Self-Assembly and Horizontal Orientation Growth of VO₂ Nanowires

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Single-crystalline vanadium dioxide (VO₂) nanostructures have attracted intense research interest recently because of their unique single-domain metal-insulator phase transition property. Synthesis of these nanostructures in the past was limited in density, alignment, or single-crystallinity. The assembly of VO₂ nanowires (NWs) is desirable for a “bottom-up” approach to the engineering of intricate structures using nanoscale building blocks. Here, we report the successful synthesis of horizontally aligned VO₂ NWs with a dense growth mode in the [1-100] quartz direction of a polished x-cut quartz surface using a simple vapor transport method. Our strategy of controlled growth of VO₂ NWs promisingly paves the way for designing novel metal-insulator transition devices based on VO₂ NWs.

Vanadium dioxide (VO₂), a representative strongly correlated electron material, is of great interest due to its first-order metal-insulator transition (MIT) at temperatures slightly above room temperature (T_C = 68 °C, where T_C is transformation temperature). This phase transition mainly features a coupled structural and electronic phase transformation from a monoclinic, insulating phase (I) at low temperatures to a rutile, metallic phase (M) at high temperatures. Meanwhile, VO₂ exhibits a drastic change in optical reflectivity across the MIT, as well as a size change of up to 1% and several orders of magnitude drop in resistivity. Exploiting these switching behaviors across the MIT, a number of applications have been demonstrated or proposed in optical switches, smart window coating, Mott transistors, memristors, sensors, and thermal actuators. Despite these expanding applications, fundamental challenges still remain for reliable MIT engineering using VO₂. For instance, the strain associated with grain boundary, dislocation, stoichiometry fluctuation and substrate clamping can broaden the phase transition temperature window. Single-crystal nanowires offer an appealing alternative to thin films because they host single domains across their entire width, and thus support single or few domain MIT. Based on this unique single domain MIT characteristic of VO₂ NWs, different aspects of the physics of MIT were discovered, and a variety of applications in actuators, gas sensors, power meters, and strain gauges were demonstrated. Due to these promising applications, VO₂ NWs have attracted a great interest as building blocks used for the fabrication of nanodevices.

Considerable effort have in recent years been expended to the control of the growth of VO₂ NWs using simple thermal evaporation methods. Usually, VO₂ NWs are preferentially grown on substrates such as silicon, oxidized silicon surface, fused quartz, etc., through a vapor-solid (VS) process. They are randomly dispersed and embedded into the substrates. Careful and selective etching is needed to release the VO₂ NWs from the substrates in order to assemble them for the aforementioned applications. This “liberation” process is typically slow with a low-yield and may damage the NWs surface. It is therefore necessary to develop an effective synthesis method of free-standing single-crystal VO₂ NWs with high densities and high aspect ratios. This kind of growth has recently been achieved by our group using rough surface quartz. Other methods that have been explored include: 1) directed and heteropitaxial growth of VO₂ NWs with high densities and high aspect ratios. This kind of growth has recently been achieved by our group using rough surface quartz. Other methods that have been explored include: 1) directed and heteropitaxial growth of VO₂ NWs with high densities and high aspect ratios. This kind of growth has recently been achieved by our group using rough surface quartz. Other methods that have been explored include: 1) directed and heteropitaxial growth of VO₂ NWs with high densities and high aspect ratios. This kind of growth has recently been achieved by our group using rough surface quartz.
challenge for nanotechnologists. In this work, we present a method to fabricate the ordered arrays of VO$_2$ NWs in a large scale on relatively inexpensive x-cut quartz substrates.

