

Mott Switching and Structural Transition in the Metal Phase of VO₂ Nanodomain

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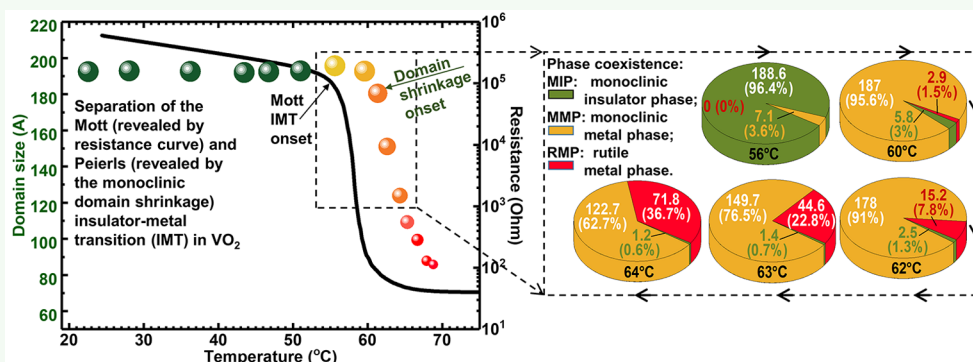
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ABSTRACT: VO₂ undergoes the insulator–metal transition (IMT) and monoclinic–rutile structural phase transition (SPT) near 67 °C. The IMT switching has many applications. However, there is an unresolved issue whether the IMT is a Mott transition or a Peierls transition. This complication is caused by metal and insulator coexistence, which is an inherent property of the IMT region. Thus, the acquired data in the IMT region are averaged over the two phases in many experiments. We overcome the issue by probing the electronic state of the monoclinic structure and by introducing a model that accounts for the coexisting phases. We reveal the Mott IMT in the nondistorted monoclinic nanodomain between 55 and 63 °C and the distortion-assisted SPT above 60 °C.

KEYWORDS: vanadium dioxide, Mott transition, electron correlation, phase coexistence, nanodomain

The thermally induced first-order transition in vanadium dioxide (VO₂) at $T_c \approx 67$ °C involves changes of both electronic and lattice structures from a low-temperature monoclinic (M marking M1) insulator to a high-temperature tetragonal rutile (R) metal.¹ The exact cause of the transition has been unknown and intensely debated for the past several decades. In particular, two competing mechanisms have been introduced as essential to induce the insulator–metal transition (IMT or electronic switching) in VO₂: the Peierls structural instability that implies formation/disappearance of the tilted vanadium dimers^{2,3} and the Mott switching that involves a sudden increase/decrease in the magnitude of the critical Coulomb interaction between electrons.^{4,5} Moreover, the combined Peierls–Mott scenarios have also been suggested.^{6,7}

On the other hand, there are numerous works suggesting that the electronic and structural transitions do not occur simultaneously.^{8–18} Their separation has been achieved by observations of the monoclinic metal phase (MMP), which unambiguously proves the Mott transition occurring prior to the M-to-R structural change. Nevertheless, the uncertainty in understanding the driving mechanism of the IMT still exists. It is attributed to the formation of the mixed phase (insulator and

metal) region inherent in the first-order phase transition. This complicates the characterization of the individual phases, thus hindering the description of the intrinsic IMT pathway.^{8,19}

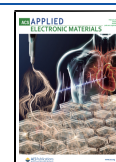
One way to reveal the IMT mechanism in VO₂ is to trace only one phase throughout the transition. For example, nanoscale infrared spectroscopy at ≈ 10 μm wavelength has been known for its capability to sense the metallic phase very effectively throughout the whole transition regime.²⁰

In this paper, we explore the electronic state of the selected monoclinic structure through measuring the X-ray absorption spectra by diffraction anomalous near-edge structure (DANES)^{21–24} experiments that use a synchrotron light source. DANES probes the electronic structure of a material by sensing the modulation of the diffraction intensities across the absorption edge of a selected V atom. The X-ray diffraction

