Vanadium Dioxide Nanowires: Growth and Characterization

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We successfully grow Vanadium Dioxide (VO_2) nanowires (NWs). We present characterization techniques, including solid gating, liquid electrochemical gating, and scanning photocurrent microscopy (SPCM). We present several novel results, including: (1) an approximate recipe for creation of n-type and p-type NWs, as well as (2) temperature modulated band bending switching in p-type NWs.

I. INTRODUCTION

Vanadium Dioxide (VO_2) is a novel material that exhibits a first-order phase transition from an insulating state to a conducting state at $T_c = 68$ °C, called a metal-insulator transition (MIT).

A. Features of Vanadium Dioxide

The transistor serves as the backbone to a large amount of technological devices, and largely functions as a switching device, allowing a signal to be switched on and off. VO_2 has thought to be promising because the observed MIT is suitable for technological adaptation. The VO_2 MIT is particularly appealing because the transition is ultrafast (occurring on the order of 100 femtoseconds [1]) and consumes low power. The MIT can be triggered by temperature, electric fields, photons, magnetic fields, and strain. Mastery of the electric field is perhaps most desirable, as this is the underlying mechanism of field effect transistors.

The MIT in VO_2 is challenging to study because the material experiences a change in primitive cell: the insulating phase is monoclinic (M1), and the conducting phase is tetragonal. Other primitive cell phases are present, such as M2, but with few exceptions [2] most research is focused on a forced dichotomy between the monoclinic and tetragonal phases of VO_2.

In addition to primitive cell geometry, the MIT is characterized by a change in reflectance. In its insulating phase, VO_2 appears light, while conductive VO_2 appears darker. This lets us identify domains using optical microscopy.

The fundamental mechanism behind the VO_2 MIT has been an open question for 50 years [1], and it is yet to be determined if the MIT is due to a Mott transition (which is controlled by electron-electron interactions and an associated critical electron density) or a Peierls transition (which is controlled by electron-phonon interactions). Research seems to currently favor the Mott picture [3], but remains inconclusive.

B. Applications of Vanadium Dioxide

Because VO_2 exhibits a transistor-like MIT, the number of applications that have been proposed approach the same level of speculation as graphene or room-temperature superconductors. Some of the suggested applications include familiar devices, such as two-terminal electronic switch devices, three-terminal (gated) electronic switch devices (Mott FETs), and optical devices. More exotic applications are in electronic oscillators, metamaterial devices, memristive devices, thermal sensors, chemical sensors, and smart windows [1].

C. Difficulties of Vanadium Dioxide

VO_2 is difficult to study from both a theoretical and experimental perspective.

The central issue is that VO_2 is classified as a strongly correlated material, which means that electron-electron interactions are complex. As a consequence, standard analytical and computational tools (such as Density Functional Theory) that rely on local density approximation are no longer reasonable. A great deal of work has been made in extending mean field theory to these regimes [4], but these models remain incomplete.

Experimentally, VO_2 is difficult largely because the carrier density must be very high to trigger the MIT and also has poor mobility, which is often measured to be $\mu = 0.1 - 1.0 \mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ [5]. Solid gate response of VO_2 is therefore very poor [6]. Measuring gate response is fundamental to device characterization, since it allows us to easily determine the majority carrier in the system. Another significant difficulty lies in the fact that bulk VO_2 will exhibit very complicated domains across the material due to the many triggering mechanisms that are inhomogeneous across the sample. This makes studying the domain interfaces in bulk VO_2 challenging.

D. Vanadium Dioxide Nanowires: a (Newer) Paradigm

In recent years, the study of NW devices has exploded. Using chemical vapor deposition techniques, researchers have been able to construct devices that have a width that is smaller than the characteristic domain size of VO_2. This creates an effectively one-dimensional environment, which allows us to probe structural issues such as band bending in a more systematic and sensible manner.

