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ARTICLE

Intermediate Metallic Phase in VO_2 Observed with Scanning Tunneling Spectroscopy

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This investigation focuses on the formation of nanoscale puddles of an intermediate metallic phase (IMP) in the metal-insulator transition (MIT) temperature regime of single-crystalline vanadium dioxide (VO_2) nanowires. The electronic structure of VO_2 nanowires was examined with scanning tunneling spectroscopy. The evolution of the local density of states of individual nanowires throughout the MIT regime is presented with differential tunneling conductance spectra and images measured as the temperature was increased. Our results show that the formation of an IMP plays an important role in the MIT of intrinsic VO_2.

Introduction

Many strongly correlated transition metal oxide (TMO) materials show a variety of phenomena such as high-temperature superconductivity, carrier-induced ferromagnetism, colossal magnetoresistance, and phase transitions including metal-insulator transitions (MITs). Vanadium dioxide (VO_2) is a strongly correlated TMO material that undergoes a MIT.[1-7] This MIT is an abrupt, first-order phase transition characterized by a change in resistivity of several orders of magnitude at a critical temperature $T_C \approx 340$ K. Vanadium dioxide is a promising material for novel nanodevices as its MIT is in the vicinity of room temperature, and is considered to be a model system to study mechanisms of MITs. Our investigation of high-quality single-crystal nanowires allowed us to examine the intrinsic properties of VO_2.

The MIT and structural phase transition (SPT) in VO_2 are often observed at the same temperature. During the SPT, the lattice structure of the high-temperature metallic rutile (R) phase undergoes dimerization and tilting of VO_6 octahedra along the R phase *c*-axis, transforming into the low-temperature insulating monoclinic (M_1) phase.[8] However, it has been revealed that a strongly correlated metallic monoclinic (M_3) phase plays an important role in the MIT of VO_2 under certain conditions. It was proposed that the SPT of VO_2 is decoupled from the MIT forming an intermediate metallic phase (IMP) above a critical hole-concentration.[1,2] The presence of an IMP has been observed experimentally,[3-5] and deemed plausible based on first principles electronic structure calculations.[4] However, no distinctly different intermediate structural phases have been identified in pair distribution function measurements of local geometric structure across the thermal phase transition.[9,10] Our scanning tunneling microscopy/spectroscopy (STM/STS) investigation of single-crystal VO_2 nanowires focuses on the electronic structure of the IMP we observed, which is distinctly different than that of the low-temperature insulating phase and the high-temperature metallic phase. It is important to evaluate the evolution of the local density of states (LDOS) of an IMP in VO_2 in order to verify emerging theoretical calculations that point to several putative intermediate phases with a reduced bandgap. To our knowledge, no direct observations of the electronic structure of an IMP have been reported and

indeed past measurements have required the application of effective medium theory to identify localized domains with discrepant optical conductivities. Understanding which mechanisms govern the MIT of this model TMO material will shed light on other TMO systems.

While there have been observations that may indicate the presence of an IMP between the insulating M_1 phase and the high-temperature metallic R phase, explanations for the observations, such as phase coexistence, current-induced conductive threads ("hot filaments"), or strain-induced nanostructures cast doubts on whether the SPT can be decoupled from the MIT and form an IMP. Phase coexistence has been observed with optical spectroscopy,[11] and with STS measurements on VO_2 thin films.[12,13] The MIT has been shown to occur as a percolation process;[11,13] it was suggested that strongly correlated nanopuddles of an IMP form in the insulating host while the high-temperature metallic phase becomes more prominent.[11]

Prior spectroscopy studies that showed the presence of an IMP lacked the spatial resolution to distinguish between nanopuddles of coexisting phases. Furthermore, Raman and infrared microscopy and spectroscopy techniques are incapable of resolving coexisting nanoscale domains such as the ones discussed below. Temperature-dependent STS has the ability to spatially map with sub-nanometer resolution the electronic structure of a sample's surface, and therefore can discern between the insulating phase coexisting with the nanoscale domains of the high-temperature metallic phase and an IMP. Thus, STS is a very attractive technique to observe nucleation and growth from metallic nanopuddles that form during the MIT in VO_2.