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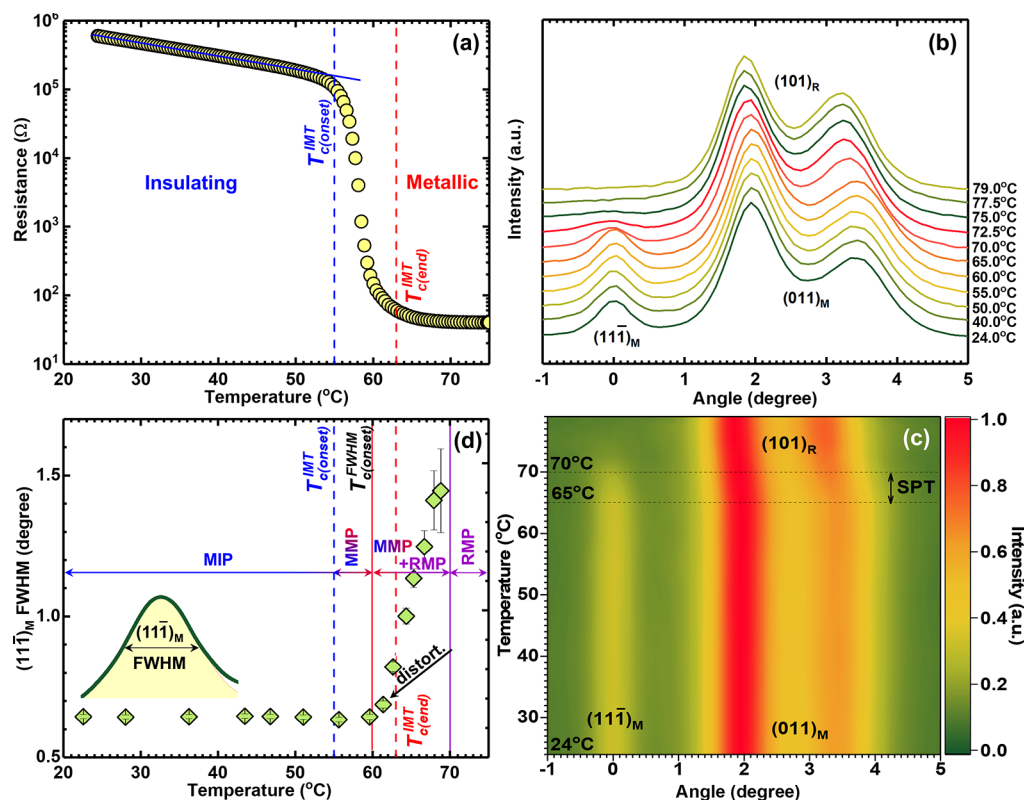


Figure 1. Evolution of the electronic and crystalline structures of VO₂ on heating. (a) The insulator-to-metal transition (IMT) revealed by a sudden resistance (r) drop between $T_{c(\text{onset})}^{\text{IMT}} \approx 55$ °C and $T_{c(\text{end})}^{\text{IMT}} \approx 63$ °C. (b, c) Evolution of the off-axis XRD peaks from the monoclinic (M) and rutile (R) VO₂. (d) Changes of the FWHM of the $(11\bar{1})_M$ peak (inset) on heating denoting the following regions: the monoclinic metal phase (MMP) region between 55 and 60 °C emerged from the monoclinic insulator phase (MIP) as a result of the Mott transition; nucleation of the rutile metal phase (RMP) at $T_{c(\text{onset})}^{\text{FWHM}} < 60$ °C revealed by the monoclinic distortion (increase of the FWHM) and, thus, the MMP+RMP region between 60 and 70 °C; the RMP region formed by the structural phase transition (SPT) above 70 °C.

intensity is proportional to the absolute square of the structure factor which is determined by the spatial arrangements of constituent atoms weighted by the atomic form factors. When the incident X-ray energy changes across absorption edge of the constitute atom, the atomic form factor is modulated significantly. X-ray absorption spectroscopy can be seen as energy-dependent X-ray diffraction with momentum transfer $Q = 0$ (straight through a sample). Thus, DANES can reveal the electronic state of the specific structure, which is an essential to clarify the complex phase-transition pathway.