II. GROWTH AND FABRICATION

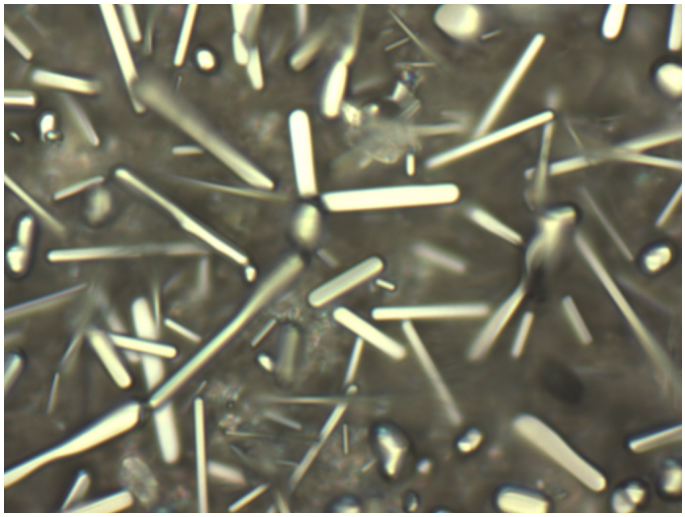
The physical mechanisms responsible for nanowire growth are complicated and not well understood. Thus, we discuss the practice and challenges of VO_2 synthesis from an especially qualitative and general perspective.

A. Growth

The VO_2 nanowires were grown using chemical vapor deposition techniques in a Lindberg Blue M furnace. We placed 30 g of a V_2O_5 powder in a quartz boat in the center of the furnace tube. An unpolished x-cut quartz substrate was placed 7 cm downstream from the boat. Unpolished quartz is frequently used to facilitate nucleation sites and promote growth of freestanding nanowires [7]. We evacuated the furnace tube to $\sim 100\,\text{mTorr}$ and flowed $k_{Ar} = 0 - 60$ sccm of argon gas, achieving a pressure of $0.9 - 1.0$ Torr. We then heat the furnace to 880°C and allow the V_2O_5 powder to evaporate into VO_2, where it is deposited on the unpolished quartz substrate. During the growth, excess O_2 is generated. By modulating the Ar concentration, we can control the vapor pressure of O_2 and thus control the doping concentration in the nanowires. We were careful to avoid the growth of solid V_2O_5 in several ways: (1) the temperature of the unpolished quartz substrate was kept over the melting point of V_2O_5 (695°C) for the duration of the growth, and (2) immediately after the growth the furnace was quickly cooled with a fan to room temperature to prevent V_2O_5 growth.

On the unpolished quartz substrate, we observed nanowires (See FIG. 1) that had a diameter of $d \approx 300\,\text{nm}$, in addition to much larger beams ($d \approx 1\,\mu\text{m}$). These nanowires are much smaller than previously reported nanowires, which have the benefit of having an improved gate response due to the increased surface area-to-volume ratio [8].

FIG. 1. Freestanding NWs on an unpolished quartz substrate. The average width of these nanowires is roughly 500 μm.



B. Fabrication

The freestanding VO_2 nanowires were mechanically transfered to a Si substrate that had a 300 nm SiO_2 thin film that served as a gate dielectric. We heated the stage, and selected nanowires that had well-defined periodic domains. The substrate was pre-patterned with large Au leads from which smaller leads could be designed and fabricated with standard electron beam lithography and metal evaporation techniques (see FIG. 2). During evaporation, the position of the sample and angle incident to the evaporator was changed periodically to insure uniform contacts. The substrate was then fixed to a stage and the leads were then patched into the measurement set up via a wirebonding process. Once fabrication is complete, we obtain VO_2 nanowire devices that are functional field effect transistors (FETs).

FIG. 2. A NW device (thin dark line in center of frame) with attached gold leads (bright yellow structures). An insulating domain (light dull area in bottom portion of NW) and metallic domain (darker upper portion of NW) are visible. The width of this NW is roughly 300 μm.

