjusts so that \(P\) is appropriate for the two phases to coexist, that
is, to lie on the phase boundary line between insulator and metal in the $(P,T)$-plane, as sketched in Fig. 1e. The stress $P$ should be zero at $T = T_c$ and negative (tensile) at higher $T$, explaining why all nanobeams become straight above ~68°C.

The nanobeam thus provides a one-dimensional analogue of the three-dimensional situation of water held at constant volume near 0°C. In this case, too, the low-$T$ phase (ice) has higher volume and lower symmetry than the high-$T$ phase (liquid water), and the fraction $x$ of ice decreases as $T$ increases in a corresponding way. It is also worth noticing that in the coexistence regime the nanobeam has zero axial stiffness, just as the ice–water mixture has diverging isothermal compressibility.

If we assume the Young’s modulus $E$ is the same for both phases then the strain $\eta(T)$ is uniform along the nanobeam and the equilibrium phase boundary line $P(T)$ is determined by

$$P(T)/E = \eta(T) = \alpha(x - x_c) + K(T - T_c) \quad (1)$$

The first term on the right represents interconversion between the phases, where $\alpha$ is the fractional increase in rutile $c$-axis length going from metal to insulator and $x_c$ is the insulating fraction at $T = T_c$. The second term represents differential thermal expansion of the VO$_2$ relative to the silicon substrate. It is an order of magnitude smaller than the first term, $K$ being about $+2.0 \times 10^{-5}$ C$^{-1}$ and assumed the same for both phases$^{1,25,27}$.

According to equation (1), for every nanobeam $x$ should have the same variation with $T$ to within an offset $x_c$ that depends on the built-in strain relative to the substrate and may vary with growth conditions. The data in Fig. 1d agree well with this prediction, supporting the assumptions made above. Moreover, we observe that $x(T)$ is nearly a straight line, with $dx/dT = -(1.10 \pm 0.05) \times 10^{-5}$ C$^{-1}$. This implies that the phase boundary line is nearly straight over the experimental temperature range so that we can simply write

$$P(T)/E = \beta(T - T_c) \quad (2)$$

where $\beta = \alpha dx/dT + K$ is the (negative) rate of change of strain with temperature. According to equation (2), $P$ will become positive when a nanobeam in coexistence is cooled below $T_c$, and upon further cooling we expect the nanobeam to buckle at the temperature $T_b$, for which $P(T_b) = P_b$. Using the Euler expression for the buckling pressure of a doubly clamped beam, $P_b = (\pi^2 E/3)H^2/L^2$, we then have

$$\beta(T_b - T_c) = (\pi^2 / 3)H^2/L^2 \quad (3)$$

Equation (3) predicts that a plot of $T_b$ versus $1/L^2$ will yield a straight line with $y$-intercept $T_c$. We construct such a plot in Fig. 1f for a series of sections of a nanobeam of thickness $H = 180 \pm 5$ nm. The data are indeed well fitted by the straight line shown, with $y$-intercept $T_c = 65.7 \pm 0.2$ °C.

This represents a completely new way of measuring the transition temperature, making use of coupling of the phase transition to nanomechanical motion. Unlike other methods it is independent of hysteresis at the transition. In fact, the more general procedure of finding lim$_{\lambda \to 0}(T_b)$ should yield $T_c$ independently of the assumptions made above, provided only that the phase boundary is well behaved. This could be used, for example, to methodically study variations in the phase boundary between samples or in response to modified external conditions.

We can also use equation (3) to obtain $\beta$ from the slope $dP_b/d(L^{-2}) = -820 \pm 20$ °C·μm$^{-2}$ of the line, giving $\beta = (\pi^2 H^2/3)/[dP_b/d(L^{-2})] = (-13 \pm 1) \times 10^{-5}$ C$^{-1}$. Using

Figure 1 | Metal–insulator transition in VO$_2$ nanobeams studied by microscopy. a, Six images of a 40-μm-long part of a single nanobeam attached as grown to an SiO$_2$ substrate, taken at the indicated temperatures during warming, showing metallic domains (darker) appearing, widening and merging. b, Scanning electron microscopy image of a suspended nanobeam device showing that longer sections are buckled at room temperature. c, Five images of one suspended nanobeam between contacts at the top and bottom separated by 20 μm. Above 68 °C it contains a single metallic domain (grey), which grows on warming until the insulating domain (purple) disappears at ~105 °C. d, Plot of the insulating fraction $x$ versus $T$ for six suspended nanobeams of various dimensions, showing that, to within a constant offset, $x$ always has the same linear variation in coexistence. e, Sketch of the phase diagram indicating part of the trajectory (red) followed on a temperature cycle starting at room temperature (left of figure). The vertical axis is uniaxial pressure $P$. The green circle indicates the point at which the nanobeam buckles on cooling. f, Plot of buckling temperature $T_b$ versus inverse square length for a nanobeam (thickness $H = 0.18$ μm, width $W = 0.9$ μm) yielding a straight line for which the $y$-intercept should be $T_c$. 