Evidence of the formation of an IMP between the insulating M_1 phase and high-temperature metallic R phase during the MIT of VO_2 has been shown. Far-field spectroscopic ellipsometry and reflectance measurements identified key electronic characteristics of a Mott transition, one of which is the divergence of the optical effective mass in metallic nanopuddles.[11] The optical conductivity extracted from these nanopuddles with effective medium theory exhibits a pseudogap and a peculiar frequency dependence that is markedly different from the high-temperature metallic phase. Qazilbash *et al.* suggested that such nanopuddles are a strongly correlated IMP based on calculated dielectric functions.[11] However, a direct measurement of localized electronic structure remains a critical gap in our understanding of these systems. A monoclinic IMP has also been observed in ultrafast pump-probe studies of the optically induced MIT in VO_2 thin films.[5,14-16] An IMP was observed after the onset of the optically induced MIT prior to the onset of the SPT, which suggests that the mechanisms governing the MIT may be different from those of the SPT.

Experimental

The samples analyzed in this work are single-crystalline VO_2 nanowires grown by a hydrothermal process through the reduction and exfoliation of layered hydrated $V_2O_4{\cdot}nH_2O$ using aliphatic alcohols,[17] and were transferred onto Cr/Au (5 nm/80 nm) thin films on Si substrates after dispersion in 2-propanol. The verification of the crystalline structure, stoichiometry, and electronic structure of our samples with x-ray diffraction, scanning electron microscopy, TEM, selected area electron diffraction, inductively coupled plasma mass spectrometry, and x-ray absorption fine structure (XAFS) spectroscopy have been previously reported.[17] The nanowires typically range in length from several hundred nanometers to 10 μm, from several hundred nanometers to 0.5 μm wide, and have an average thickness of 160 nm.[17] Nanowires of binary and ternary vanadium oxides grown by hydrothermal methods are comparable to epitaxially grown samples in terms of the magnitude and abruptness of the metal—insulator transition. Indeed, greater than four orders of magnitude decrease in resistance have been observed at the critical MIT temperature for hydrothermally grown VO_2 nanowires.[17,18,19] Indeed, it is thought that the migration of defects to proximal surfaces allows for highly crystalline nanowires to be stabilized by hydrothermal methods and indeed such methods have allowed for the first observations of colossal MITs in the ternary vanadium oxide bronzes β'-$Cu_{0.65}V_2O_5$ and δ-$K_{0.5}V_2O_5$.[18,19] The hydrothermal process yielded free-standing single-crystal nanowires with a reduced T_C and broadened MIT hysteresis. Since the nanowires are simply cast onto the substrate in solution, no strong substrate coupling is expected allowing these materials to serve as excellent model systems for interrogation of intrinsic MIT phenomena. The cooling and heating T_C values obtained with differential scanning calorimetry were found to be 305 K and 335 K, respectively.[17] The origin of the reduction of T_C in our VO_2 nanowires is not certain. However, defects, strain-induced effects, reduced dimensionality, or a combination of these factors may be responsible.[13,17,20] Specifically, structural transformations are often nucleated at defects (such as dislocations), which in nanowires tend to migrate to surfaces. The absence of a defect with adequate potency to nucleate a transition to the monoclinic phase could explain the supercooling of the high-temperature rutile

(austenite) phase. The dramatic reduction of T_C in nanowires and nanoparticles as compared to 2D thin films and 3D single-crystals may also be due to a strongly modified percolation threshold at reduced dimensions.[7,17,20]

An Omicron variable-temperature ultra-high vacuum STM was used to study the temperature dependence of STS on VO_2 nanowires during heating cycles. Mechanically cut Pt-Ir alloy tips were used for tunneling measurements. STM topography, *I-V* and differential tunneling conductance (*dI/dV-V*) curves were obtained simultaneously with a modulation bias technique. A step in the voltage sweep for *dI/dV* is 10 mV, the sample bias voltage is −1.5 V, the tunneling current is 1.1 nA, and the pixel size is 3.85 x 3.85 nm^2. In order to repeatedly image the same area of the same nanowire, thermal drift was manually compensated for in the measurements.

