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**Stability of the M2 phase of vanadium dioxide induced by coherent epitaxial strain**

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Tensile strain along the  $c_R$  axis in epitaxial VO<sub>2</sub> films raises the temperature of the metal insulator transition and is expected to stabilize the intermediate monoclinic M2 phase. We employ surface-sensitive x-ray spectroscopy to distinguish from the TiO<sub>2</sub> substrate and identify the phases of VO<sub>2</sub> as a function of temperature in epitaxial VO<sub>2</sub>/TiO<sub>2</sub> thin films with well-defined biaxial strain. Although qualitatively similar to our Landau-Ginzburg theory predicted phase diagrams, the M2 phase is stabilized by nearly an order of magnitude more strain than expected for the measured temperature window. Our results reveal that the elongation of the  $c_R$  axis is insufficient for describing the transition pathway of VO<sub>2</sub> epitaxial films and that a strain induced increase of electron correlation effects must be considered.

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The abrupt metal insulator transition (MIT) near room temperature in VO<sub>2</sub> is believed to be a cooperative Mott-Peierls transition, which is further complicated by the appearance of an intermediate insulating phase under certain conditions. This monoclinic M2 phase is a known Mott insulator suggesting that electron-electron interactions may play an important role in determining the transition pathway [1–3]. In unstrained stoichiometric VO<sub>2</sub>, the structural phase transition accompanying the MIT is from the high temperature rutile phase to the monoclinic M1 phase, which causes both zigzagging of the vanadium chains and the formation of V-V dimers along the rutile  $c$  ( $c_R$ ) axis [4,5]. In the M2 phase, only half the vanadium chains zigzag, while the other half form V-V dimers [6,7]. This structure is known to be stabilized in large single crystals at intermediate temperatures by low level chemical doping (e.g., with Cr or Al) or uniaxial pressure along the [110] direction, however the electron correlation effects have not been simultaneously investigated [1,2,6,8–10].

Recently, uniaxial strain studies of VO<sub>2</sub> nanobeams have determined that VO<sub>2</sub> has a triple phase point at 65 °C at ambient pressure, where the two insulating monoclinic phases

and the metallic rutile phase can coexist [11,12]. Applying compressive strain along the  $c_R$  axis lowers the transition temperature ( $T_{MIT}$ ), whereas tensile strain along  $c_R$  raises the transition to the metallic phase with the M2 phase stabilized between the M1 and rutile phases. In thin films, the M2 phase has only been observed when using symmetry mismatched substrates, which tend to have low lattice strain and high defect concentrations [13–20]. Because of this, no clear relationship between thin film strain and the stabilization of the M2 phase can be deduced from existing reports. Understanding how this phase can be stabilized with epitaxial strain is necessary for a real understanding of how the MIT of VO<sub>2</sub> can be modulated.

Rutile TiO<sub>2</sub> substrates, isomorphic to the metallic phase of VO<sub>2</sub>, offer a means to obtain well-defined biaxial tensile strain with lattice mismatches up to a few percent. It is well known that  $T_{MIT}$  can be tailored by  $\pm 40$  °C by choice of substrate orientation in thin ( $\leq 40$  nm) VO<sub>2</sub>/TiO<sub>2</sub> films [21]. This correlates well with tensile or compressive strain along the  $c_R$  axis, however there has been no evidence of the M2 phase reported in these films.

Here we present a combined study of polarization and temperature dependent soft x-ray absorption spectroscopy (XAS) with hard x-ray photoelectron spectroscopy (HAXPES) of high quality epitaxial VO<sub>2</sub> films on TiO<sub>2</sub>(001) and (100) oriented substrates. Using the sensitivity of XAS at the O

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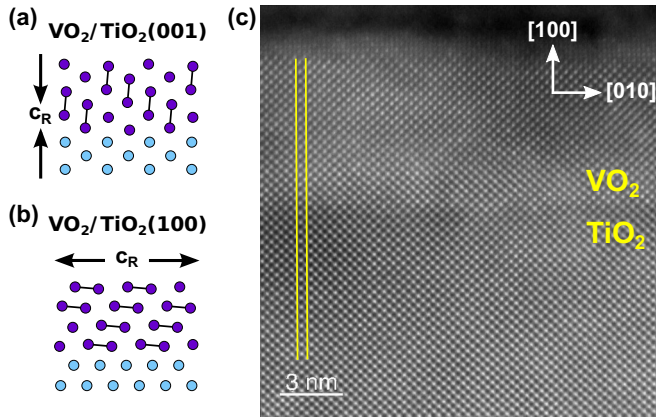


