Hubbard Gap Modulation in Vanadium Dioxide Nanoscale Tunnel Junctions

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ABSTRACT: We locally investigate the electronic transport through individual tunnel junctions containing a 10 nm thin film of vanadium dioxide (VO₂) across its thermally induced phase transition. The insulator-to-metal phase transition in the VO₂ film collapses the Hubbard gap (experimentally determined to be 0.4 ± 0.07 V), leading to several orders of magnitude change in tunnel conductance. We quantitatively evaluate underlying transport mechanisms via theoretical quantum mechanical transport calculations which show excellent agreement with the experimental results.

KEYWORDS: Atomic force microscopy, metal–insulator transition, vanadium dioxide, density functional theory, non-equilibrium Green’s function, tunnel junction

Vanadium dioxide (VO₂) is a correlated electron material that exhibits a metal-to-insulator transition (MIT) with up to 6 orders of magnitude change in in-plane resistivity near room temperature (~340 K) in unstrained films.¹ The MIT can be externally triggered using thermal,² electronic,³ optical,⁴ or strain stimuli.⁵ It has also been demonstrated by time-resolved optical pumping that this transition is as fast as 75 fs.⁶ In the insulating state, VO₂ has an optically measurable Hubbard gap of 0.6 eV,⁷ which abruptly collapses as VO₂ undergoes an insulator-to-metal transition. The collapse of the Hubbard gap and ultrafast switching holds promise for high speed correlated tunnel transistors.⁸ This increases the interest to investigate nanostructures that contain VO₂.

In this work we investigate nanoscale tunnel junctions that contain a thin layer of VO₂. Our structures incorporate an electrically insulating film on top of a thin VO₂ film between metallic contacts. This layout allows us to directly study the out-of-plane electronic transport behavior through a thin film of VO₂ throughout its phase transition.

When VO₂ is in the metallic state, such a metal–insulator–metallic VO₂–metal structure essentially acts as a metal–insulator–metal tunnel junction. In this state direct tunneling is expected to be the dominating underlying transport mechanism⁹ as electrons can tunnel directly from one metallic layer, through the insulating barrier into the next metallic layer (Figure 1a). When VO₂ is in its insulating state, a bandgap E₉ opens in the VO₂ film (Figure 1b). This bandgap eliminates states near the Fermi level previously used for the electronic transport, thus significantly lowering the tunneling current through the structure. This bandstructure is fundamentally different from conventional semiconductor based tunnel junctions where the electronic transport is dominated by band-bending and the Fermi level movement.⁹

Such metal–tunnel barrier–VO₂ tunnel junctions were first demonstrated by Martens et al.,¹⁰ on devices with diameters of several hundred micrometers and using atomic layer deposition (ALD) at temperatures of 200 °C and higher. Martens et al. could show approximately 1 order of magnitude conductance change when thermally driving these devices across the MIT.

In this work, we investigate the electronic transport through nanoscale tunnel junctions fabricated via low temperature (110 °C) ALD. We locally investigate the temperature

Received: June 3, 2014
Revised: August 25, 2014
dependence of the electrical conductance for individual nanopillars and observe a change in conductance of roughly 2 orders of magnitude as the VO$_2$ film goes through the MIT. To quantitatively understand the quantum transport in these tunnel junction devices, we carry out nonequilibrium transport calculations under the framework of density functional theory (DFT) combining with nonequilibrium Green’s function (NEGF) methods.

The sample under investigation is a multilayer nanopillar array of VO$_2$ tunnel junctions. A schematic side view is shown in Figure 2a. The substrate consists of electrically conducting 500 μm thick (001) Nb-doped TiO$_2$ from CrysTec. On this substrate we deposit a 10 nm ± 5 Å thick epitaxial VO$_2$ film via reactive oxide molecular beam epitaxy using a Veeco GEN10 array of VO$_2$(NEGF) methods. Patterns of about 20 pA for which we correct in all measurement data. For each temperature and each nanopillar, we record 20 individual IV traces. The raw data show a constant instrument originated current offset of about 20 pA for which we correct in all measurement data. For each temperature and each nanopillar, we record 20 individual IV traces under identical conditions, the average of which is then used for further evaluation.

Using this method we record the current $I$ through a nanopillar versus sweeps of the applied voltage $V$, so-called IV traces. The raw data show a constant instrument originated current offset of about 20 pA for which we correct in all measurement data. For each temperature and each nanopillar, we record 20 individual IV traces under identical conditions, the average of which is then used for further evaluation.

Figure 3a–c shows IV traces recorded over a temperature range from 260 to 360 K in 5 K temperature steps for three individual nanopillars (A–C). We observe two distinctly different shapes of IV traces: traces recorded above a transition temperature $T_c$ show a continuous increase of current with applied voltage. This is the signature shape of the IV trace in the ON state where direct tunneling takes place from the Pd-layer through the tunnel barrier posed by the dielectric into the metallic VO$_2$ layer. Typical currents are of the order of 1 nA at $V = 0.4$ V.