This approach allows us to experimentally manifest the metal phase that emerges in the nondistorted monoclinic structure (i.e., Mott transition) on heating and to observe the further monoclinic distortion by means of the monoclinic nanodomain's size reduction due to the rutile phase nucleation. Moreover, we theoretically support the observed Mott-type IMT in VO₂ by deducing the "Mottian" characteristics of the MMP, such as the divergence of the Brinkman–Rice effective mass and large correlation strength. Also, on the basis of the extended Brinkman–Rice picture,^{8,19} we succeeded in developing the mixed phase model able to distinguish and quantify the properties of the coexisting phases in the transition region. Thus, it enables us to observe the evolution of the individual phases in the vicinity of the IMT in VO₂.

Figure 1a shows the resistance vs temperature curve measured upon heating of a VO₂ film on the r -plane Al₂O₃ substrate. The curve demonstrates a noticeable deviation from the Arrhenius law (solid blue line) and an electronic transition characteristic between $T_{c(\text{onset})}^{\text{IMT}} \approx 55$ °C and $T_{c(\text{end})}^{\text{IMT}} \approx 63$ °C

with a resistance drop of almost 4 orders of magnitude. Figures 1b,c depict the evolution of the off-axis diffraction peaks obtained by measuring the in-situ synchrotron-based X-ray diffraction (XRD) on heating. Here, the left peak gradually disappears while the center and the right peaks quite maintain their intensities. The left peak can be assigned to the monoclinic $(11\bar{1})_M$ peak, the center peak to $(011)_M$ from one of the twin domains, and the right side peak to $(011)_M$ from the other twin domain (see details in the Supporting Information).²⁵ Although the $(011)_M$ and $(11\bar{1})_M$ peaks from the monoclinic structure disappear with an increasing temperature, the rutile phase $(101)_R$ peaks simultaneously develop close to the $(011)_M$ peaks. Because of a broad peak width, $(011)_M$ and $(101)_R$ are not resolved as separate peaks. Hence, a gradual increase of $(101)_R$ concomitant with a decrease of $(011)_M$ is apparent from the shift of peak positions across the SPT, as clearly shown between 65 and 70 °C in Figure 1c.

To examine the SPT, we selected the $(11\bar{1})_M$ peak (Figures 1b,c), which is unique to the monoclinic structure, and traced its changes on heating. Figure 1d shows the progression of the full width at the half-maximum (FWHM) of $(11\bar{1})_M$ (see the inset of Figure 1d) throughout the phase transition, which is plotted on the same x -axis scale as the resistance curve in Figure 1a for a convenient comparison of the two processes. Notably, the temperature difference between $T_{c(\text{onset})}^{\text{IMT}} \approx 55$ °C and the starting temperature of the monoclinic structure distortion (a shrinkage of a monoclinic nanodomain) $T_{c(\text{onset})}^{\text{FWHM}} > 60$ °C (red solid line in Figure 1d) is about 5 °C (Figures 1a,d). This observation implies the existence of the monoclinic