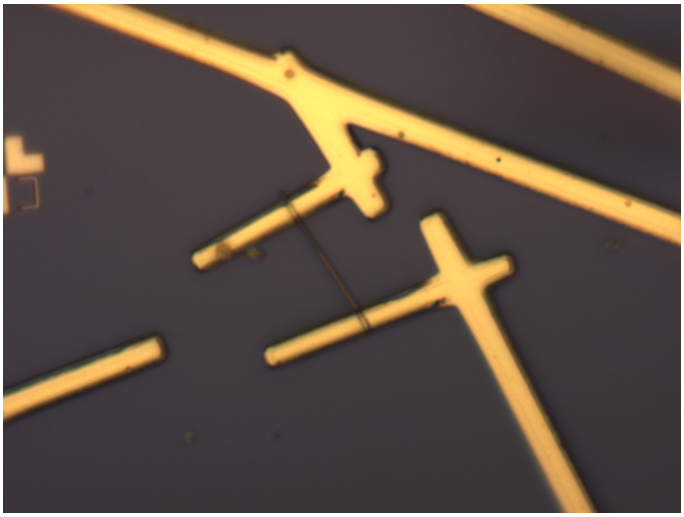
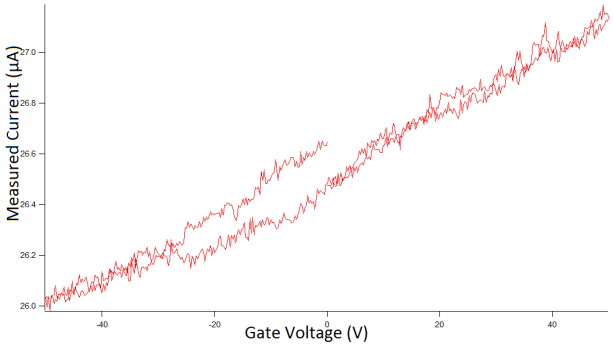


FIG. 3. The gate response of a PbS NW device. Because this curve is very linear, we can strongly conclude that the majority carriers are electron quasiparticles and that the device is n-type.



III. MEASUREMENT AND RESULTS

We primarily used two characterization techniques to study the VO_2 nanowires: (1) electrochemical gate scan, and (2) Scanning Photocurrent Microscopy (SPCM). Before committing to either electrochemical gating or SPCM, we first measured the voltage-current relationship and discarded devices showing nonlinear responses to ensure that all contacts were Ohmic.

A. Solid Gating

The gate measurement is a fundamental semiconductor characterization technique, ubiquitous in all aspects of research in industry and academia. In this setting we can use a gate scan to determine the majority carrier in the nanowire, which tells us if the device is n-type (electron quasiparticle carriers) or p-type (hole carriers). If the slope is positive, then the device is n-type, if the slope is negative then the device is p-type.

By using the SiO_2 thin film as a dielectric, we can apply a voltage to the Si substrate and induce a potential across the device and the substrate. This allows us to modulate the carrier density of the device, and we can then determine the majority carrier type by reading off the slope of the curve. In measuring more than 40 devices with various values of k_{Ar}, we determined a correlation between k_{Ar} and majority carrier.

k_{Ar} (sccm)	Doping Type
0	p-type
30	p-type & n-type
60	n-type

Unfortunately, due to the poor mobility of VO_2 (typical measured value $\mu = 0.04\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) and conductivity (typical measured value $\sigma = 0.6\,\mathrm{S\,m^{-1}}$), though some devices show acceptable solid gate response, it is often inconclusive (see FIG. 4), and requires more extreme experimental techniques.

B. Electrochemical Gating

Electrochemical gating provides the means in which one can push the carrier concentration of a device into new regimes. This involves applying a minuscule droplet of polyethylene glycol (PEO) with 5% $KClO_4$ by weight. The PEO is packed with free ions, and by applying a voltage to the device (via an electrode that overlaps with the pool of PEO), we achieve a similar carrier density modulating capacitance. The essence in gating is encoded in the simple formula for a parallel plate capacitor:

$$C = \frac{\epsilon A}{d},$$

where C is the capacitance of the device, ϵ is the absolute permittivity of the device, A is the surface area, and d is the distance between plates. Because the distance between the two "plates" (that is, between the ions in the liquid and the NW) is significantly reduced (compared to the distance between the NW and the Si substrate), we have dramatically more efficient charge injection and observe an increase in conductivity by two orders of magnitude.

We kept the stage at $T = 35K$, which is slightly above the melting point of the PEO. With skilled application via micromanipulator, we were able to achieve a droplet size of roughly $20 - 100\mu\,\mathrm{m}^2$.