Below $T_c$, the shape of the IV traces abruptly changes and shows a region of current blockade around 0 V. The width of this current blockade region (Hubbard gap) is $0.4 \pm 0.07$ V. Outside of this blockade region, the current through the structure rises with increasing applied voltage. This is the
signature shape of the IV trace in the OFF state where typical currents are of the order of 0.02 nA at $V = 0.4$ V.

The $T_c$ for pillars A and B is $285 \pm 5$ K and $290 \pm 5$ K for Pillar C. A slight variation in $T_c$ for different nanopillars could be due to a variation in local strain, temperature, or film thickness. We extract the conductance $G(V_E)$ here defined as $G(V_E) = (I(V_E))/V_E$ at distinct evaluation voltages $V_E$ (Figure 4a) and plot its value versus the measurement temperature $T$(Figure 4b). For each individual pillar we observe that for both $G$ and the quantum mechanical transport in VO$_2$ applications, a promising transport property that could be used to achieve a tunnel conductance at low applied voltage takes place. This is a magnitude. The precise magnitude of the change depends on $V_E$, at which the comparison is carried out. Figure 4 traces for temperatures between 260 to 340 K in 5 K steps as indicated in the legend for three different nanopillars (A, B, C).

(figure 4b). For each individual pillar we observe that for both regions, $T > T_c$ and $T < T_c$, the conductance is nearly independent of temperature. This indicates that the dominant temperature dependent process that influences the conductance is the phase transition in VO$_2$ at $T_c$. All other transport processes show only a very weak temperature dependence. At $T_c$, the conductance changes by approximately 2 orders of magnitude. The precise magnitude of the change depends on the voltage $V_E$ at which the comparison is carried out. Figure 4 shows that, when VO$_2$ undergoes a MIT at $T_c$, a large change in tunnel conductance at low applied voltage takes place. This is a promising transport property that could be used to achieve a steep slope switching characteristics in future device applications.

To make a direct comparison between the measurements and the quantum mechanical transport in VO$_2$ based tunnel junction devices, we carry out nonequilibrium transport calculations by using density functional theory combining with the non-equilibrium Green’s function formalism, as implemented in the simulator Atomistic Toolkit. Before performing the transport calculations, first-principle calculations of both high-temperature rutile (Figure 5a) and low-temperature monoclinic (M1) (Figure 5c) crystal structure (in bulk form) of VO$_3$ are carried out by DFT+U where $U$ is the Hubbard electron–electron correlation parameter. In our computations, different lattice parameters of both VO$_2$ crystal structures as determined by Eyert et al. have been considered. We adopt the Perdew–Burke–Ernzerhof functional under generalized gradient approximation for the exchange correlation along with double-$\zeta$-double polarized basis set for the electron wave function. These electron wave functions are usually comparable to well-converged plane wave basis sets, whereas the core electrons are defined by norm-conserving pseudopotentials. The computed projected density of states (PDOS) for both crystal structures is shown in Figure 5. It is well-understood that the high-temperature rutile crystal structure leads to metallic behavior. Lowering of the crystal symmetry from rutile to M1 results in a formation of V–V dimers along the rutile c-axis, which splits the nonbonding $d$-orbitals into occupied and unoccupied states. Due to the Mott insulator nature of the M1 VO$_2$, the conventional DFT cannot open a band gap. With the addition of Hubbard $U$ term, the $d$-orbitals split into a lower Hubbard band (LHB) and an upper Hubbard band (UHB) and eventually produce a Mott–Hubbard gap. The electronic state as projected in our PDOS computations agrees well with the orbital distributions as shown by Quackenbush et al. From our first-principles study, we observe that $U = 4$ eV produces a Mott gap of 0.56 eV, which is in excellent agreement with the experimental as well as previous theoretical results of 0.63 eV. Therefore, we considered DFT+U instead of conventional DFT along with NEGF formalism in our transport calculations of the M1 phase.
The atomistic view of the VO$_2$ based tunnel junction device used for our transport calculations is shown in Figure 6a. We consider a simplified device architecture by implementing a 2 nm thick HfO$_2$ film instead of two different dielectric materials as a tunnel barrier in order to reduce the computational cost by minimizing the number of different interfaces. The VO$_2$ thickness is 2.9 nm for M1 and 2.8 nm for the rutile crystal structure where we consider the low-temperature M1 crystal structure for the VO$_2$’s OFF state below $T_c$ and the high-temperature rutile crystal structure for its ON state above $T_c$.