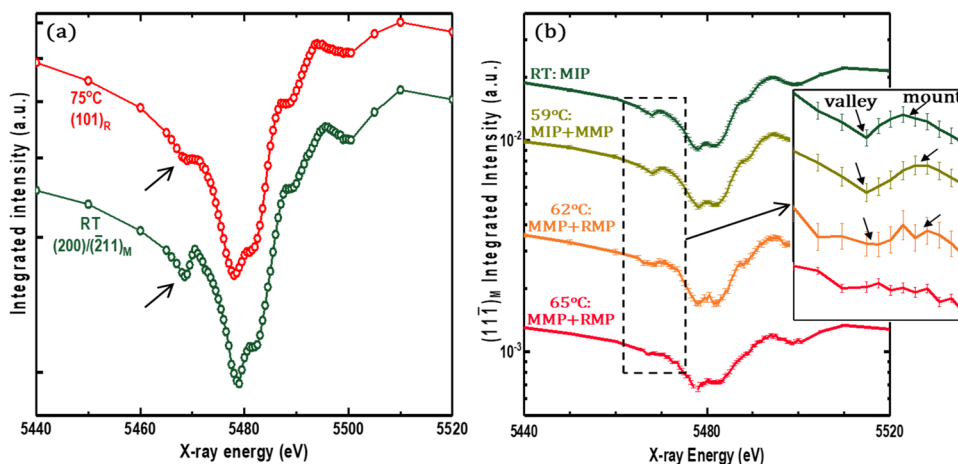


Figure 2. DANES at the V K edge from the VO_2 film on Al_2O_3 . (a) Integrated intensities of the diffraction peaks from the monoclinic insulating (RT, $(200)/(\bar{2}11)_M$) and rutile metallic (75 °C, $(101)_R$) phases of VO_2 vs the incident X-ray energy. Errors in the intensities are smaller than the symbols size. (b) Integrated intensities of the $(111)_M$ peak of VO_2 as a function of the incident X-ray energy and temperature. Inset: magnified pre-edge regions from (b) for an X-ray energy range of 5465–5472 eV with designated “valley” and “mount” areas of the distinguishable profile changes observed at 59 °C due to the emergence of the monoclinic metallic phase (MMP) from the monoclinic insulator phase (MIP) and further, above 62 °C, due to the nucleation of the rutile metal phase (RMP).

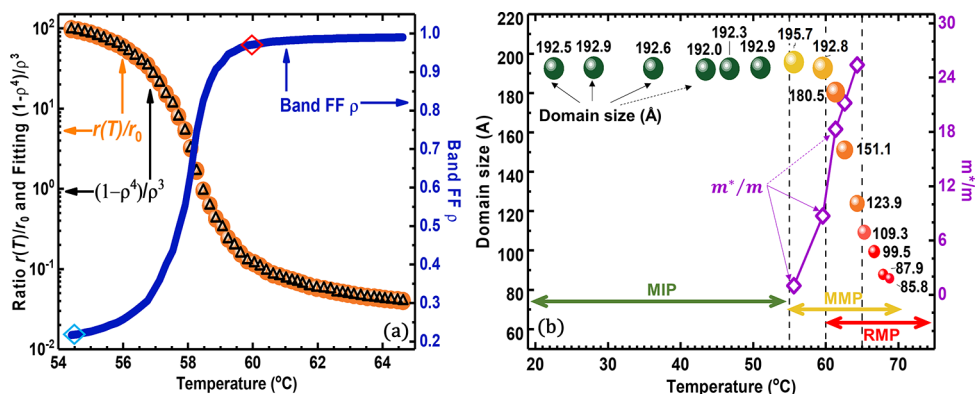


Figure 3. Analyzing the resistance and tracking the changes of the VO_2 monoclinic nanodomains size upon heating. (a) The temperature dependence of the band-filling factor (band FF or ρ , $0 < \rho \leq 1$; blue solid line)^{8,19} extracted from the resistance curve in Figure 1a. The experimental resistance $r(T)/r_0$ curve (orange balls) overlaps with the calculated $(1/\rho^3)(1 - \rho^4)$ curve (black open triangles) (details in the Supporting Information). (b) Temperature dependence of the monoclinic domain size (left y-axis) and the carriers' effective mass (right y-axis). The regions of the monoclinic insulator phase (MIP), monoclinic metal phase (MMP), and rutile metal phase (RMP) and their coexistence are also shown.

metal phase (MMP) between 55 and 60 °C and, thus, the isostructural Mott IMT. Above 60 °C (Figure 1d), the peak broadening is observed due to the distortion of the monoclinic structure. We assume that this distortion is caused by the local emergence (nucleation) of the rutile metal phase (RMP) that gradually spreads upon further heating until the SPT is complete above 70 °C (Figure 1c).