**Results**

Figure 1a shows a schematic of the reactor setup and the formation temperatures of as-prepared products. Two kinds of morphologies, namely nanowires (NWs) in region I (750–800°C) and microplates (MPs) in region II (800–850°C), are observed. Fig. 1b shows a representative XRD spectrum of the products on substrates. The XRD peaks can be indexed to the low-temperature and monoclinic structure of VO$_2$ (JCPDS card 72-0514). It is noted that besides the (011) and (022) peaks which appear in the in-plane growth of VO$_2$ NWs, there are no other peaks such as (002), (020), (013), (200), (-212), (-311), (300), etc. This fact suggests a preferential orientation of the VO$_2$ products with the (011) plane parallel to the surface of the quartz substrate which resulted from the epitaxial growth. Figs. 1c and d show the representative optical images of as-grown products. High density VO$_2$ NWs were the dominating products in the low-temperature deposition zone (I). In contrast with the randomly oriented in-plane growth of VO$_2$ NWs on other reported substrates, such as silicon, oxidized silicon surface, fused quartz, etc., the present VO$_2$ NWs only grow along one direction. The diameters of VO$_2$ NWs normally range from tens to hundreds of nm and their lengths are several tens of micrometers. The diameters and densities of VO$_2$ NWs are shown to be temperature dependent. Low growth temperatures resulted in small diameters and a low density of VO$_2$ NWs. High growth temperatures favor the fusing of NWs and enhance their lateral growth leading to an MP morphology as shown in Fig. 1c. The grown embedded VO$_2$ MPs in the substrates have an irregular shape with a submicrometer thickness and size of tens of micrometer. Rich domain patterns are observed in these VO$_2$ MPs which can be attributed to the twining of a low-temperature phase or to the formation of two mixed monoclinic phases. This manifests the existence of the elastic strain induced in the MPs by the substrate upon the following cooling process.

Figure 2a shows a typical SEM image of NW products at the deposition temperature of 800°C. The image has a weak contrast due to the poor electrical conductivity of VO$_2$ and the quartz substrate. The NWs density is quite high and they appear to integrate together forming a NW film. Fig. 2b is an AFM image of VO$_2$ NWs grown at a low deposition temperature of 750°C. There are two distinct features for the as-grown VO$_2$ NWs: 1) there is no overlap between two NWs when they meet, that is, one NW growth front is stopped by another NW. 2) There are obvious traces of grooves left aside the two ends of each VO$_2$ NW due to the dissolution of SiO$_2$ during the growth process. All the VO$_2$ NWs are in the monoclinic phase as confirmed by the micro-Raman spectra of nanowires and quartz substrate in Fig. 2c. The Raman spectrum at room temperature shows characteristic vibration modes for the monoclinic insulating phase of VO$_2$. Comparing with the previous work on thin films and bulk crystals, the Raman peaks at room temperature are identified as 148(A$_g$), 194(A$_g$), 225(A$_g$), 313(B$_g$), 396(A$_g$) and 613(A$_g$) cm$^{-1}$. There are no peaks related to V$_2$O$_5$ and other stoichiometries. This is consistent with our XRD data and following TEM results.

The interface between the root of a single VO$_2$ nanowire and quartz substrate was investigated by cross-section TEM imaging (see Fig. 3a). The TEM sample was prepared using focus ion beam (FIB) milling with the cross-section plane perpendicular to the VO$_2$ NW growth direction. The cross-section of VO$_2$ NW shows a rectangular shape and the VO$_2$/quartz interface is flat. Figs. 3b–d show the selected area electron diffraction (SAED) patterns taken from the NW, quartz substrate and the interface, respectively. The SAED pattern P1 was indexed to be monoclinic VO$_2$. The diffraction spots were clear and round and the pattern did not change as the electron beam moved along the nanowire indicating that the whole nanowire is a single crystal without stacking faults. The HRTEM image in Fig. 3e taken from the NW shows clear lattice fringes, again confirming the good crystallinity of the NW. The marked lattice spacing of 0.451 nm corresponds to the inter-plane spacing of the (010) and (001) planes of monoclinic VO$_2$ crystals. From the above SAED
studies (Figs. 3b–d), the orientation relationships between VO₂ NW and the quartz substrate can be identified as below:

\[
\begin{align*}
(011)_{\text{VO}_2 \text{ monoclinic}} & \parallel (11-20)_{\text{quartz}}, \\
[100]_{\text{VO}_2 \text{ monoclinic}} & \parallel [1 - 100]_{\text{quartz}}.
\end{align*}
\]