Differential tunneling conductance (*dI/dV*), which is proportional to the LDOS,[21] was obtained as a function of tip-sample bias at every pixel over the same area of an individual nanowire at incrementally increased temperatures. This process was repeated for separate nanowires. In order to observe the transition of the LDOS, *dI/dV-V* curves were obtained at fixed temperatures around the heating T_C. The *dI/dV-V* curves obtained are consistent with reported *dI/dV-V* curves for the insulating M_1 phase and the high-temperature metallic R phase obtained indirectly from *I-V* curves on VO_2 thin films [Figs. 1(b), 1(f), and 2(b)].[12,13]

Results

Our STS results on VO_2 nanowires show that distinct nanoscopic regions exist in the nanowires with a reduced gap that we attribute to the coexistence of an IMP with the insulating phase and the high-temperature metallic phase in the MIT temperature regime. The insulating and metallic phases can be distinguished with *dI/dV-V* curves and images at a fixed finite sample bias. Here we present the spatial distribution and evolution of the LDOS of nanowires: nanopuddles ascribed to an IMP appear in the MIT temperature regime, and the high-temperature metallic phase percolates from them.

Figure 1 shows *dI/dV-V* curves and images obtained by repeatedly measuring the same area of a nanowire at 320 K, 335 K, and 343 K. The purple and blue areas in the *dI/dV* images in Figs. 1 and 2 represent insulating areas: purple areas correspond to a full energy gap [Figs. 1 and 2], and blue areas correspond to a reduced energy gap at the fixed sample bias near the Fermi level chosen for the *dI/dV* images. Likewise, metallic areas are represented by the cyan, green, yellow, and red areas which have increasingly larger *dI/dV* values at the fixed sample bias chosen for the *dI/dV* images. For ease of qualitative interpretation, the curves of Figs. 1 and 2 are color coordinated with their respective *dI/dV* image color scales. For clarity the *dI/dV-V* curves, other than the full gap curves, have been vertically offset. In order to better visualize the evolution of the IMP LDOS with increasing temperature, two areas in each of *dI/dV* images in Fig. 1 where nanopuddles of the IMP formed (and their corresponding *dI/dV-V* curves) have been labelled as Areas 1 and 2. The marked Areas 1 and 2 of Fig. 1and their respective *dI/dV* curves correspond exactly to the same locations across the series of images.

In Fig. 1(a), we show the *dI/dV* image at 320 K (below T_C), which displays a predominantly insulating surface. Figure 1(b) shows *dI/dV-V* curves which correspond to the *dI/dV* image of Fig. 1(a), and most of Fig. 1(a) displays a full or reduced energy gap, including those of Areas 1 and 2. Figure 1(a) also has small areas which display negligible, or no energy gap, along with some small metallic areas. Such areas that exhibited a reduced energy gap and metallic domains were commonly observed in these nanowires, even below the cooling T_C. The wide range of *dI/dV* characteristics has been observed in previous STS temperature studies of VO_2 thin films.[12,13] The origin of these persistent metallic domains may be due to: crystal faults, vacancy defects, strain effects that permit stabilization of the high-temperature phase,[22] or a combination of these factors.[13,17]