It is typical of electrochemical gating techniques to exhibit a change in majority carrier. This is usually referred to as the chemical doping regime (see FIG. 5), and is achieved by driving the gate voltage past some threshold. When this occurs the NW and electrochemical fluid will react and create oxygen vacancies or hydrogenation at the VO_2 surface, which changes the doping type of

FIG. 4. The gate response of a VO_2 device. Since the profile of the curve is highly nonlinear, we cannot make any conclusive statements about the majority carrier or doping type.

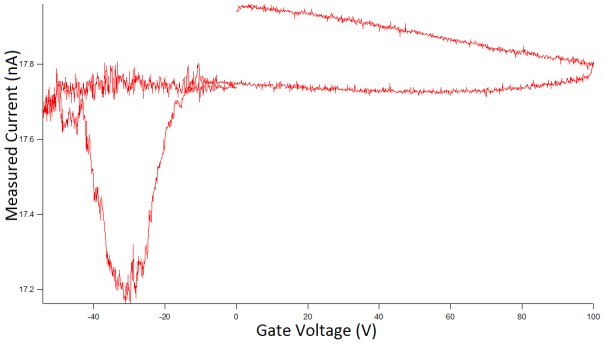
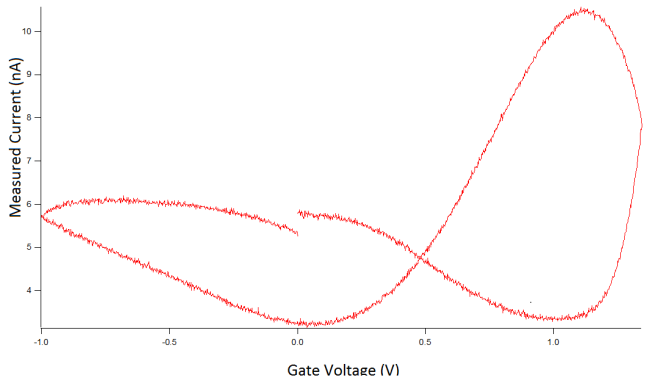


FIG. 5. Gate response of a p-type VO_2 NW device with electrochemical gating techniques. The standard gate response is visible, as well as the electrochemical doping regime.



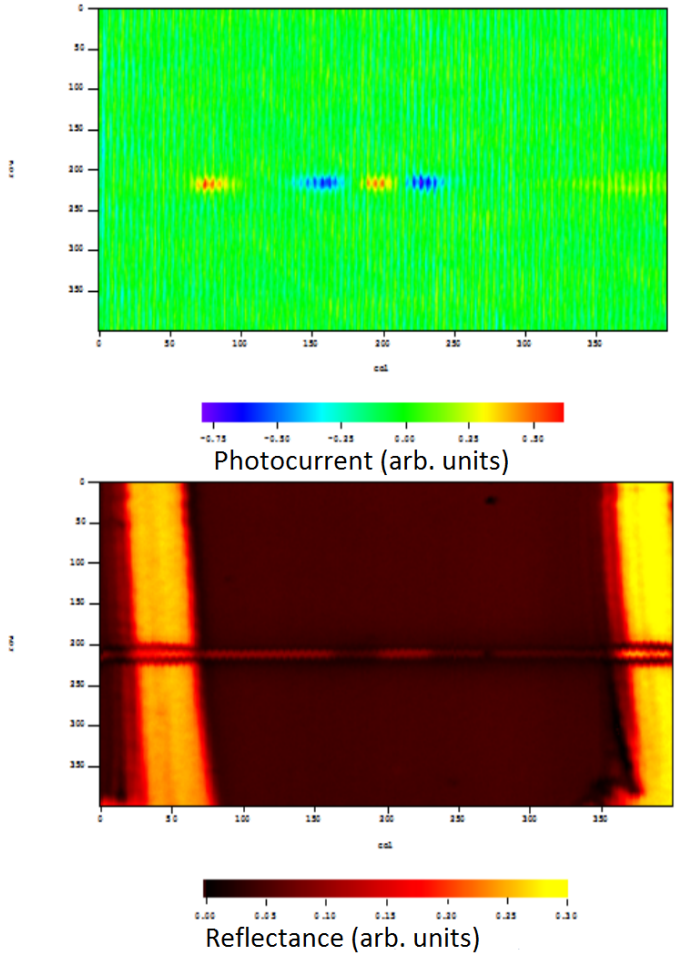
the wire. If the voltage is reduced, then oxygen may be readsorbed into the NW reversibly.