Figure 2a shows the two representative DANES profiles obtained by measuring the intensities of the monoclinic $(200)/(\bar{2}11)_M$ peak at room temperature and the rutile $(101)_R$ peak at 75 °C, while changing the incident X-ray energy across the V K edge. As inferred by comparing the profiles, a significant difference can be found in the pre-edge region around 5468 eV, as marked by the black arrows in Figure 2a. In particular, a dip in diffraction intensity is flattened in the metallic rutile phase compared to the insulating monoclinic one. A similar observation has been previously reported for XANES measurements.²⁶ Therefore, the pre-edge region is clear evidence of the electronic structure change.

Figure 2b shows the DANES profiles of $(11\bar{1})_M$ taken at various temperatures through the transition. Along with the gradual reduction in the overall signal intensity, we first recognize a subtle, but notable difference in the shape of the “mount” between the DANES profiles taken at room temperature (RT) and 59 °C. This indicates the local emergence of the metallic puddles within the nondistorted monoclinic insulating phase (MIP), as observed in Figures 1a,d between 55 and 60 °C. Previously, the metallic puddles have been visualized in the transition regime by the nanoscale infrared spectroscopy.²⁰ In addition, at 62 and 65 °C, both the “valley” and “mount” of the profiles undergo significant changes showing a lower contrast variation similar to that from the metallic rutile phase at 75 °C (Figure 2a). This resemblance between the DANES profiles in the monoclinic metallic and rutile metallic phases provides clear evidence that the monoclinic insulating VO_2 film has switched to the monoclinic metallic state; this is pivotal for defining the Mott transition in VO_2 .

We further analyze the detected phases of VO₂ on the basis of the obtained experimental information. First of all, we develop an inhomogeneous mixed phase model to reveal the metal fraction in the film and apply it to fit the resistance curve in Figure 1a. The corresponding experimental resistance ratio ($r(T)/r_0 = 1250 \Omega$; r_0 is the Drude resistance), as shown in Figure 3a (the solid orange balls), is closely fitted by a calculated $(1/\rho^3)(1 - \rho^4)$ curve (open black triangles), as explained in the Supporting Information; the IMT resistance is fitted for the first time. Here ρ (blue curve) is defined as the band-filling factor (band FF)^{8,19} of $0 < \rho \leq 1$, and it is extracted from the resistance curve. ρ indicates the fraction of band filling with electrons in k -space, and it also indicates the extent of the metal phase in an inhomogeneous system with insulator and metal phases in real-space (see the Supporting Information). The ρ values in k -space and real-space are equivalent. For instance, $\rho = 1$ means half-filling in k -space and the electronic structure of a metal with one electron per atom in real-space. This reveals that the metal phase exists all over the measurement region. In the case of $\rho = 0.5$, the metal phase is 50% in the measurement region (the other 50% is the insulator phase), and the conduction band is filled by one-half of half filling as per average over the coexisting phases. A change from $\rho \approx 0.23$ at about 55 °C, i.e., the metal phase share in the measurement region is 23% (see the blue diamond in Figure 3a) and insulator 77%, to $\rho \approx 0.97$ at 60 °C, i.e., nearly metal (the red diamond in Figure 3a), reveals that the IMT has already occurred at the sharp resistance reduction region.

In addition, we estimate the coherent domain size by using the Scherrer formula²⁷ and the FWHM of the (111)_M peak shown in Figure 1d. The details of the calculations are given in the Supporting Information, while the evolution of the monoclinic nanodomains size in the wide temperature range of 23–69 °C is plotted in Figure 3b.

