Distinct Electronic Structure of the Electrolyte Gate-Induced Conducting Phase in Vanadium Dioxide Revealed by High-Energy Photoelectron Spectroscopy

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ABSTRACT The development of new phases of matter at oxide interfaces and surfaces by extrinsic electric fields is of considerable significance both scientifically and technologically. Vanadium dioxide (VO2), a strongly correlated material, exhibits a temperature-driven metal-to-insulator transition, which is accompanied by a structural transformation from rutile (high-temperature metallic phase) to monoclinic (low-temperature insulator phase). Recently, it was discovered that a low-temperature conducting state emerges in VO2 thin films upon gating with a liquid electrolyte. Using photoemission spectroscopy measurements of the core and valence band states of electrolyte-gated VO2 thin films, we show that electronic features in the gate-induced conducting phase are distinct from those of the temperature-induced rutile metallic phase. Moreover, polarization-dependent measurements reveal that the V 3d orbital ordering, which is characteristic of the monoclinic insulating phase, is partially preserved in the gate-induced metallic phase, whereas the thermally induced metallic phase displays no such orbital ordering. Angle-dependent measurements show that the electronic structure of the gate-induced metallic phase persists to a depth of at least ~40 Å, the escape depth of the high-energy photoexcited electrons used here. The distinct electronic structures of the gate-induced and thermally induced metallic phases in VO2 thin films reflect the distinct mechanisms by which these states originate. The electronic characteristics of the gate-induced metallic state are consistent with the formation of oxygen vacancies from electrolyte gating.

KEYWORDS: VO2 · ionic liquid electrolyte gating · orbital polarization · X-ray photoelectron spectroscopy

Because of its electronic and structural phase transitions near room temperature, VO2 has been of intense interest from a fundamental physics viewpoint,1 where it acts as a model system to investigate the interactions between spin, charge, and orbital degrees of freedom, and as a material for future electronic devices.2–8 The mechanism driving the metal-to-insulator transition (MIT) is still debated; both electron correlation and lattice distortion effects are expected to play a role.5,9 The interplay between the crystal structure and electronic properties is depicted in Figure 1. In the tetragonal rutile phase, the V 3d t2g orbitals are crystal-field split into an a1g (d5) orbital and doubly degenerate egπ orbitals.3–5,10 The d5 states are situated parallel to the rutile c-axis and originate from the overlapping d orbitals of V atoms within neighboring oxygen octahedra. The egπ states hybridize with the O 2p orbitals (V–O overlap) to form bonding (π) and antibonding (π*) states. As shown in Figure 1b for the rutile structure, both the d5 and π* bands cross the Fermi energy (Ef). In the rutile → monoclinic phase transition, V atoms dimerize and the V–V dimers rotate with respect to the rutile c-axis (Figure 1a), resulting in the d5 bands (formed by V–V overlap) splitting into bonding (d5) and antibonding (d5*) states. The displacement of V atoms within their oxygen octahedra also leads to an increased overlap between the V 3d and oxygen orbitals.
O 2p states resulting in the π* band being pushed to higher energy and thereby opening an energy gap in the monoclinic phase, as shown in Figure 1b.4,10 The strong temperature-driven modulation of the density of states (DOS) at $E_F$ leads to large changes in the transport properties (Figure 1c).