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the estimate\(^{29}\) \(E \approx 140\) GPa, we can then quantify the stress in the nanobeam: the phase boundary slope is \(\beta E \approx -18\) MPa °C\(^{-1}\), and the largest tension, reached at \(T = T_m \approx 110\) °C, is \(P_m = \beta E(T_m - T_c) \approx -0.7\) GPa. For \(T > T_m\) the nanobeam is fully metallic and thermal expansion causes the tension to decrease again, at a rate \(dP/dT = K \epsilon \approx +2.5\) MPa °C\(^{-1}\), as indicated in Fig. 1e. Also, using this value for \(\beta\) we find \(\alpha = (\beta - K)/(d\epsilon/dT) = 1.36 \pm 0.15\%\). The discrepancy with the accepted value\(^{25}\) of \(\alpha = 1.0\%\) could be partly due to the phases having different elastic moduli or to the intermediate M2 insulating phase (see below).

Measurements of the two-terminal electrical resistance \(R\) in the coexistence regime yield a number of interesting results. Figure 2a shows the characteristics on repeated thermal cycling of four nominally equal sections (A–D) of a single nanobeam. Each comprises smooth \(R\) versus \(T\) curves punctuated by sudden jumps. On warming from \(T_{\text{room}}\) \(R\) initially decreases in a semiconducting manner. It drops sharply at a temperature \(T_s \approx 65–68\) °C when a metallic region appears and the nanobeam becomes straight. Subsequently, in the coexistence regime, as the insulating region shrinks \(R\) decreases steadily to a much smaller value at \(T_m \approx 105\) °C at which the insulator disappears. The coexistence curve is reproducible on sweeping up and down at 6 °C min\(^{-1}\) as long as \(T\) is kept below \(T_m\). On the other hand, on cooling from above \(T_m\) each section remains fully metallic down to a lower temperature \(T_s\) at which an insulating region suddenly appears and \(R\) jumps up to the coexistence curve. \(T_s\) varies greatly between sections, from \(78\) °C (section A) to \(55\) °C (section D).

During further cooling, \(R\) increases smoothly until the nanobeam buckles at \(T_b \approx 57.5\) °C. Below that, the temperature \(T_s\) at which \(R\) returns to the insulating curve also varies, as several conformations are possible after the nanobeam initially buckles downwards and collides with the substrate. When sweeping at 6 °C min\(^{-1}\), \(T_s\) and \(T_m\) vary within a range of 2–5 °C between sweeps, whereas \(T_b\) and \(T_m\) are reproducible to within the measurement accuracy of \(\pm 0.1\) °C.

The supercooling of the homogeneous, uniformly stressed metallic phase to \(T_s\), which can be more than 50 °C below the phase boundary, is represented by the green lines on the phase diagram in Fig. 2b. This intrinsic supercooling (as opposed to the persistence of metallic domains due to inhomogeneous strain fields in larger samples) is much larger than has been reported previously\(^5\) and indicates high crystal uniformity. The large variations in \(T_s\) between nanobeams could reflect the availability of imperfections at which the insulating phase can nucleate. This system offers new opportunities for investigating the kinetics of a first-order phase transition in a quasi-one-dimensional geometry, for example by studying the process of insulator nucleation at \(T_s\) or the disappearance of the insulating domain at \(T_m\) (see inset to Fig. 2a).

In Fig. 3 we plot the resistivity \(\rho_i\) (along the rutile c-axis) of a number of nanobeams in their fully insulating state obtained simply using \(\rho = RA/L\), where \(A = WH\). Studies of the dependence on \(L\) have shown that contact resistance is negligible. \(\rho_i\) is

Figure 3 | Collected resistivity measurements for ten nanobeams of various dimensions. The insulator resistivity \(\rho_i\) shows an activation energy \(E_a = 0.30\) eV (dashed line is \(e^{E_a/RT}\)). Plotted using symbols are measurements of the resistivity \(\rho_m\) of the insulator in coexistence. To within error they all show a temperature-independent value of \(12 \pm 2\) Ω cm.