C. Scanning Photocurrent Microscopy

Scanning photocurrent microscopy is confocal microscopy method that exploits a focused laser as excitation source. SPCM is used to probe local electronic structure and charge transport properties. Our experimental set-up is comprised of a 532 nm continuous wave laser focused by an objective lens and scanned across the device via mirrors attached to galvanometers. Reflection and photocurrent signals were simultaneously recorded to map out a two-dimensional map of the device. A detailed account of SPCM measurement and set up can be found in [8] and [9].

As the laser is a local excitation source, we were careful to ensure that the power did not exceed the threshold to cause an MIT in the device being measured. At $T = 74°C$ (FIG. 6) and zero bias voltage, we observed a localized domain near a contact due to the Schottky junction at the contact. In general, a Schottky junction between a metal and an insulator causes a photocurrent signal on either sides of the domain. By examining this current, we can infer how the band structure has changed locally (usually referred to as band bending) and then infer what type of majority carrier is present in the NW. More information about band structure and its fundamental importance in solid state physics can be found in [10]. By examining the band bending, we see it is consistent with a p-type device. We then increased the temperature to $T = 95°C$ (FIG. 7) and observed several new metallic domains emerge that had alternating polarities that suggested band bending in a Schottky junction between a metal and p-type semiconductor. The signal is also reduced as the temperature increases. We ramped the temperature to $T = 137°C$, where we observed the polarity of the domains flip (FIG. 8). This is not obvious without realizing that the nanowire is also displaced

FIG. 6. Photocurrent and reflectance measurement at $T = 74°C$. Note that the domains are visible in the reflectance image. The preamplifier is connected to the lead on the right hand side of the NW.



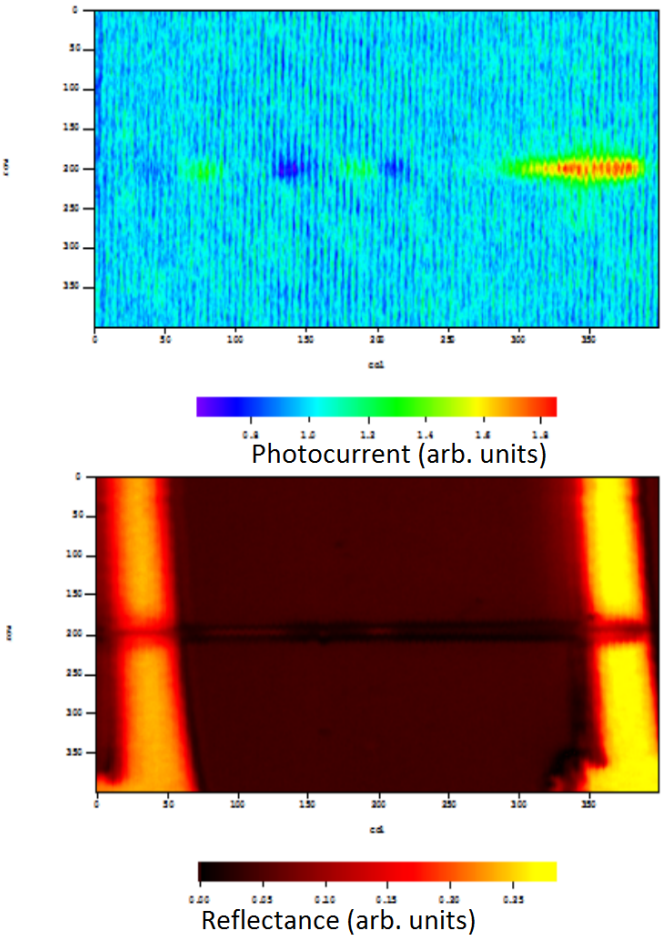
slightly to the left between FIG. 7 and FIG 8. This corresponds to a change to an n-type semiconductor. We believe this is due to the creation of oxygen vacancies in the devices. The polarity flipping is reversible since we returned to p-type band bending when we ramped the temperature back down to room temperature. This makes sense, because oxygen may be readsorbed into the device and remove oxygen vacancies.