FIG. 1. Schematic representations of the crystal structure of epitaxial  $\text{VO}_2$  film grown on (a)  $\text{TiO}_2(001)$  and (b)  $\text{TiO}_2(100)$ , showing the orientation of the V-V dimers. (c) ADF STEM image of a 7.5 nm  $\text{VO}_2/\text{TiO}_2(100)$  epitaxial film viewed along the  $[001]$  axis.

$K$  edge to the presence of the V-V dimers, we are able to distinguish between each of the three phases (M1, M2, and R). We determine the  $\text{VO}_2/\text{TiO}_2(001)$  with a compressed  $c_R$  are absent of intermediate phases and maintain a MIT similar to unstrained  $\text{VO}_2$ , aside from the lowered  $T_{\text{MIT}}$ . In stark contrast, the  $\text{VO}_2/\text{TiO}_2(100)$  films with elongated  $c_R$  have a stable M2 phase between the M1 and R endpoints, while the HAXPES displays evidence of a more Mott-like transition with increased electron correlation effects. These results are generally in good agreement with nonthin film studies, however we note a significantly larger strain than predicted is required to stabilize the M2 phase for the same temperature window. This discrepancy is attributed to additional consequences of the biaxial nature of thin film epitaxial strain and reveals that tailoring the MIT of  $\text{VO}_2$  is not exclusively determined by the  $c_R$  lattice constant.

A set of high quality epitaxial  $\text{VO}_2$  thin films were grown on rutile (001) and (100)  $\text{TiO}_2$  single crystal substrates by reactive MBE by a codeposition method under a distilled ozone background pressure [22,23]. The XAS and HAXPES presented here were collected from a representative 10 nm  $\text{VO}_2/\text{TiO}_2(001)$  film and a 5 nm  $\text{VO}_2/\text{TiO}_2(100)$  film. These thicknesses were chosen to ensure the  $c_R$  lattice constant is either contracted or elongated, respectively, as shown schematically in Fig. 1. Details regarding sample growth and characterization as well as spectroscopy measurements are provided in the Supplemental Material [24]. Electrical transport measurements of these films show a change in resistivity of  $\Delta R/R = 10^{3.09}$  centered at  $19.1^\circ\text{C}$  for  $\text{VO}_2/\text{TiO}_2(001)$  and  $\Delta R/R = 10^{2.94}$  centered at  $77.6^\circ\text{C}$  for  $\text{VO}_2/\text{TiO}_2(100)$ . This confirms a similar orientation-dependent tuning of the MIT as previously reported [21]. XAS of the O  $K$  edge was measured in total electron yield (TEY) mode. The photon energy axes were calibrated using the Ti  $L_{2,3}$  and O  $K$  absorption edge features of a rutile  $\text{TiO}_2$  single crystal. From prior studies we have determined that for films of  $\geq 5$  nm thickness there is no spectral contamination originating from the  $\text{TiO}_2$  substrate [25]. The HAXPES measurements were performed using a photon energy of  $h\nu = 4$  keV with a resolution of

0.45 eV. The binding energy axes were referenced to the Fermi edge of Au foil.