The discrepancy with the accepted value\(^3\) of 12 Ω cm for the supercooling regime.

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consistent between samples and its T dependence gives an activation energy $E_a = 0.30 \pm 0.01$ eV, indicated by the dashed line. Interestingly, this activation energy corresponds to that expected for an intrinsic semiconductor with precisely the established optical gap $E_g = 0.60$ eV of VO$_2$. This is in contrast with the anomalously large and sample-dependent activation energies of up to 0.45 eV reported in the literature to bulk insulating VO$_2$, which are most likely influenced by domain structure or imperfections that are absent in the nanobeams.

We also plot the resistivity $\rho_n$ of the metallic phase obtained in the same way for one nanobeam in its fully metallic state. Consistent with the literature we find that $\rho_n$ increases slowly with $T$ and that at the transition $\rho_n \approx 2 \times 10^2 \rho_m$. The kink in $\rho_n$ at $107 \degree C$, indicated by an arrow, occurs at the boundary between the supercooled and stable metallic phase. We do not know its origin, although we note that recent experiments have indicated that structural transitions may occur within the metallic phase under hydrostatic pressure or transiently after ultrafast excitation.

In the coexistence regime we expect $R$ to have four contributions:

$$R = \frac{\rho_i L}{A} + (1 - x)\frac{\rho_m L}{A} + R_c + R_{dw} \quad (4)$$

where $\rho_i$ and $\rho_m$ are the insulator and metal resistivities in coexistence, and $R_c$ and $R_{dw}$ are the resistances of the contact to the insulator and of the domain wall, respectively. Because $\rho_i > \rho_m$, the second term is negligible. At $T_m$, when the insulating domain disappears, there is usually a small sharp drop in $R$ of around 50 k$\Omega$ (see inset to Fig. 2a). We have yet to determine whether this reflects the resistance of the domain wall, the minimum insulating domain size, or the contact to the insulator, but in any case it implies that $R_c + R_{dw} \leq 50$ k$\Omega$. Because $R$ is usually greater than 1 M$\Omega$ for measurable $x$, to good accuracy we can thus write

$$R = \rho_i x L / A \quad (5)$$

As a result, the resistance can act as a probe of the position $xL$ of the interphase wall. We find that $R$ can be stable to within 0.1%, limited by the thermal stage stability; hence it can be used to detect motion of the wall with an accuracy of less than 10 nm in a device with $L = 10 \mu$m, offering the possibility of detecting small effects of perturbations such as electric field on the transition. Applying this idea, we found no change in $R$ on applying up to 50 V to the silicon substrate, indicating that the screening length within the semiconductor is less than the minimum nanobeam thickness, ~30 nm, and implying that Mott transistor action will be difficult to achieve.

Most interestingly of all, by using equation (5) we can determine $\rho_i$ from $R$ using values of $x$ obtained by optical inspection. The results are included in Fig. 3. We find that $\rho_i = 12 \pm 2 \Omega$ cm for all the nanobeams, independent of $T$ to within measurement error. This is in sharp contrast with the activated behaviour of $\rho_i$, which strongly suggests carrier activation across an unchanging gap. It implies that the carrier density in the insulator becomes independent of $T$ once the nanobeam enters coexistence; that is, in coexistence the changing strain causes the gap to increase in just such a way as to counteract the effect of thermal activation on the carrier density. In other words, the phase boundary corresponds to a contour of constant insulator carrier density in the $P$–$T$ plane.

This remarkable result is unlikely to be a coincidence, especially considering recent evidence that the excited carrier density in the insulator is important when the transition is induced optically. Rather, it implies that the transition temperature is closely linked to the equilibrium carrier density in the insulating phase. This is consistent with a driving role for electron–electron interactions in the MIT, as in a Mott transition that occurs when the density-dependent screening reaches a critical strength. In contrast, a phonon-driven mechanism would not be expected to be sensitive to the non-degenerate carrier density in the insulator.

Metal–insulator transitions have been studied in bulk systems for decades and are still not fully understood. As reported here, the greatly improved reproducibility, uniformity and level of control that is possible in single-domain samples can shed new light on such transitions and other aspects of strongly correlated electron physics. Further work is ongoing to understand the various new phenomena that have been observed in VO$_2$ nanobeams, including the appearance of the intermediate M2 insulating state during the transition between the M1 and metallic phases, which among other things explains the larger-than-expected change $\alpha$ in the unit cell length reported above.

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**Author contributions**

J.W. performed the experiments with assistance from Z.W., W.C. and D.H.C. D.H.C. guided the work and did the majority of the analysis and writing.

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