It is therefore confirmed that the NW is surrounded by \{011\} faces and its axis is along the [100] monoclinic direction. The NW growth direction is aligned with [1-100] quartz. During the growth process, the VO₂ phase is rutile. This is because the deposition temperature is higher than \(T_c\) while it changes to the monoclinic phase after cooling to room temperature. Here, it is necessary to study the lattice match relationship between the two phases of VO₂ and the quartz substrate. With regard to this orientation relationship, VO₂ has a good lattice match with the quartz in both the metal rutile and insulator monoclinic phases as shown below:

\[
\begin{align*}
1 \times d_{(1000)/\text{quartz}} (0.426 \text{ nm}) & \approx 3 \times d_{(002)/\text{VO}_2 \text{ rutile}} (0.428 \text{ nm}), \text{ the lattice mismatch is 0.5\%, the normal directions of these two planes are parallel to [1-100]_{\text{quartz}};} \\
3 \times d_{(0001)/\text{quartz}} (1.622 \text{ nm}) & \approx 5 \times d_{(110)/\text{VO}_2 \text{ rutile}} (1.610 \text{ nm}), \text{ the lattice mismatch is 0.8\%, the normal directions of these two planes are parallel to [0001]_{\text{quartz}};} \\
1 \times d_{(1000)/\text{quartz}} (0.426 \text{ nm}) & \approx 3 \times d_{(-402)/\text{VO}_2 \text{ monoclinic}} (0.430 \text{ nm}), \text{ the lattice mismatch is 0.9\%, the normal directions of these two planes are parallel to [1-100]_{\text{quartz}};} \\
3 \times d_{(0001)/\text{quartz}} (1.622 \text{ nm}) & \approx 5 \times d_{(011)/\text{VO}_2 \text{ monoclinic}} (1.600 \text{ nm}), \text{ the lattice mismatch is 1.4\%, the normal directions of these two planes are parallel to [0001]_{\text{quartz}}.}
\end{align*}
\]

The calculated lattice mismatches between rutile VO₂ and quartz are only 0.5% along the [1-100] quartz and 0.8% along the [0001] quartz direction for the VO₂ rutile phase. It is known that VO₂ NWs have a preferred growth direction along [001] VO₂ rutile. The above anisotropic lattice mismatch relationships definitely determine the fast growth of VO₂ NW along the [1-100] quartz direction due to the best lattice match relationship while the width of NWs along [0001] quartz direction is limited due to a larger lattice mismatch. This rationale supports the self-assembled oriented growth of VO₂ NW on x-cut quartz substrate. Similar anisotropic lattice mismatch relationship between quartz and monoclinic phase VO₂ is kept after cooling down to room temperature. In case of VO₂ MPs, the observed linear domain patterns along the [1-100] quartz direction (Fig. 1d) can be attributed to the elastic strain caused by the synergistic effect of the large lattice mismatch 0.8%/1.4% (high T/room T) perpendicular to the [1-100] quartz direction and the large difference in expansion coefficients between these two crystals (about two orders of magnitude)\(^1\).

We did not observe horizontally aligned growth of VO₂ NWs on z-cut (0001) quartz. This is a strong indication of the important role of the surface crystallographic plane in determining the direction of NW growth. As such, compared with z-cut (0001) quartz, the x-cut (11-20) quartz is shown to be a superior substrate for VO₂ growth due to the lattice match relationship. A similar growth behavior was found for the horizontal growth of ZnO NWs on x-cut sapphire through a metal-catalyzed vapor-liquid-solid (VLS) growth mechanism\(^2\). Fig. 4(a) schematically illustrates the growth direction of NWs and the VO₂ [001] rutile direction relative to x-cut (11-20) quartz. Fig. 4b proposes a model derived from the SAED results. In this model, the (110) plane of VO₂ rutile is considered parallel to the a-plane of quartz. Only in this arrangement will V atoms (small red circles) have a reasonable overlap with oxygen atoms (large navy blue circles) of quartz. Interestingly, the two crystals appear to have a better match in the ±[1-100] quartz direction which coincides with
the observed NW growth direction. In this figure, only V atoms which match with the oxygen atoms of the quartz are shown.