For an in-depth analysis of the epitaxial nature of our  $\text{VO}_2/\text{TiO}_2(100)$  films, STEM and high resolution XRD measurements were conducted. Cross-sectional scanning transmission electron microscopy (STEM) of  $\text{VO}_2/\text{TiO}_2(001)$  specimens have previously shown abrupt interfaces and well-defined epitaxial growth where  $(001) \text{VO}_2 \parallel (001) \text{TiO}_2$  and  $[100] \text{VO}_2 \parallel [100] \text{TiO}_2$  [22,26]. Here we confirm  $\text{VO}_2/\text{TiO}_2(100)$  to have a similarly well-defined epitaxial relation of  $(100) \text{VO}_2 \parallel (100) \text{TiO}_2$  and  $[001] \text{VO}_2 \parallel [001] \text{TiO}_2$ . Figure 1(c) shows an annular dark field STEM image of a  $\text{VO}_2/\text{TiO}_2(100)$  specimen viewed along the  $[001]$  axis, with a (100) film surface. The film has a top surface layer which looks like it belongs to another phase. This is likely due to ion milling damage induced during sample preparation. The undamaged thickness of the film is 6.9–7.0 nm, and the total thickness of the film is 7.5 nm. In addition to the sharp and well-ordered interface, the whole of the film shows comprehensive structure. As highlighted by the yellow lines, the image shows the columns of vanadium ions maintain their alignment with the titanium ions of the substrate all the way to the damaged surface layer with no sign of dislocations. Additionally, these films display a high quality interface with limited titanium diffusion and maintain MITs in films as thin as 1 nm [22,23,25].

Reciprocal space maps were measured around the  $(2,0,0)$  specular and  $(2,1,1)$  off-specular Bragg peaks of the  $\text{TiO}_2(100)$  substrate and are shown in the Supplemental Material [24]. The  $\text{VO}_2$  Bragg peak is overlapped with  $\text{TiO}_2(2,1,1)$  peak in the in-plane direction, confirming that the in-plane structure of the  $\text{VO}_2$  film is fully strained to the in-plane structure of the substrate. From analysis of the Kiessig fringes along the  $(H,0,0)$  direction, using a pseudorutile unit cell, the lattice constant along the surface normal is estimated to be  $a_R = 4.47 \text{ \AA}$ . This is in good agreement with the intensity profile along the  $(H,1,1)$  direction. This indicates that the out-of-plane lattice spacing is indeed contracted from its bulk state in these strained films, demonstrating coherent epitaxial strain. From this we confirm an in-plane tensile strain of  $\epsilon_{c_R} = 3.74\%$  and  $\epsilon_{b_R} = 0.86\%$  up to a film thickness of 7.5 nm in our  $\text{VO}_2/\text{TiO}_2(100)$  films.

In order to monitor the behavior of the V-V dimers across the phase transformations of  $\text{VO}_2$  we employed soft XAS. XAS at the O  $K$  edge probes the conduction band via dipole transitions into the unoccupied O  $2p$  density of states near  $E_F$ . Because of the high degree of O  $2p$ -V  $3d$  covalent mixing, this technique is sensitive to the unoccupied V  $3d$  states associated with the formation of V-V dimers [27,28]. This so-called  $d_{\parallel}$  feature in the XAS spectrum emerges for the low temperature insulating phase and is routinely considered a signature of the monoclinic M1 structure. Furthermore, since only every other vanadium ion chain forms V-V dimers in the M2 structure, as compared to the full dimerization in the M1 structure, this technique is expected to also be a sensitive probe of the M1/M2 phase transition.

First, polarization dependent XAS was performed for both  $\text{VO}_2$  film orientations in the low temperature M1 phase (see the Supplemental Material [24]). The general features in the XAS spectra are consistent with previous studies and show