In Fig. 1(c), we show the 335 K (T_C) *dI/dV* image featuring (red) nanopuddles that formed in Areas 1 and 2, which were part of the insulating host matrix, shown in Figs. 1(a) and 1(b). Figure 1(d) shows the 335 K *dI/dV-V* curves which correspond to the *dI/dV* image of Fig. 1(c), some of which closely resemble the *dI/dV-V* curves of the insulating M_1 phase and the metallic R phase reported in literature.[12,13,23,24] However, at 335 K the *dI/dV-V* curves of the metallic nanopuddles which formed in Areas 1 and 2 display distinctly different LDOS than reported for the R phase. The nanopuddles of Areas 1 and 2 in Figs. 1(c) and 1(d) subsequently at 343 K, shown in Figs. 1(e) and (f), transformed into areas that match the reported metallic R phase. Thus, we consider that the LDOS of the nanopuddles in Areas 1 and 2 at 335 K [Figs. 1(c) and 1(d)] to be that of an IMP or IMPs.[3-5,11]

There are several distinctions between the *dI/dV-V* curves of the IMP and the high-temperature metallic phase. First, the IMP *dI/dV-V* curves tend to have a large shoulder in the valence band, and a smaller shoulder in the conduction band. The shoulders of the IMP *dI/dV-V* curves are consistent with the shifts in the valence and conduction bands observed both experimentally and computationally.[15,25] Second, the *dI/dV-V* curves reported for the R phase in literature and high-temperature metallic phase we observed in our measurements tend to be more smooth and symmetric about the Fermi level as compared to the *dI/dV-V* curves of the IMP.[12,13] Third, the IMP *dI/dV-V* curves tend to have larger values near the Fermi level as compared to the high-temperature metallic phase. This supports the