It has long been of interest to induce a metallic state in VO$_2$ below the MIT temperature, $T_{MIT}$, for example, by light or by electric fields. Using conventional field-effect transistor geometries in which the channel is formed from VO$_2$ and gated with conventional gate dielectrics, the electric fields are not sufficiently large to change the electronic state of VO$_2$. However, using ionic liquid electrolyte gate dielectrics, which provide much larger electric fields at the liquid/channel interface, Jeong et al.8 and Nakano et al.11 have found that a VO$_2$ channel can be gated to a metallic state below $T_{MIT}$. However, whereas Nakano et al.11 claimed that the metallic state resulted from a collapse of the Mott insulating energy gap due to electrostatically induced electrons at the oxide surface, Jeong et al.8 showed that the metallic state in the VO$_2$ channel was non-volatile and persisted when the gate voltage was reduced to zero and even after the ionic liquid was completely removed from the VO$_2$ surface. Using a wide variety of characterization techniques and studies, Jeong et al.8 provided strong evidence that the metallicity in VO$_2$ arises from the formation of oxygen vacancies due to an electric-field-induced oxygen migration during the gating process. Moreover, these authors showed this process to be reversible.8 In the scenario of Jeong et al.,8 there is no reason to expect that the structure of the metallic state of gated VO$_2$ is the same as that of the thermally induced metallic phase, but Nakano et al.11 claimed that the gate-induced metallic phase has the same rutile structure as that of the high-temperature metallic state. It is thus very important to determine the crystal and electronic structure of the gate-induced metallic phase in VO$_2$. Here we perform high-energy X-ray photoelectron spectroscopy (HAXPES) on electrolyte-gated VO$_2$ thin films at various temperatures to elucidate its electronic structure. HAXPES has a key advantage over conventional photoelectron spectroscopy in that high-energy photons excite high kinetic energy electrons which have a long inelastic mean free path and correspondingly large escape depth and thus a high bulk sensitivity.12–15

**RESULTS**

A schematic of the measurement setup and device used is shown in Figure 2a (see Experimental Methods for details). Panels b–e and f,g of Figure 2 show, respectively, the valence band (VB) and the V 2p spectra measured at various photoemission angles and temperatures. Measurements were performed on the same sample in the pristine monoclinic (120 K) and rutile (350 K) phases as well as the gated (120 K) state. The VB spectra from these different states are compared in Figure 2b. The rutile phase is obviously metallic, exhibiting a coherent peak at $\sim$0.3 eV below the Fermi level, consistent with previous work.9 The
monoclinic structure, on the other hand, shows a peak at \( \sim 0.9 \) eV below \( E_F \). The VB spectrum of the gated structure is broadened in comparison to the monoclinic structure and exhibits a shift to lower binding energy of about 200 meV and additional spectral weight at \( E_F \).

The dependence of the relative photoemission intensity of the 3d bands on the light incidence angle was also investigated. Inspection of the 3d band photoemission (Figure 2b) shows that the intensity at the peak maximum in the monoclinic phase is much higher than that in the rutile phase at the peak maximum for low incidence angles. The 3d band of the gated phase exhibits a peak photoemission intensity between that of the rutile and monoclinic. This behavior may be a consequence of the orbital polarization in this compound.\(^{16}\) In the rutile phase, the nondimerized V atoms possess a homogeneous spatial distribution of 3d states, as sketched in the inset of Figure 2c. The \( d_\pi \) and \( \pi^* \) states (2p–3d hybridized) are occupied. Therefore, the photoemission intensity does not present a strong dependence on the light electric field direction. By contrast, the monoclinic phase has a strong dimerization of V atoms resulting in a strong orbital polarization. That is, only the \( d_\pi \) band is occupied at energies near \( E_F \). The light electric field at low incident angles couples with the \( d_\pi \) states, resulting in an enhanced photoemission intensity in comparison to high incident angles (Figure 2d). In the gated phase, the angular dependence is smaller, which can be ascribed to a partial orbital polarization (Figure 2e). A smaller orbital polarization is a direct consequence of the reduced V dimerization, as shown schematically in Figure 1d. Indeed, this result is consistent with recent structural measurements of electrolyte-gated \( \text{VO}_2 \) using \textit{in situ} synchrotron X-ray diffraction.\(^{17}\)
In Figure 2f, the rutile V 2p_{3/2} peak is located at \(-515.9\) eV, consistent with the V^{4+} oxidation state in VO_{2}, and is significantly broadened in comparison to the other two peaks.\(^8\) This broadening has been attributed primarily to the absence of V dimerization;\(^9\) metallic screening effects also play a role.\(^6\) At low temperatures, the transition to the monoclinic phase can be easily identified by the decreased V 2p_{3/2} peak width. The gated film at 120 K presents a similar V 2p_{3/2} spectra as the monoclinic phase, with the exception of a shoulder at lower binding energy. Figure 2g shows the gated V 2p spectra measured at different emission angles. Data collected at quasi-normal emission (\(\theta = 85^\circ\)) have essentially the same features as the off-normal emission (\(\theta = 30^\circ\)), pointing to the homogeneity of the gated phase over a relatively thick region (>40 Å). Comparison between gated and pristine spectra collected in both photoemission and reflection modes also play a role.\(^6,9\) At low temperatures, the transition to the monoclinic phase can be easily identified by the decreased V 2p_{3/2} peak width. The gated film at 120 K presents a similar V 2p_{3/2} spectra as the monoclinic phase, with the exception of a shoulder at lower binding energy. Figure 2g shows the gated V 2p spectra measured at different emission angles. Data collected at quasi-normal emission (\(\theta = 85^\circ\)) have essentially the same features as the off-normal emission (\(\theta = 30^\circ\)), pointing to the homogeneity of the gated phase over a relatively thick region (>40 Å). Comparison between gated and pristine spectra collected in both photoemission and reflection modes.