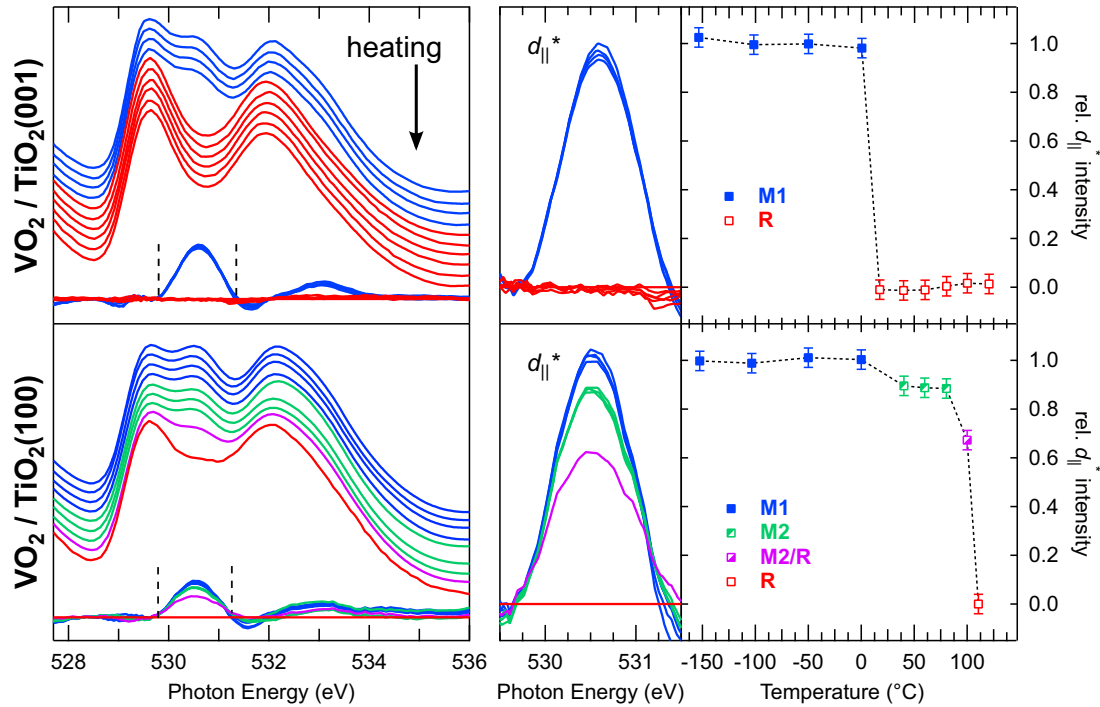


FIG. 2. (Left) Temperature dependent O  $K$ -edge XAS measurements of  $\text{VO}_2/\text{TiO}_2(001)$  and  $\text{VO}_2/\text{TiO}_2(100)$  with (right) an expanded view of the  $d_{\parallel}$  feature and its peak intensity as a function of temperature.

no observed energetic shifts or broadening of the unoccupied bands owing to epitaxial strain [27–29]. Due to the highly directional  $d_{x^2-y^2}$  orbital, the  $d_{\parallel}$  feature shows a strong angular dependence and even completely disappears for polarization geometry  $\vec{E} \perp c_R$ . Because of this, the  $d_{\parallel}$  is slightly less pronounced in the (001) oriented films owing to the constraints of the near grazing incidence geometry required for  $\vec{E} \parallel c_R$ .

Temperature dependent XAS measurements were then carried out for both  $\text{VO}_2$  films and are shown in Fig. 2. Each collected raw spectrum has been normalized to the local maximum of the  $\pi^*$  feature ( $\sim 529.5$  eV), and are vertically offset for clarity with temperature increasing from top to bottom. Below these are each difference spectra to represent the spectral changes as temperature is increased. This shows the  $d_{\parallel}$  band as a symmetric peak centered at 530.5 eV in both strain orientations.

To highlight the more subtle changes in the  $d_{\parallel}$  region, an expanded view is also shown for each film orientation alongside the integrated peak intensity as a function of temperature. The error bars plotted for the integrated peak intensity represent a 99.6% confidence level. From this it is clear that the (001) oriented films display only two phases. The  $d_{\parallel}$  feature is identical at all lower temperatures and then vanishes near room temperature and for all higher temperatures. This is consistent with a transition from the M1 to R phase near room temperature with no evidence of any intermediate phases. In contrast, the (100) oriented films display more intricate changes as the temperature is increased. At low temperatures the  $d_{\parallel}$  feature is again observed as a symmetric peak, however, in this case, it shows intermediate intensities before it completely vanishes. The first reduction in intensity occurs before 40 °C and remains as a stable plateau at least up to 80 °C. Subsequently, there

is an additional point at which the intensity is diminished further before completely vanishing upon reaching the high temperature phase. The endpoints are similar to the (001) orientation and are consistent with the M1 and R phases. The stable intermediate phase is interpreted as the M2 phase, where the reduced intensity of the  $d_{\parallel}$  feature reflects the decreased participation in the V-V dimerization. Following this assignment, the single spectrum collected at 100 °C is likely representative of spatial coexistence between the M2 and rutile phases [24]. This demonstrates that the intermediate M2 phase can indeed be stabilized via coherent epitaxial strain and is only observed in the (100) strain case, i.e., when the  $c_R$  lattice constant is elongated.

