Evidence for Ionic Liquid Gate-Induced Metallization of Vanadium Dioxide Bars over Micron Length Scales

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ABSTRACT: It has recently been shown that the metal–insulator transition in vanadium dioxide epitaxial films can be suppressed and the material made metallic to low temperatures by ionic liquid gating due to migration of oxygen. The gating is only possible on certain crystal facets where volume channels along the VO₂’s rutile c-axis intersect the surface. Here, we fabricate bars with the c-axis in plane and oriented parallel to or perpendicular to the length of the bars. We show that only bars with the c-axis perpendicular to the bars, for which the volume channels are accessible from the sides of the bar, can be metallized by ionic liquid gating. Moreover, we find that bars up to at least 0.5 μm wide can be fully gated, demonstrating the possibility of the electric field induced migration of oxygen over very long distances, ~5 times longer than previously observed.

KEYWORDS: Metal insulator transition, ionic liquid gating, metallization, epitaxial oxide films, vanadium dioxide
metallization of the oxide material but could lead to important technological applications, such as neuromorphic devices and membranes for oxygen separation.

To avoid patterning of the deposited VO₂ films which can lead to damage affecting its electrical properties, we patterned the underlying TiO₂ substrate before depositing the VO₂ film to create the bars. The TiO₂ (100) single crystal substrates were patterned by e-beam lithography to create arrays of mesas separated by 40 nm deep trenches. The trenches were 2 mm long. The widths of the mesas and the spacings between them were each designed to be 0.25, 0.5, or 1 μm. Subsequently a VO₂ layer is deposited on the patterned TiO₂ substrate to form arrays of VO₂ bars on top of the mesas. The trench is much deeper than the thickness of the deposited VO₂ layer. Thus, these VO₂ bars have exposed edges (i.e., side walls) which are used to ionic liquid gate the bars. Since there are no volume channels that are connected to the top surface of the VO₂, only the edges can gate them, based on our previous studies. Furthermore, the VO₂ film deposited within the trench has no exposed edges and is therefore not gateable. In any case, by design, only the bars are electrically connected to the source and drain contacts, as discussed further below, and not the VO₂ layers at the bottom of the trenches. Each bar forms an electric double layer transistor (EDLT). Many bars were connected to common source and drain contacts so that the electrical properties of an array of EDLTs was measured. This allowed for any variations in properties of the bars to be averaged out in a single measurement. Each of these arrays comprises a single device. Two distinct device types were fabricated for transport—device T—and synchrotron X-ray diffraction—device

Figure 1. VO₂ bar devices. (a) Schematic diagram of part of one device that is composed of a series of VO₂ bars oriented along the (010) rutile axis. The (100) VO₂ layers are shown in blue, and the corresponding (100) TiO₂ substrate is shown in pink. Schematic layouts are on a 10 × 10 mm² area substrate of (b) T devices and (c) X devices. The different arrangements of the atoms within the rutile structure on the exposed (001) and (010) edges are schematically illustrated at the top and bottom of the layout in b. Also illustrated is the oxygen that exits the (001) but not the (010) edges during the ionic liquid gating. The inset in c illustrates the array of bars within a single device. (d) Typical atomic force microscopy image and (e) line scans showing cross sections of two sets of bars; top: 1 μm wide bars spaced 1 μm apart and bottom: 0.5 μm wide bars spaced 0.25 μm apart.
X—measurements. The arrays were 100 μm wide for device type T and 300 μm wide for device type X. Each of the devices was surrounded by a “moat”, namely, a trench 100 μm wide to ensure electrical isolation of each device. The moats were spaced 25 μm apart.

Figure 1a shows a schematic diagram of one device that is covered with ionic liquid. For device type T, four sets of nine devices, each with trenches of different widths and spacings, and patterned in close proximity to each other, were formed, as shown in Figure 1b, two sets with the bars oriented along, and two sets with the bars oriented perpendicular to the in-plane rutile c-axis. For device type T each device was gated independently by placing a droplet of ionic liquid selectively on a single device with a micropipette. Another droplet of ionic liquid was placed on the gate electrode, and additional ionic liquid was dispensed to connect the device and gate droplets while avoiding contact to the other devices present on the substrate. For device X all the devices were gated in parallel. The layout of the devices and their connections are shown in Figure 1c. For the T devices two gate electrodes ∼1 × 10 mm² were fabricated on opposite sides of the substrate.