It is important to note that the spectra for the gated films measured at 120 K cannot be fit as a combination of the monoclinic and rutile spectra (Figure S2). Therefore, the shoulder in the V 2p_{3/2} peak and the modifications in the VB after the gating process are due to a structural change, which is different from that observed in the pristine VO_{2} monoclinic \(- rutile structural phase transition. In the gated sample, the shoulder at lower binding energy in the V 2p_{3/2} peak is consistent with the presence of vanadium atoms in the +3 valence state; this leads to V 2p_{3/2} peaks with larger energy broadening than the monoclinic pristine phase, such as typically found in Magnéli phases.\(^8,18,19\) Additionally, the broadening and shift in the VB spectra of the gated sample is also consistent with the reduced oxygen content in the Magnéli phases, for example, V_{2}O_{3} and V_{3}O_{11} (Figure S2).\(^8,18,19\) V_{2}O_{3} and V_{3}O_{11} have nondimerized and partially dimerized V\(_{-V}\) bonds, respectively, and the broadening of the V 2p_{3/2} peak and shift in the VB spectra have been attributed to this reduction in V\(_{-V}\) dimerization.\(^19\) Based on these observations and the dependence of the VB intensity on light incidence angle, we suggest that the gated structure may also exhibit larger V\(_{-V}\) interatomic distances than the monoclinic phase (Figure 1d–f).

Figure 3 compares the spectra from the gated sample measured at temperatures above (350 K) and below (120 K, same as Figure 2b) the MIT of the pristine film. At 350 K, the V 2p spectrum of the gated film resembles that of the pristine rutile structure. This may indicate structural similarities between the rutile phase and the gated phase at high temperature. However, the VB spectra of the gated film at all temperatures show distinct features that are not associated with the rutile or the monoclinic phase, further demonstrating the distinct electronic structure in the gated state.

According to the photoemission spectra measured at different emission angles (Figure 2g), the electronic structure of the gate-induced metallic phase is not limited to the surface, but rather extends to a thickness beyond that examined by HAXPES (here >40 Å). As discussed above, the electronic structure of this phase is consistent with the model of Jeong et al.,\(^8\) who have proposed that oxygen vacancies are induced by electrolyte gating of VO_{2}. To better understand the effect of the formation of oxygen vacancies in the pristine VO_{2}, density functional theory (DFT) calculations were performed with the VASP\(^20\) program package using the Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional\(^21\) taking 12.5% of exact exchange (labeled as HSE-0.125), the Perdew, Burke, Ernzerhof (PBE) functional,\(^22\) and a rotationally invariant implementation of the PBE+U functional.\(^23\) In the case of PBE+U, the Hubbard on-site repulsion U and J exchange interaction was included using U_{\text{eff}} = U - J = 3.32 eV in accordance with ref 24 (more details are presented in the Supporting Information). Theoretical efforts to simulate the experimental observations are complicated by the strong electron correlation effects in VO_{2}.\(^5,25\) This issue notwithstanding, we have applied DFT calculations in a simplified model of the gated phase, in which we concentrate our efforts on capturing general trends in the structural modifications and electronic structure induced by oxygen removal. When O is removed, the structural changes extend far beyond the first coordination shell and are quite substantial in the whole supercell volume (see Figure 4a). Our calculations indicate that, besides the atomic structure, the electronic structure is also strongly affected by oxygen vacancy creation. For an O1-type vacancy (oxygen vacancy between dimerized V atoms), the flow of the bond charge density shows that the two valence electrons of the removed oxygen atom (see the blue isosurface in Figure 4b) are redistributed over the whole volume of the simulation cell (see the red isosurface in Figure 4b). This charge density is rather delocalized and could serve as a charge carrier, leading to conductivity in the oxygen-deficient structure. The calculated DOS computed with either PBE+U or HSE-0.125 hybrid functionals provides qualitatively similar results, showing that compared to pristine VO_{2} (Figure 4c), the oxygen vacancies lead to a broadening of the V 3d states and a reduction in the band gap compared to the monoclinic phase (Figure 4d). This
Modification in the DOS leads to the emergence of new states in energy positions above the Fermi energy of the monoclinic structure, in agreement with very recent dynamical mean-field theory simulations and with the increased spectral weight near E_F observed in the HAXPES valence band spectra of the gated films (Figure 2c).