IV. DISCUSSION

These results are novel. P-type NW devices have not previously been reported, and we believe we are the first group to report a recipe that establishes a causal link between growth conditions (specifically the partial pressure of O_2 in the furnace) and doping type.

Despite the increased efficiency of the electrochemical gating method, we still observe considerable hysteresis. This does not have a simple solution, as increasing the voltage will push the device further into the electrochem-

FIG. 7. Photocurrent and reflectance measurement at $T = 95^{\circ}$C. The large blob next to the lead on the right is attributed to thermoelectic effects.



ical doping regime and will be irreversible. Nonetheless, we are still able to extract useful information about the doping type with electrochemical gating.

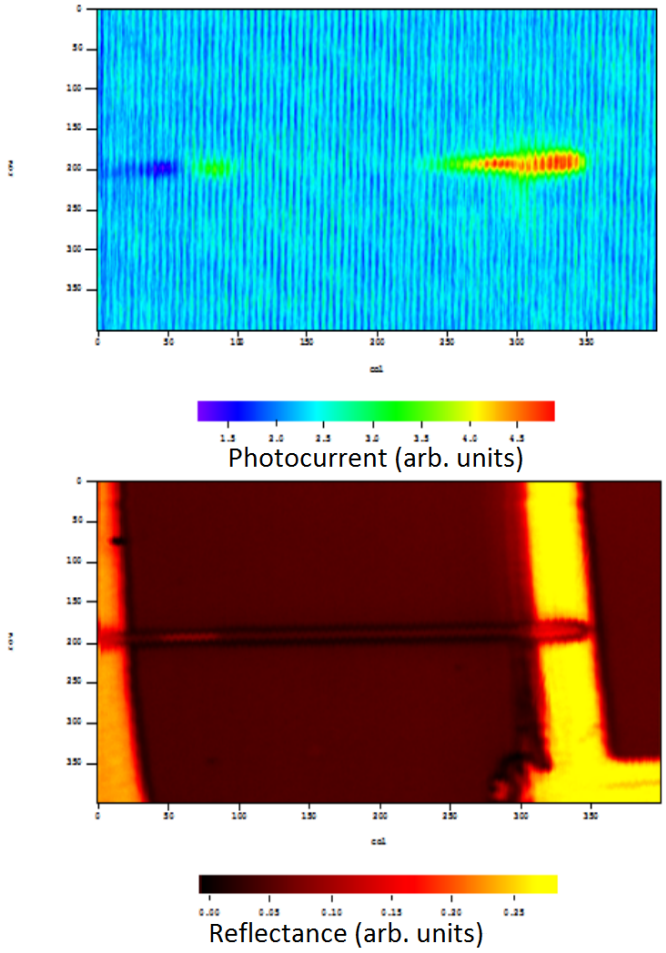
Our SPCM results provide the strongest evidence that the NW devices were p-type. Our observation of temperature dependent polarity flipping also suggests that the p-type nature may be related to surface oxygen adsorbtion.

V. CONCLUSION AND FUTURE OUTLOOK

We obtained several novel and exciting results. We successfully characterized our VO_2 via electrochemical gating. We also observed temperature driven polarity flipping in domains, which both provides solid confirmation of doping type and weakly suggests that the MIT in VO_2 is Mott-type.

It is possible that fabrication of suspended VO_2 nanowire devices could help reduce the effects of strain on the devices, but it is likely that the majority of strain

FIG. 8. Photocurrent and reflectance measurement at $T = 137^{\circ}$C.



in the devices is due to the electrical contacts themselves. Investigations into strain in VO_2 have been successfully implemented [2], but understanding of strain effects on electronic structures and electric field induced MITs is lacking.

We also would like to investigate surface states in VO_2: because surface states are generically less mobile than bulk states, it is possible that further insight into surface states may allow their mitigation and eventually improve gate response.

It would also be nice to perform Hall measurements on NW devices. This has been reported for other NW devices [11], and successful implementation in a VO_2 NW system would provide further information about charge carriers and transport phenomena. This is also considered to be a rather difficult experiment to implement.

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