In particular, Figure 3b shows the temperature dependence of the sizes of the monoclinic nanodomains, which are approximately the same (within the measurement uncertainty), about 192–195 Å, before and immediately after the IMT. In other words, the domain size conservation is observed in the temperature range 23–60 °C, irrespective of the electronic state switching from the insulator to metal above 55 °C. However, when the temperature exceeds 60 °C, the nanodomains start to decrease in size due to the nucleation and growth of the rutile phase.

To estimate the contribution of each individual phase in the coexistence region, we assume the domain-size conservation and set it to be equal to 195.7 Å, which corresponds to the domain at 56 °C (near the IMT onset). The contribution of the other phases to the 195.7 Å monoclinic domain reduction (domain shrinkage) on heating is taken into account by applying the inhomogeneous mixed phase model with the band filling factor ρ given in Figure 3a. The pie charts in Figure 4 show the resulting share of the MIP, MMP, and RMP phases via the calculated sizes of their nanodomains and relative percentage. The domain sizes along with the ρ values are also given in Table 1.

It is worth emphasizing the importance of the obtained result regarding the distinction between the coexisting phases and the observation of the Mott transition within the nondistorted monoclinic structure. Note that we associate the observed MIP–MMP transition with the thermal excitations of impurity donor atoms coming from, for example,

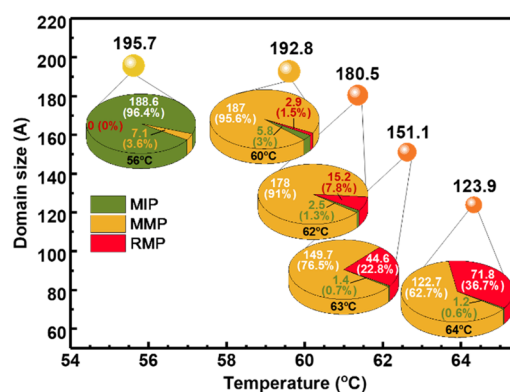


Figure 4. Calculated share and percentage of the monoclinic insulating phase (MIP), monoclinic metal phase (MMP) and rutile metal phase (RMP) coexisting within the VO₂ nanodomains (extracted from Figure 3b) in the IMT temperature range 56–64 °C.

oxygen deficiency (the indirect IMT). This results in a collapse of the Hubbard d -gap in the MIP phase formed by the critical on-site Coulomb repulsive energy U_c between $3d^1$ electrons.^{11,28} The collapse of the d -gap induces free carriers by way of the avalanche in the nondistorted MIP. These carriers mutually scatter each other when their concentration tends to the metal one ($\sim 10^{22} \text{ cm}^{-3}$). Moreover, we speculate that these scatterings, regarded as correlation, further promote the divergent rise of the effective mass of carriers, m^*/m ,^{8,19} as shown in Figure 3b.

In addition, from the effective mass, we obtain another important IMT characteristic that is the correlation strength, κ_{BR} , in the Brinkman–Rice (BR) picture.²⁹ The extended Brinkman–Rice picture applied to inhomogeneous systems^{8,19} reveals the extent of the band-filling factor ρ . The corresponding calculations, given in the Supporting Information, determine the correlation strength of $\kappa_{BR} \approx 0.98$ at $\rho \approx 0.99$ at the MMP (near 65 °C) and $m^*/m \approx 1/(1 - \rho^4) \approx 25$. The large effective mass is consistent with that in a previous paper,³⁰ which justifies that the extraction of ρ from resistance is correct. Note that although a large correlation strength is obtained, it may be incorrect because the BR picture is applied at zero temperature in the absence of thermal phonons.^{8,19} The analyzed effective masses, the correlation strength, and all of the parameters for their calculations are shown in Table 1.