**Discussion**

One-dimensional nanostructures such as carbon nanotubes, Si NWs, ZnO NWs, etc., can receive a perfect control over diameter, density, position and orientation using the VLS growth mechanism with the appropriate metal catalysts and substrates. In contrast, the thermal evaporation VS growth of VO2 NWs shows a poor controllability. Our work demonstrates that a special type of substrate, x-cut (11-20) quartz, facilitates the controlled growth of VO2 NWs at a lower cost, higher density, larger length, and better alignment. As revealed by prior experimental and theoretical studies, the nucleation rate is at its maximum when the fit between the lattices of nucleus and the substrate surface is at the highest. Here, we also found that x-cut (11-20) quartz substrate can cause a much higher NW surface density than other lattice matched substrates though they also have a lattice fit relationship with VO2. Thus, the nucleation and growth behavior of VO2 NWs is sensitive not only to the lattice match but also to the chemical identity of quartz substrates. This finding is consistent with the fact that the silicon dioxide surface favors the nucleation and growth of VO2 NWs. In addition, the utilization of V2O5 evaporation source provides a much higher vapor pressure because it has a much lower melting point of 690 °C than that of VO2 (1967 °C). As a result, the combination of the x-cut (11-20) quartz surface and V2O5 provides an excellent seeding and fast growth environment. Strelcov et al. has shown that silicon dioxide-based substrates, especially quartz, favor a high aspect ratio growth. In our case, the competitive growth of NWs with a superior high nucleation density suppresses the elongation of NWs by physically stopping the growth fronts, as observed in Figs. 1c and 2b, leading to the NW’s aspect ratio of less than 50. Our work advances a rational growth of VO2 NWs with regards to cost, orientation and surface density while the control over diameter, position and aspect ratio still remains a challenge and needs further investigations.

In conclusion, we report the horizontally aligned and dense growth mode for VO2 NWs on the polished x-cut quartz surface using a simple vapor transport method. It is shown that the product morphology ranges from MPs to NWs depending on the deposition temperature. The growth direction of NWs is along the [1-100] quartz direction as identified by the HRTEM and SAED observations. Here, the self-assembly of VO2 NWs is attributed to an epitaxial crystal growth on the naked crystal plane of x-cut quartz. The combination of the low-melting-point source V2O5 and lattice matched quartz substrates greatly facilitates the nucleation and enhances the growth rate. This approach is potentially a means for self-alignment of VO2 NWs in the lithography industry to design novel metal-insulator transition devices based on VO2 NWs such as near infrared linear polarizers and microactuators.

**Methods**

VO2 NWs were grown using a simple vapor transport method in which V2O5 powder was placed in a quartz boat at the center of a horizontal tube furnace as seen in Fig. 1a. Argon (Ar) gas flow transported the V2O5 atoms to the quartz substrate where crystal growth took place. The reaction product was collected on the substrate which was placed close to the source quartz boat at the downstream location (Substrate is shown in Fig. 1a). The growth was carried out in the following condition: evaporation temperature ~ 880 °C, Ar carrier gas flow rate ~ 6.8 scm (standard-state cubic centimeter per minute), pressure ~ 5 torr, and evaporation time ~ 2 hours or more. We observed a distinct VO2 growth direction on x-cut quartz, which resulted in the growth of NWs on the basal plane of the substrate in a direction. The horizontal growth is shown to be highly dependent on the orientation of used quartz substrates: only x-cut polished quartz offers a high-density, oriented growth while polished quartz with other orientations gives randomly dispersed NWs grown embedded in the substrates as reported previously. The size distribution, lattice structure and crystal orientation of the as-synthesized products were characterized by optical microscopy (CASCADE CMPS-8881), scanning electron microscopy (SEM, Quanta 3D FEG), x-ray diffraction (XRD, Siemens D5000), and transmission electron microscopy (TEM, FEG CM200), as well as a Raman spectroscopy (INVIA, using a 488 nm Ar ion laser).

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Author contributions
C.C. designed the research, performed sample fabrication, analysed the results and wrote the paper. H.G., K. L., D.F. and J.Z. performed the TEM, the Raman, the XRD and AFM characterization and the paper revision. A.A. and H.S. incorporated in the interpretation of experimental results and final paper polishing.

Additional information
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