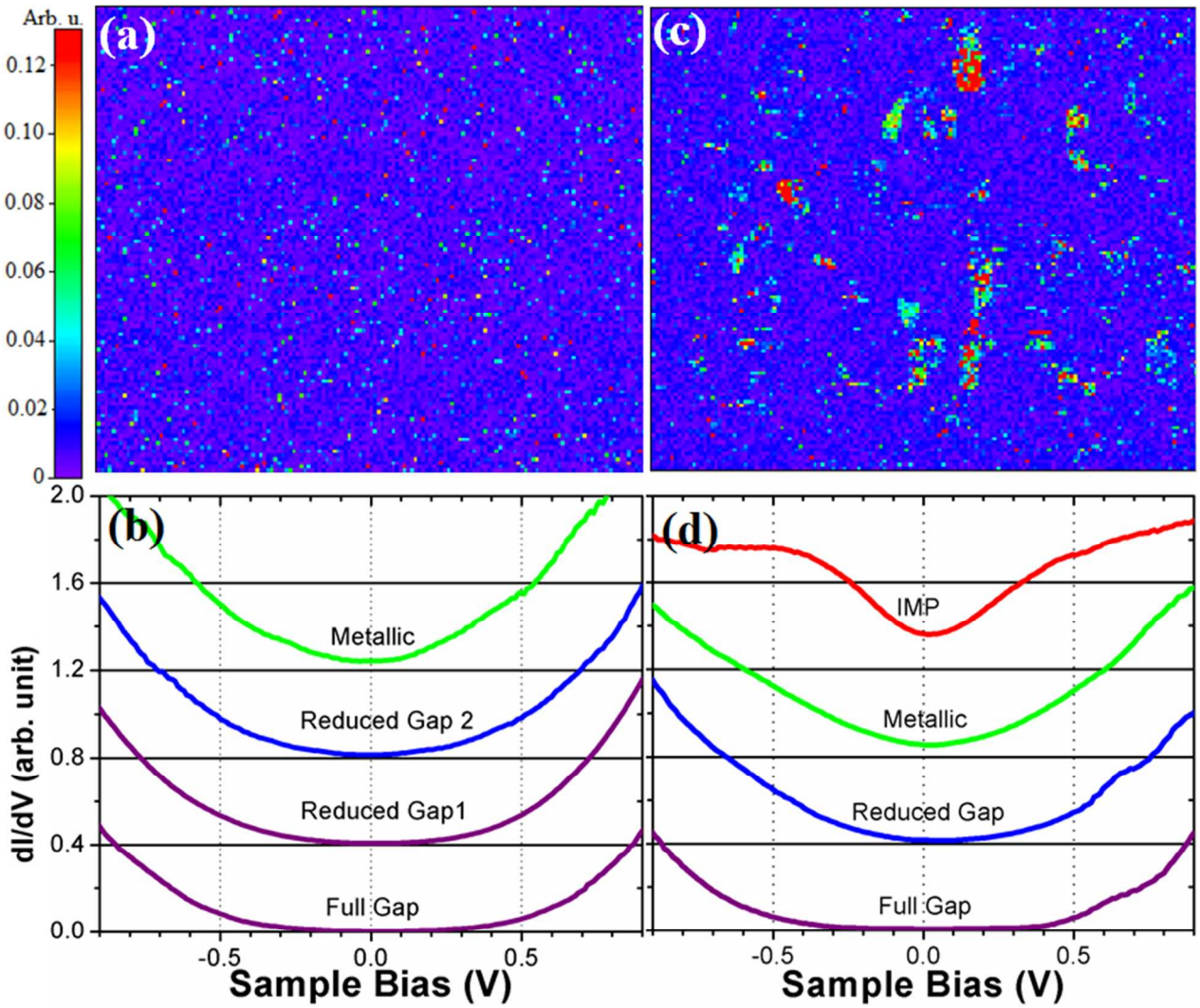

Figure 1. (a) and (c) show *dI/dV* images (fixed sample bias of +0.05 V) of the same area of a second VO_2 nanowire. The color scale applies to the *dI/dV* images. (b) and (d) show *dI/dV-V* curves which correspond to the *dI/dV* images (a) and (c), respectively. For clarity the *dI/dV-V* curves, other than the full gap curves, have been vertically offset. (a,b) and (c,d) were obtained sequentially at 320 K and 348 K, respectively. Image sizes are 500 x 400 nm^2.

suggestion of an IMP having much larger conductivity values relative to the high-temperature metallic R phase.[11,26]

We present evidence that suggests that the change from the low-temperature insulating phase to that of the IMP with increasing temperature may be accompanied by an insulating state with a reduced energy gap. Similarly, the LDOS of the IMP might not abruptly change to that of the high-temperature poor-metal as temperature is increased. It is plausible that there are further intermediate states in temperature (Area 2 of Figs. 1(c) and 1(d)) between the IMP we observed (Area 1 of Figs. 1(c) and 1(d)), and the high temperature poor-metal. The specific Fermi surface of the intermediate metallic phases is likely also affected by the strain state and compositional inhomogeneities (such as slight variations in oxygen stoichiometry), although the intermediating role of these states is clear from their evolution to metallic character with increasing temperature. We further note that the specific spectroscopic signature of the IMP is likely to be influenced by their spatial extent and proximity to metallic and full gap phases. These explanations account for the noted discrepancies between the spectra's of Areas 1 and 2 in Fig. 1(d).

Figure 2 presents *dI/dV* results obtained by repeatedly measuring the same area of a nanowire at 320 K and 348 K. Just as Fig. 1(a) and (b), the *dI/dV* results at 320 K of Figs. 2(a) and 2(b) show that below T_C the insulating phase is dominant. The spatial distribution of areas exhibiting a reduced energy gap can be seen more clearly in Fig. 2 than in Fig. 1. As expected, Figs. 2(c) and 2(d) show that above T_C the high-temperature metallic phase has become more prevalent, but has not become dominant. Some of the nanopuddles in Fig. 2(c) appear to have already transformed from the IMP to the high-temperature metallic phase at 348 K. The spatial variations of the MIT critical temperature of our nanowires may be related to varied surface strain states.