CONCLUSION

In conclusion, by exclusively probing the electronic structure of the monoclinic nanodomains, we demonstrated the Mott transition that occurs via the emergence of the monoclinic metal phase (MMP). This is independent of the structural distortion responsible for the Peierls transition. We also discovered that the size of the monoclinic nanodomain reaches a maximum just before rapid reduction, which corresponds to the structural distortion. In addition, the MMP and the RMP are mixed in the distorted region above 60 °C, which is due to the structural transition from the MMP to the RMP required to stabilize the metallic phase. Therefore, the extent of the RMP increases with increasing temperature. The MMP is the key in developing numerous applications such as the ultrafast IMT switches, oscillating devices, Mott transistors, optoelectronic devices, neuromorphic devices, IMT qubits, and so on. Furthermore, we consider that the previously suggested conclusions^{6,7} on the metal–insulator transition in VO₂,

Table 1. Temperature-Dependent Values of the Band-Filling Factor (ρ), Domain Sizes of Different Phases (MIP, MMP, and RMP)^a, Effective Mass (m^*/m), and Correlation Strength (κ_{BR})

temp (°C)	$\rho = n_{\text{carrier}}/n_{\text{tot}}$	distortion of the structure	monoclinic domain size ^d (Å)	MIP size ^e (Å)	MMP size ^f (Å)	RMP ^g (Å)	m^*/m ^h	$\kappa_{BR} = U/U_c$
56	0.036	no	195.7	188.6	7.1	0	1	ND at $\rho < 1$ ⁱ
60	0.970	no	192.8	5.8	187.0	2.9	8.7	0.941
62	0.986	yes	180.5	2.5	178.0	15.2	18.3	0.972
63	0.988	yes	151.1	1.4	149.7	44.6	21.2	0.976
64	0.990	yes	123.9	1.2	122.7	71.8	25.4	0.980
66	n/a	yes	109.3	0	109.3	86.4	n/a	n/a
67	n/a	yes	99.5	0	99.5	96.2	n/a	n/a
68	n/a	yes	87.9	0	87.9	107.9	n/a	n/a
69	n/a	yes	85.8	0	86.8	109.9	n/a	n/a

^aThe distortion of the structure means the shrinkage (size reduction) of the monoclinic nanodomain. ^bAs the temperature increases, the increase of ρ translates into percolation. ^c $n_{\text{tot}} = 1.69 \times 10^{22}/\text{cm}^3$ is given by the inverse volume of the tetragonal rutile. ^dMonoclinic domain sizes are obtained from analyzing the X-ray diffraction. ^eMIP is the monoclinic insulator phase. ^fMMP is the monoclinic metal phase. ^gRMP is the rutile metal phase. The MIP, MMP, and RMP sizes were obtained by subtracting the domain size from the monoclinic domain size of 195.7 Å. ^hEffective mass (m^*/m) is defined as the following: $m^*/m = 1/(1 - \rho^4)$, where ρ is the band-filling factor, i.e., the extent of the metal phase. ⁱBecause the Brinkman–Rice picture is applied at half-filling of one electron per atom when $\rho = 1$, in the $\rho < 1$ case, $\kappa_{BR} = U/U_c$ is not determined (ND).

which is a combination of the electron–electron interaction (Mott transition) and electron–phonon interaction (Peierls transition), are caused by the combined observation of both the distorted monoclinic metal phase and the rutile metal phase in the measurement region.

Our approach to probe the electronic properties of a specific crystallographic phase can be applied to a variety of phase change materials (NbO_2 , V_2O_3 , Fe_3O_4 , InSe , etc.) and multiphase systems, thus paving the way for understanding their intrinsic properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaelm.0c00983>.

VO_2 synthesis, device fabrication, resistance and X-ray diffraction measurements, DANES setup, θ – 2θ XRD measurements, VO_2 domain size calculation, extraction of the band-filling factor ρ from the resistance data using the inhomogeneous model, physical meaning of ρ , derivation of the metal resistance from the Drude model, analysis of the “Mottian” characteristics of VO_2 (PDF)

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Author Contributions

C.-Y.K. and T.S. contributed equally to this work.

Author Contributions

C.-Y.K., T.V.S., and H.-T.K. established the research plans, conducted the experiments, analyzed the data, and wrote the article. J.C.C. assisted with the sample fabrication and the DANES experiment.

Notes

The authors declare no competing financial interest.

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