CONCLUSION
In summary, valence band and V 2p photoemission spectra reveal that the gate-induced metallic state in VO_2 has a distinct electronic structure from that of the rutile metallic phase of the pristine film. In our experiments, we observe broadening of the valence band in the gated state to lower energies, which we speculate is due to the formation of oxygen vacancies since broadening of the valence band is characteristic of Magnéli phases that have reduced oxygen content in comparison to VO_2. We conclude that the monoclinic structure and the associated orbital degeneracy of the insulating phase is retained but modified by electrolyte gating, as summarized schematically in Figure 1d,e. The V–V distance is increased in the gated phase and is consistent with the creation of oxygen vacancies, as proposed by Jeong et al. (Figure 1d). Larger V–V distances imply a smaller d orbital overlap, decreasing the d band splitting without lifting the orbital polarization. This is accompanied by a charge redistribution due to the removal of oxygen, populating empty states at E_F (Figure 1e). Additionally, the gated sample shows a substantial increase in spectral weight at E_F, reflecting the enhanced conductivity at low temperatures (Figure 1f). The observed electronic structures are consistent with an electrochemical reaction in VO_2 leading to the formation of oxygen vacancies over a relatively thick region, in agreement with the results reported in ref 8.

EXPERIMENTAL METHODS
An epitaxial VO_2 thin film and device were prepared on (001) TiO_2. The VO_2 thin film is 10 nm thick with a MIT temperature of 290 K and a rms roughness of 10 Å. Further details are available in ref 8. An X-ray excitation energy of 3 keV (P09, PETRA III, DESY) was used to study the VO_2 film in its pristine and gated states (120–350 K). At this excitation energy, the probing depth can be varied from ~40 to ~20 Å by increasing the angle of emission (θ) from 90° (normal) to 30° (off-normal). A linear background was subtracted from the V 2p spectra, which was...
then normalized by the V 2p subarea. VB spectra were normalized by the photoemission intensity at the high-energy tail of the O 2p band (energy ∼2.8 eV).

The sample was gated by applying V_g = 2.1 V at 330 K (above the MIT) and then sweeping the temperature from 330 to 10–330 at 3 K/min. Gating was performed under vacuum ex situ, leading to a conducting state (gated VO_2) as evidenced by a conductivity increase of 3 orders of magnitude (Figure 1f).

Since Jeong et al. have shown that the conducting state in VO_2 persists even after electrolyte removal, HAXPES is used to probe the electronic structure of the gate-induced metallic phase after the liquid electrolyte was removed by washing the sample with isopropyl alcohol. This allowed for measurements of the VB and core states of VO_2 thin films with a high signal-to-noise ratio.

Conflict of Interest: The authors declare no competing financial interests.

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Supporting Information Available: Temperature-dependent HAXPES, comparison of gated and weighted average spectra, O 2p HAXPES spectra, Magnéli phase valence band comparison, sample transport properties, and ab initio calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