To confirm the assignment of the intermediate M2 phase observed for the  $\text{VO}_2/\text{TiO}_2(100)$  we performed hybrid DFT using the HSE06 functional [30] of the M1, M2, and R phases of  $\text{VO}_2$  as described by Eyert [31]. Spin polarization was explicitly included only for the M2 phase in order to obtain a band gap, while the M1 and R calculations are not spin polarized [31,32]. The  $t_{2g}(\pi)$  projected density of states for both the M1 and M2 phase are presented in Fig. 3 (see the Supplemental Material for details [24]). The  $d_{x^2-y^2}$  orbital, associated with the  $d_{\parallel}$  feature in the O  $K$  edge, is found at 1.6 eV above  $E_F$  in the M1 structure. For the M2 structure, this  $d_{x^2-y^2}$  orbital is projected separately for each unique vanadium atom; V1 representing the dimerized chains, and V2 representing the evenly spaced zigzagged chains. The behavior of the unoccupied  $d_{x^2-y^2}$  orbital is clearly altered compared to the M1 phase. The lower DOS of this orbital in the M2 phase indeed reflects the reduced participation in the V-V dimerization, reaffirming that the  $d_{\parallel}$  feature is largely derived from the dimerized vanadium ions.

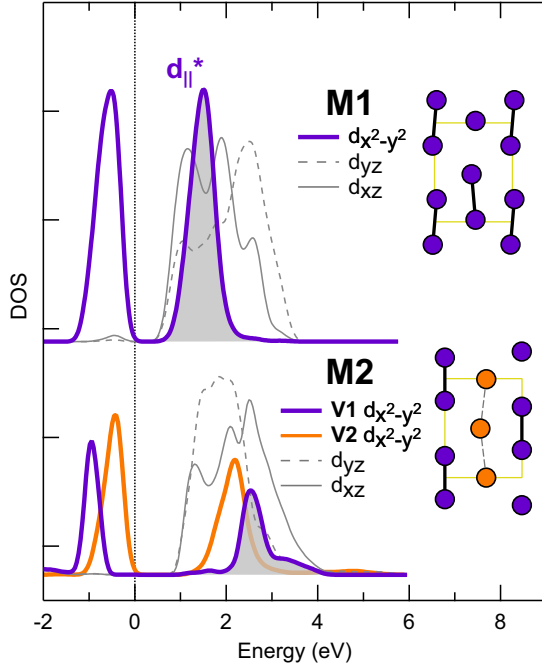


FIG. 3. The  $t_{2g}(\pi)$  projected DOS comparing the M1 and M2 phase calculated by hybrid DFT. The highlighted region indicates the  $d_{||}$  band in each structure arising from dimerized vanadium ions.

Further confirmation of the existence of the M2 phase in the (100) strained films is supported by Landau-Ginzburg theory. The predicted structural phase transformations in  $\text{VO}_2$  as a function of biaxial strain are described here using a six-order Landau polynomial (see the Supplemental Material for details [24])

$$F(\eta, \epsilon) = A2(T - T_C)\eta^2 + A4\eta^4 + A6\eta^6 + \frac{1}{2}c_{ijkl}(\epsilon_{ij} - \eta^2\epsilon_{ij}^0)(\epsilon_{kl} - \eta^2\epsilon_{kl}^0), \quad (1)$$

where  $T_C$  is the Curie temperature under stress-free condition,  $A2$ ,  $A4$ , and  $A6$  are constants,  $\eta$  is a normalized order parameter describing the R to M1 transformation, R to M2 transformation, and M2 to M1 transformation,  $\epsilon_{ij}$  is the total strain,  $\epsilon_{ij}^0$  is the stress-free transformation strain at transition temperature  $T_0$ , and  $c_{ijkl}$  is the elastic stiffness tensor [33]. For a thin film clamped on the substrate in the  $x_1$ - $x_2$  plane, by applying the thin film boundary condition we obtain the new transition temperature