To simulate the transport across the VO$_2$ tunnel junction, we construct a Pd/HfO$_2$/VO$_2$ supercell. To construct the supercell with different materials (i.e., VO$_2$/dielectric/metal), we use a slab of VO$_2$ along the [001] orientation in both the rutile (metallic) and M1 (insulating) phase of VO$_2$. This orientation is the same as that of VO$_2$ used in the experimental tunnel junction structures. Further, this particular choice of orientation removes any dangling bonds at the VO$_2$ interface and eliminates the effect of any resulting surface states. To minimize the number of atoms in the supercell, we use the monoclinic phase of the HfO$_2$ dielectric. The lattice parameters for HfO$_2$ used in the simulation are reported by Zhou et al.$^{17}$ While constructing the supercell, the $b$ and $c$ axes of the HfO$_2$ lattice are swapped, enabling the strain to be minimized. The supercell is then completed by adding [001] Pd. The resulting transverse lattice constants for the supercell are $a = 1.404$ nm, $b = 1.404$ nm (rutile VO$_2$ supercell) and $a = 1.404$ nm, $b = 1.7906$ nm (M1 VO$_2$ supercell). In the rutile VO$_2$ phase, the corresponding strain on HfO$_2$ at the HfO$_2$/[001] rutile VO$_2$ interface is 1.13%, and the strain on Pd metal at the Pd/HfO$_2$ interface is 1.79%. The corresponding values of strain for the M1 case are 1.53% and 1.74%.

As depicted in Figure 6a, we have also considered the transverse directions (xy-plane) as periodic to unite the bulk nature of different materials. To relax the structural interface of this tunnel junction, structure optimization has been done by quasi-Newton scheme$^{18}$ until all the forces acting on atoms become smaller than 0.001 eV/Å. In the transport computations we employ DFT+NEGF to the atomic structure of both the device and the electrodes in a self-consistent manner. The conductance of the device has been calculated as

$$G = \frac{2e^2}{h} \sum_i T(E_i, k_{\|})$$

Figure 6. (a) Atomistic structure of VO$_2$ based tunnel junction where the transport direction is along the z-axis and the direction perpendicular to the z-axis (xy-plane) is periodic in nature. (b) The schematic depicting the tunneling transport mechanism and (c) the corresponding transmission (normalized to the area) when VO$_2$ is in the insulating state. (d, e) Schematic and the corresponding transmission (normalized to the area) when VO$_2$ is in its metallic state.
Bloch wave vector, and are anti-Hermitian components of the self-energy terms of the $i$ through distinct, individual VO results.

conductance (Figure 7b) agrees well with our measurement $6e$). When comparing the experimentally measured transition along with the electronic phase transition in VO, $6d$, allowing for controlled direct tunneling from the Pd-layer electronic states throughout the whole structure line up (Figure 7).

Figure 6b shows the schematic of the tunneling mechanism in VO-based tunnel junction when VO$_2$ is in its insulating M1 state. As VO$_2$ opens a bandgap when lowering the temperature, eliminating the electronic states in the VO$_2$ around the Fermi energy, the external voltage has to be high enough to compensate for the missing electronic states near the Fermi energy in VO$_2$ to allow transport through the structure. This is also reflected in the transmission (Figure 6c).

Above $T_c$ when VO$_2$ is in its metallic rutile crystal structure, electronic states throughout the whole structure line up (Figure 6d), allowing for controlled direct tunneling from the Pd-layer through the tunnel barrier into the metallic VO$_2$ layer (Figure 6e). When comparing the experimentally measured $G$ vs $V$ traces (Figure 7a) in both ON and OFF states, we find that the signature shape of the computed quantum mechanical tunnel conductance (Figure 7b) agrees well with our measurement results.

In conclusion, we are able to accurately measure IV traces through distinct, individual VO$_2$ nanopillars while also allowing the benefit of topographic imaging. In the future this might allow us to simultaneously investigate the topographic phase transition along with the electronic phase transition in VO$_2$ that we investigate in this work. The VO$_2$ nanotunnel junctions show an abrupt change in conductance of approximately 2 orders of magnitude when VO$_2$ undergoes its phase transition from the insulating (OFF) state to its metallic (ON) state. This MIT occurs at $T_c = 287.5 \pm 7$ K. When VO$_2$ is in the electrically insulating state, the IV traces show a region of suppressed current (Hubbard gap) of a width of 0.4 ± 0.07 V. We have performed ab initio transport calculations through DFT+NEGF formalism by considering both rutile and M1 phase for the ON and OFF states, respectively. To incorporate the Mott properties in the M1 phase, we use $U = 4$ eV which results in a very good agreement between the experimental Hubbard gap value and calculated bandgap value of 0.56 eV. Our theoretical quantum mechanical transport calculations show very good agreement with the experimental results in terms of the shape of the GV traces. Our results are a step toward the future use of correlated oxide based tunnel junctions with high on-off conductance ratios for both memory and logic applications.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

M.H. thanks the DFG fellowship (HU-1960/1-1) for their support. All authors would like to thank Prof. Hoffman (Harvard University) for allowing the use of her facilities to carry out the measurements. R.G. and S.D. thank the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA for their financial support. NS, HP, and DGS were funded by Office of Naval Research through award N00014-11-1-0665. This work was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant No. ECCS-0335765).

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