The trenches were patterned using e-beam lithography with poly(methyl methacrylate) resist (950k molecular weight, 5% solution in anisole). This resist was spun onto the 10 × 10 mm² samples at 2000 rpm spin speed followed by baking at 120 °C for 120 s. In order to prevent charging during e-beam exposure, a charge dissipation top coat was added consisting of the aquaSAVE conducting polymer solution (Mitsubishi Rayon Co., Ltd.), spun at 1500 rpm followed by baking at 90 °C for 60 s. The patterns were exposed using a Vistec/Leica VB6 e-beam machine with a 5 nA beam, taking 150 min per sample. After the water rinse of the aquaSAVE and 120 seconds resist development in a 1:3 solution of methyl-isobutyl ketone—isopropyl alcohol solution, the samples were etched in a PlasmaTherm Versaline ICP etch tool under the following conditions: pressure of 5 mT, BCl3 flow rate of 45 sccm (standard cubic centimeter per minute), SF₆ flow rate of 5 sccm, a coil RF power of 300 W, and a platen RF power of 50 W. The total etch time was 75 s. Following this etch, the resist was stripped in hot NH4F solution, the samples were etched in a BOE solution for 50 s. Next, they were annealed again for 1 h, and then ion milled for 90 s in an Oxford IonFab before ion beam deposition of 5 nm of ruthenium followed by 65 nm of gold. Finally, the samples underwent liftoff in hot NMP for 30 min. The gate electrodes, ∼1 × 10 mm² in area, for the T devices were fabricated later by a shadow masking technique using the same metal layers as the contacts.

Atomic force microscopy (AFM) images of two type T devices with bar widths of 1 and 0.5 μm and spacings of 1 and 0.25 μm, respectively, are shown in Figure 1d. The surface of the VO2 films on top of the bars is very smooth with a root-mean-square (rms) roughness of ∼0.5 nm, whereas it is slightly rougher, with an rms roughness of ∼0.7 nm within the trenches, where the TiO2 substrate had been ion-milled prior to the VO2 deposition. AFM line profiles shown in Figure 1e confirm the depth of the trench to be ∼40 nm.

Transmission electron microscopy samples were prepared by cross-sectional focused ion beam milling using a Ga ion beam on selected bars. Typical results are shown in Figure 2 for a bar with channels perpendicular to the length of the bars. The images were taken using a JEOL ARM200 microscope. A low magnification image is shown in Figure 2a and a high-resolution, high-magnification image is shown in Figure 2b and c. The high-resolution image along the (010) zone axis clearly shows that the rutile c-axis is oriented perpendicular to the length of the bar and in the plane of the bar (see schematic in Figure 2c). The high-resolution image shows that the VO2 film is epitaxial with the rutile TiO2(100) single crystal substrate so that the VO2 unit cell is expanded along the c-axis by ∼3%. The clamping of the VO2 lattice to the substrate likely accounts for the small structural changes found from in situ synchrotron X-ray diffraction studies.

Ionic liquid (IL) gating transport experiments on type T devices were performed in a Quantum Design DynaCool Physical Property Measurements System. The IL used for these experiments was 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM-TFSI). The devices and the IL were separately baked at 120 °C in a high vacuum chamber at 10⁻⁸ Torr prior to the gating experiments, to eliminate any contaminants, such as water. A droplet of IL was placed on the substrate such that it covered an entire set of nine devices and the adjacent gate electrode. A single device from the set was selected for IL gating by ultrasonically wire bonding 25 μm diameter gold wires to its source and drain contacts. A gate voltage (V_G) of +2.6 V and a source drain voltage (VSD) of +0.1 V were applied at 300 K, where the VO2 is in its insulating state. After 8 h of gating V_G was reduced to 0 V, and the device
resistance was measured as a function of temperature at a scan rate of 3 K/min. Figure 3a and b shows typical resistance versus temperature measurements, before and after gating, for two devices, one with bars parallel and one with bars perpendicular to the VO$_2$ rutile $c$-axis. These devices each have 140 bars, 0.5 μm wide, spaced by 0.75 μm.

Figure 3a shows that gating of the device for which the rutile $c$-axis is parallel to the length of the bars results in small changes in the device’s electrical properties. The MIT of the device is slightly reduced in temperature. In contrast, Figure 3b shows that gating of the bars in which the rutile $c$-axis is perpendicular to their length results in a complete suppression of the device’s MIT, and the device becomes metallic to the lowest temperature measured. Moreover, upon gating, the resistance of the device at temperatures above its MIT increases from 3.6 to 4.5 kΩ. The fact that no remnant MIT is observed for the bars with the rutile $c$-axis perpendicular to their length means that the entire volume of all the bars in this device were metallized. Furthermore, this shows that the ionic liquid gate induced metallization occurs up to a depth of 0.5 μm, the width of the bars.

The observation that the bars have a very different response to ionic liquid gating depending on the orientation of the rutile $c$-axis has several implications. First, these results are consistent with our previous studies that showed that VO$_2$ is metallized, not by electrostatic effects, but rather by electric field induced migration of oxygen along the volume channels within the rutile structure along the $c$-axis. Second, it is possible to achieve a volume metallization of VO$_2$ (100) by gating from sidewalls as long as the sidewalls are perpendicular to the rutile $c$-axis. In this case the volume channels are oriented perpendicular to the sidewalls with access to the EDL and the ionic liquid. The sidewalls have VO$_2$(001) facets. On the other hand, when the sidewalls have (010) facets, as is the case for the bars with the rutile $c$-axis oriented along their length, we find almost no gating effect. In both cases the top surfaces of the bars have (100) facets, and therefore, if these surfaces played a role in the gating, we would have seen metallization, independent of the orientation of the bar edges. Moreover, our findings on bars with rutile $c$-axis oriented along their length are consistent with a previous study where no IL gating effect was observed on nanobeams whose $c$-axis was oriented along the nanobeam axis. Third, the gating effect occurs over a very long length scale of at least 0.5 μm. This also indicates the high quality of the VO$_2$ films used in this study as the open volume channels must extend over this same length scale.