$$T_0 = \frac{(A4 + \Delta A4)^2}{4A2A6} + (T_C + \Delta T_C), \quad (2)$$

with  $\Delta T_C = \frac{T_0}{\Delta H} [ \frac{c_{13}^2}{c_{33}} (\epsilon_{11}^0 + \epsilon_{22}^0) (\epsilon_{S1} + \epsilon_{S2}) - (c_{11}\epsilon_{11}^0 + c_{12}\epsilon_{22}^0)\epsilon_{S1} + (c_{12}\epsilon_{11}^0 + c_{11}\epsilon_{22}^0)\epsilon_{S2} ]$  and  $\Delta A4 = -\frac{c_{13}^2}{2c_{33}} (\epsilon_{11}^0 + \epsilon_{22}^0)^2 + 2c_{66}\epsilon_{12}^0{}^2 + c_{12}\epsilon_{11}^0\epsilon_{22}^0 + \frac{c_{11}}{2} (\epsilon_{11}^0{}^2 + \epsilon_{22}^0{}^2)$ , where  $\epsilon_{S1}$  and  $\epsilon_{S2}$  are substrate mismatch strain along  $x_1$  and  $x_2$  directions, respectively. By rotating the coordinate system, we thus can easily get the strain-temperature phase diagrams for both strain cases reflecting epitaxial  $\text{VO}_2$  on  $\text{TiO}_2(001)$  and (100).

Comparing the tensile sides of each phase diagram in Fig. 4, we find good qualitative agreement with experiment. As the

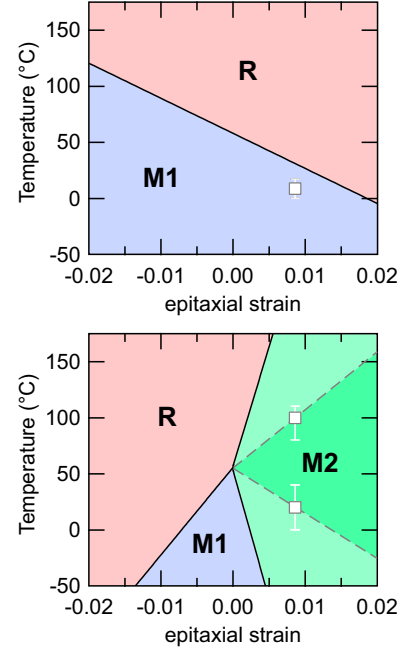


FIG. 4. Transformation temperature as a function of mismatch strain for (001)  $\text{VO}_2$  (top) and (100)  $\text{VO}_2$  (bottom) thin films. In the (001) case, the epitaxial strain is equal in the  $a_R$  and  $b_R$  directions, while in the (100) case, the  $x$  axis represents the epitaxial strain along the  $b_R$  direction ( $\epsilon_{S1}$ ), with the strain along  $c_R$  direction ( $\epsilon_{S2}$ ) fixed to  $4.35\epsilon_{S1}$  in order to reflect the anisotropic epitaxial strain. The white boxes (along with dotted lines to guide the eye) represent experimentally determined transformation temperature values.

temperature increases, M1 transforms to R directly in (001) films, while M1 transforms first to M2 and then to R in (100) films. The M2 phase has a larger stress-free transformation strain (1.57%) along  $c_R$  than that of M1 (1.00%), thus the large  $c_R$  tensile strain of the (100) films should favor the M2 phase over M1 and stabilize it for a wide temperature range. However, the epitaxial strain of a (100) film is very anisotropic, i.e., 0.86% along the  $b_R$  direction and 3.74% along  $c_R$ , and we find significant differences in experimental transformation temperatures. For this measured temperature window in which the M2 phase is stable, the strain on  $c_R$  observed in our films is nearly an order of magnitude higher than expected. This large discrepancy indicates that the effects of biaxial epitaxial strain alone are insufficient to accurately describe these phase transformations. There may be additional consequences to the epitaxial strain, such as changes in bandwidth and thus correlation strength that may have a large impact on the transformation temperatures.