The specific critical transition temperature of the nanowires depends not just on the size (and the strain state) but also the thermal history. Consequently, supercooling of the metallic state and superheating of

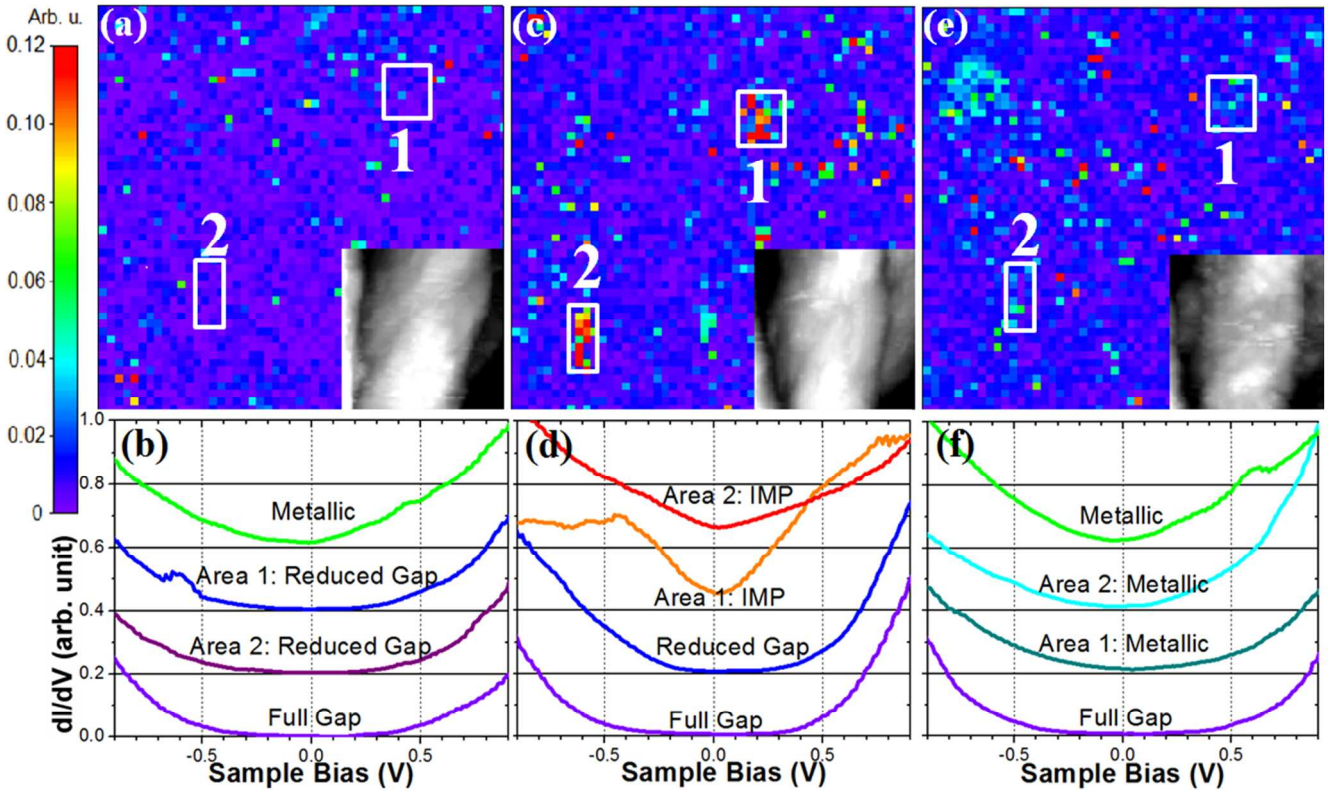

Figure 2. (a), (c) and (e) show *dI/dV* images (fixed sample bias of +0.1 V) of the same area of the first VO_2 nanowire. (b), (d) and (f) show *dI/dV-V* curves which correspond to *dI/dV* images (a), (c) and (e), respectively. The marked Areas 1 and 2 and their respective *dI/dV* curves correspond exactly to the same locations across the series of images. The color scale applies to the *dI/dV* images. (a,b), (c,d) and (e,f) were obtained sequentially at 320 K, 335 K, and 343 K, respectively. For clarity the *dI/dV-V* curves, other than the full gap curves, have been vertically offset. The insets show the concurrently obtained STM topography images. Image and inset sizes are 200 x 200 nm^2.

the insulating state is often observed for specific domains within these systems. For the nanowire in Fig. 2, the specific surface examined appears to have a relatively elevated transition temperature.

