Supporting Information for

Axially Engineered Metal-Insulator Phase Transition by Graded Doping VO₂ Nanowires

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1. Device fabrication for electrical measurements free of strain.

Figure S1. Suspended pad based microdevice used for electrical measurements. Scheme of the device structure (a), SEM images showing the top view of the device (b), FIB-deposited Pt/C composite to bond the NW onto the pad (c), and optical images of the fabricated devices with an undoped VO_2 NW (d) and a graded doped $W_xV_{1-x}O_2$ NW (e). Scale bars: 50 µm (b), 5 µm (c), 20 µm (d), 20 µm (e).

2. Close-up optical image of a root-cantilevered NW as a micro-thermometer.



Figure S2. Progressive M domain growth with increasing temperature in a graded doped W_xV_1 . $_xO_2$ NW. The wire length is ~35 μ m.

3. Length shrinkage of a $W_x V_{1-x} O_2$ NW: the basis for micro-actuation.



Figure S3. Optical images showing length change by complete phase transition of a graded doped $W_x V_{1-x} O_2$ NW. The overall length decreases by ~ 1% between the M and the I phases.

4. Suggested mechanism for the axially graded doping of W in VO₂ NWs.



Figure S4. (a) A sketch showing the typical W fraction along the graded W-doped VO₂ NW. (b) Mechanism of growing free-standing VO₂ NWs on rough quartz substrates using V_2O_5 powder as the source. ^{S1} At the growth temperature when VO₂ nucleates and grows out of the V_2O_5 droplet, owing to capillary force, the VO₂ NWs are initially bound onto the local substrate surface. However, at later times, following the surface roughness, the NWs grow out of the surface plane and become free-standing. (c) A schematic showing various temperature profiles we tried for the NW synthesis. (d) The structural model of the VO₂ rutile (M phase); [001] projection (viewed along the c_R axis), and [110] projection.

Our graded doped $W_x V_{1-x} O_2$ NWs show "V"-shape W doping profile along the axial direction, as sketched in **Fig. S4a**. The mechanism of axially graded doping of W in the VO₂ NWs is not fully understood, but an explanation is given below.

First, we note that these NWs were grown catalyst-free, ^{S2} and the rough geometry of substrate surface is exploited to facilitate the growth of free-standing NWs, as shown schematically in **Fig. S4b**.^{S1} Otherwise, most of the NWs are grown firmly clamped onto, or half-embedded into the surface, imposing large strain to the NWs and influencing their MIT behavior. ^{S2} Liberating the NWs from the substrate by chemical etch is possible, but gives low yield and may damage the surface of the NWs.

Secondly, in **Fig. S4c** we show a few possible temperature profiles we tried for the growth. In route B, the sample was taken out of the tube furnace abruptly (within ~ seconds) after the 880°C growth. In all other routes, the temperature ramping up and down processes were on the order of 50°C/min, and were controlled by the temperature controller of the furnace. We observed that i) No NWs were grown at all in route E; ii) NWs were grown in route A, B, C and D, and surprisingly they all yielded NWs with similar lengths; iii) all A, B, C and D growths led to "V"-shape W doping in VO₂ NWs; and iv) the average W doping levels were the highest for route A and the lowest for D.

We now discuss two possible W doping mechanisms: W incorporation during the NW growth, and W doping by axial diffusion after the NW growth.

1) W incorporation during the NW growth. In this picture, the W atoms are incorporated into the VO₂ NW while the NW is forming. Because tungsten oxide has different vapor pressure from that of V₂O₅, it is possible that W incorporation is more efficient at relative low temperatures slightly below 880°C. In this way both the root and the tip of the VO₂ NW were heavily doped with W, because they are the parts of the NW that formed at slightly lower temperatures (i.e., during the temperature ramping up and ramping down processes).

However, our observation iii above shows that the NWs were still doped as the "V"shape W profile even in absence of the temperature ramping down process (route B). This is contradicting with the idea that W atoms were incorporated during the NW formation. This idea is also inconsistent with the observation ii. We therefore propose:

2) W doping by axial diffusion after the NW formation. In this picture, the VO_2 NWs were rapidly grown, and then W diffuses along the axis of the NW from the two ends towards the center, fed by the tungsten oxide vapor and assisted by the high temperature.

This is consistent with all the observations above. V_2O_5 micro-droplets are transported to the substrate at high temperatures, and an un-doped VO₂ NW rapidly forms from each liquid V_2O_5 droplet when temperature approaches 880°C. This NW stops to grow when its V_2O_5 droplet is depleted even if the V_2O_5 vapor supply continues; therefore, longer growth time at 880°C (from routes D to C to A) does not grow longer NWs. The formation of VO₂ NW is too fast for significant amount of W to be doped in, therefore, these rapidly formed VO₂ NWs are nominally un-doped or only lightly doped. Instead, W atoms axially diffuse from the two ends of each already-grown VO₂ NW toward the center, resulting in a "V"-shape W doping profile. This diffusion process is fed by the abundant tungsten oxide vapor and assisted by the high temperature of the furnace.

The diffusion is mostly axial instead of radial along the NWs because of diffusion anisotropy. The high-temperature crystal structure (rutile phase) of the VO₂ NWs has large openings along the NW axis (c_R) direction acting as diffusion channels for the W atoms, but the V and O atoms are much more closely packed in the NW radial direction (i.e., directions perpendicular to c_R) (**Fig.S4d**); this allows a much easier axial diffusion than radial diffusion. In TiO₂ which has a similar rutile structure, it has been reported that some cations diffuse more easily along the c-direction channels.^{S3-S5} Such quasi-one-dimensional diffusion warrants further investigation and may be used to achieve other novel structures.

References

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