To investigate any such modification to the electronic structure in the highly anisotropic  $\text{VO}_2/\text{TiO}_2(100)$  strain case, we employed HAXPES. Figure 5 shows the HAXPES spectra of the topmost valence band states for each film orientation recorded both above and below their respective  $T_{\text{MIT}}$  (as determined from resistivity measurements). The valence band of  $\text{VO}_2$  consists of a broad O  $2p$  band (2–9 eV) and a smaller feature near  $E_F$  that is predominantly V  $3d$  in character (see the Supplemental Material for full VB spectra [24]). This V  $3d$  feature displays dramatic changes across the MIT. Here we

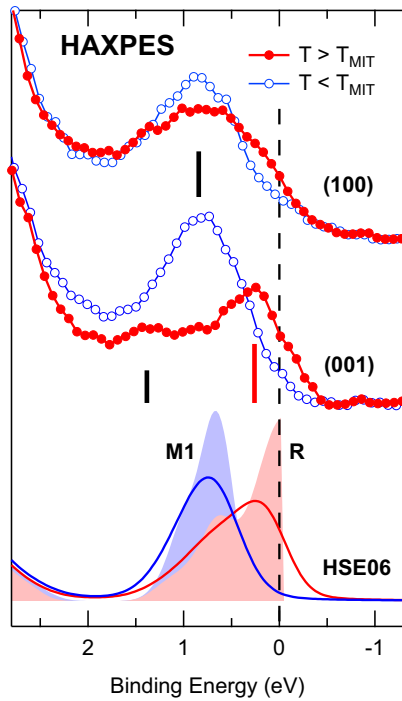


FIG. 5. Valence band HAXPES of  $\text{VO}_2/\text{TiO}_2(100)$  and  $\text{VO}_2/\text{TiO}_2(001)$  collected above and below  $T_{\text{MIT}}$ . (Bottom) HSE06 hybrid DFT calculations showing the total DOS for the M1 and R phase. Solid bars indicate the coherent (red) and incoherent (black) contributions to the V  $3d$  feature.

also observe clear differences between the two strain cases. The  $\text{VO}_2/\text{TiO}_2(001)$  spectra shows a single peak near 1 eV in the insulating phase that shifts towards  $E_F$  above  $T_{\text{MIT}}$  resulting in a clear metallic Fermi edge. This is consistent with our hybrid DFT predicted spectra, and shows the (001) oriented films are in good agreement with bulk  $\text{VO}_2$  and other reports of  $\text{VO}_2/\text{TiO}_2(001)$  [28,29,34–36]. Also in the metallic phase, there is some additional weight above 1 eV that is not captured in the DFT band calculations. This broad feature is the so-called “incoherent peak” associated with the lower Hubbard band [35].

Now looking to the  $\text{VO}_2/\text{TiO}_2(100)$  spectra for the metallic phase, this incoherent peak is much more pronounced and is observed at the same binding energy as the insulating peak, near 1 eV. In this case, there is only a small transfer of spectral weight across the MIT resulting in small density of states at  $E_F$  in the metallic phase and is consistent with previous observations of  $\text{VO}_2/\text{TiO}_2(100)$  films [25,37]. This behavior is more typical of a Mott insulating system, indicating that the electron correlations are more dominant in the (100) oriented films [38,39]. Doping  $\text{VO}_2$  with tungsten has also been observed to induce more Mott-like spectral signatures, although in the present case these effects are purely strain induced [40]. This increase in electron correlation effect is likely a consequence of the distortion of the rutile phase induced by the epitaxial strain in  $\text{VO}_2/\text{TiO}_2(100)$  films. We consider this to be responsible for the discrepancy between the predicted and observed phase transformation temperatures. Further support is provided by a strain-induced orbital selective

Mott transition explicitly considering the effects of electron correlations in  $\text{VO}_2$ , as proposed by Mukherjee *et al.* [41].

We have demonstrated here that the intermediate M2 phase can indeed be stabilized via coherent epitaxial strain where the  $c_R$  axis is elongated. This result can largely be explained by the change in  $c_R$  lattice constant, however the temperature window in which the M2 phase is stable is quantitatively different than predicted for  $\text{VO}_2/\text{TiO}_2(100)$  films. This discrepancy is a consequence of the increased electron correlations in the  $\text{VO}_2/\text{TiO}_2(100)$  films as compared to  $\text{VO}_2/\text{TiO}_2(001)$ , indicating that the more Mott-like MIT character needs to be explicitly considered. Due to the well-defined epitaxial strain in these films, we can now provide an explanation for the inconsistent appearance of the M2 phase in thin  $\text{VO}_2$  films where the biaxial strain and possible renormalization of the electronic structure are not explicitly considered. This work demonstrates that by use of epitaxial strain, it may be possible to further strain-tune the degree of electron correlation in  $\text{VO}_2$ .

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