Insulating domains still remained in our nanowires above T_C, which is consistent with STS results on VO_2 thin film.[12,13] The insulating regions observed near and above T_C exhibited energy gaps similar to those of the insulating ground state. While the *dI/dV* image at 343 K, shown in Fig. 1(e), indicates that the high-temperature metallic phase has become more prominent than at 320 K and 335 K [Figs. 1(a) and 1(c), respectively], it is not dominant and indeed a percolating network of metallic domains has not formed. Figures 1 and 2 both indicate that the overall metallicity of the surfaces increases as the temperature is increased through the MIT regime. However, it is quite possible that as the temperature is increased through the MIT regime, changing surface strain states may result as domains in the majority of the nanowire undergo the MIT. These changes may cause regions of the surface which exhibited spectra of the high-temperature poor-metal at slightly lower temperatures to partially revert back to regions with reduced band gaps even though the temperature increased. In other words, the intermediate metallic phase can be captured for some regions of the nanowires depending on the strain state, whereas in other regions the strong thermodynamic driving force for the structural and electronic phase transitions preclude observation of intermediate stages.

Discussion

We consider several explanations for the presence of an IMP in our nanowires. Our use of high-quality nanostructures produced by a hydrothermal process without a growth substrate or high synthesis temperatures may have revealed the intrinsic character of VO_2. This may be due to the lack of strong substrate coupling, since the nanowires are simply cast onto the substrate in solution and not directly coupled to the substrate. The presence of an IMP in our experiments with high-quality nanowires may also be due to our use of a Cr/Au coated substrate. It has been shown that an IMP will be induced above the electronic MIT temperature (below the SPT temperature) if sufficient electrons have been removed from the VO_2 valence band,4 and similarly through an interface charge transfer effect between Au TEM grids and VO_2 nanowires grown by a vapor transport deposition technique.3 A series of intermediate phases with distorted structure have been identified between the M_1 and R phases in XAFS measurements at the V K-edge that have been predicted to have reduced gaps.[10] Such phases could also give rise to the STS signatures observed here. The nanoscale domains we observed are well below the spatial resolution of other spectroscopic techniques that would have permitted structural elucidation, such as Raman microprobe imaging. The lack of an IMP in previous VO_2 STS temperature studies may be due to strain effects from the use of substrates for thin film growth, or because said substrates were insulating.[12,13,25,26]

Inserting Graphics

Graphics should be inserted where they are first mentioned (unless they are equations, which appear in the flow of the text). They can be single column or double column as appropriate.

Conclusions

In summary, we have studied the IMP that forms in VO_2 nanowires by measuring *dI/dV* directly with a modulation bias technique. We demonstrated direct evidence that nanopuddles of an IMP formed in the insulating phase, and that these nanopuddles evolved into the high-temperature metallic phase as the temperature was increased through the MIT regime. Our LDOS measurements of the IMP are qualitatively consistent with the surprisingly metallic LDOS of the IMP (relative to the poor-metal rutile phase) which Yuan *et al.* calculated.4 In the absence of a structural probe with a comparable spatial resolution, we are uncertain whether or not the observed IMP forms when the SPT is decoupled from the MIT, by an interface charge transfer effect,3 or if it is the same as the reported strongly correlated metallic,[11] M_3,3 or photo-induced phases.[14-16] Nevertheless, this work provides the first direct observation of the localized electronic structure as VO_2 nanowires undergo a MIT.

Acknowledgements

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