Figure 3c shows a series of IL gating experiments that were performed on a type T device that had wider bars. This device had 50 bars, each ~1 μm wide, spaced ~1 μm apart, with the rutile $c$-axis perpendicular to the length of the bars. Temperature dependent resistance measurements were performed on this device in its insulating state and after gating in vacuum for...
3, 6, and 12 h. A significant reduction in the MIT was observed, but the metallization was not complete even after gating for 12 h. Note that between each gating experiment the sample was removed from vacuum into air and the IL was removed by rinsing in iso-propyl alcohol (IPA) for 5 min and blow drying in nitrogen. We found that during this process the device resets itself to its initial insulating state as confirmed by transport measurements. The sample was baked in vacuum at 100 °C for several hours to remove any residual water before performing the subsequent gating experiment.

We note that TiO$_2$ has the same rutile structure and correspondingly volume channels as VO$_2$; earlier it has been found that ionic liquid gating has a similar crystal facet dependence, but the metallization is confined to a thin surface layer (∼2 nm thick), and the conductivity of this metallized layer is 100 times smaller than the conductivity of the metallized VO$_2$. Moreover, the effect is volatile so that when $V_G ≈ 0$ the TiO$_2$ has reverted to its insulating state. Thus, the TiO$_2$ substrate does not play a role in our VO$_2$ gating experiments.

Type X devices were fabricated to investigate structural changes of the VO$_2$ bars upon IL gating. X-ray diffraction (XRD) measurements were carried out, in situ, at the Stanford Synchrotron Radiation Laboratory (SSRL) at room temperature in a purpose-built electrochemical cell. Type X sample had a total of 18 devices with 9 devices in which the rutile $c$-axis of VO$_2$ was parallel and 9 devices in which the rutile $c$-axis of VO$_2$ was perpendicular to the length of the bars. The devices were 300 μm wide in order to accommodate the width of the focused X-ray beam. Source and drain contacts were formed from ∼1 mm × 10 mm wide stripes of 5 nm Ru/65 nm Au that were deposited along opposite sides of the 10 mm × 10 mm substrate. These contacts were connected to the source and drain of each of the devices, in parallel (see Figure 1c). Thus, all the devices on one Type X sample were gated simultaneously. The same ionic liquid, HMIM-TFSI, was used as for the transport measurements.

The XRD measurements were carried out using a monochromatic X-ray beam with an energy of 12 keV. Figure 4a and b shows XRD $θ$–$2θ$ patterns for two devices each with 300 bars, ∼2 mm long, 0.5 μm wide at a spacing of 0.5 μm. For one device the rutile $c$-axis is parallel, and for the other device, perpendicular to the length of the bars. For both devices, the XRD data in the out-of-plane direction show sharp substrate peaks at 53.4° (TiO$_2$(400)) and a broader diffraction peak from the VO$_2$ film at ∼54.7° (VO$_2$(400)). After gating for 12 h at $V_G$ = 2.6 V, no shift in the film’s diffraction peak is observed for the set of bars parallel to the $c$-axis, whereas a shift of ∼0.4° is observed for the bars perpendicular to the $c$-axis. A shift of the peak position to a lower $2θ$ angle represents an expansion of the out-of-plane lattice parameter. While this peak shift is very significant, it is much smaller than we have previously observed when gating a (001) oriented VO$_2$ film from its surface in which the film is found to expand by 3% or more out-of-plane. Here the bars cannot expand in plane along the (001) axis since their lattice is clamped to the TiO$_2$(100) substrate and is therefore already expanded by ∼3%.

We have clearly demonstrated that bars of crystalline VO$_2$ can be converted from an insulating to a metallic state by ionic liquid gating from the side walls of the bars over substantial distances of more than 0.5 μm. We note that the area of the surface of the bars exposed to the ionic liquid is about 20 times larger than the area of the side walls, yet our results show that negligible gating takes place through these surfaces. Gating occurs only when the side walls are properly crystallographically oriented, when the volume channels in the VO$_2$’s rutile structure are oriented perpendicular to the side walls. These results are a clear manifestation of the oxygen vacancy formation mechanism that gives rise to the ionic liquid gating metallization. These results are important because not only do they demonstrate that oxygen vacancies can be induced even at large distances from the EDL but that the process takes place over considerable time. This could be useful for several technological applications, perhaps most interestingly for neuromorphic computing devices where analogue devices are needed. Another potential application is the use of VO$_2$ membranes for oxygen separation driven by ionic liquid gating on one or both sides of the membrane. Once an oxygen vacancy gradient is established across the membrane the process could be much faster than the initial process of setting up this gradient.

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Notes
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■ REFERENCES
