Strain Induced Orbital Dynamics Across the Metal Insulator Transition in Thin VO$_2$/TiO$_2$ (001) Films

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Abstract

VO$_2$ is a strongly correlated material, which undergoes a reversible metal insulator transition (MIT) coupled to a structural phase transition upon heating ($T$ = 67 °C). Since its discovery, the nature of the insulating state has long been debated and different solid-state mechanisms have been proposed to explain its nature: Mott-Hubbard correlation, Peierls distortion, or a combination of both. Moreover, still now, there is a lack of consensus on the interplay between the different degrees of freedom: charge, lattice, orbital, and how they contribute to the MIT. In this manuscript, we will investigate across the MIT the orbital evolution induced by a tensile strain applied to thin VO$_2$ films. The strained films allowed to study the interplay between orbital and lattice degrees of freedom and to clarify MIT properties.

Keywords Orbital dynamics · VO$_2$ strained films · Auger yield · Metal-insulator transition

1 Introduction

The vanadium ([Ar] 3d$^3$4s$^2$) element is very reactive and can be synthesized in many mixed valence oxides with different oxidation states and stoichiometry, e.g., VO, V$_2$O$_3$, V$_3$O$_5$, VO$_2$, V$_6$O$_{13}$, V$_4$O$_7$, and V$_2$O$_5$. This class of oxides bears the seed of a strong electronic correlation and has been widely studied since the early times of X-ray spectroscopy. The electronic transport and the spectroscopic properties of V$_2$O$_3$ [1] and VO$_2$ [2], as well as the complex local structure of V$_2$O$_5$ [3] have always attracted interest, and still today, their investigation is a hot topic in materials science, [4–6] with many potentials for technology applications [7]. Among the vanadium oxides, VO$_2$ is one of the most stimulating systems. It exhibits a reversible, temperature-triggered (67 °C) metal insulator transition (MIT) coupled to a structural phase transition (SPT) from the high-temperature tetragonal metal phase to the low-temperature monoclinic insulator phase characterized also by a clear nanoscale phase separation [7–9]. Since its discovery in the late 50s [10], the nature of the VO$_2$ MIT has been the object of debate within the scientific community. A transition driven by the strong electron correlation, i.e., the Mott-Hubbard transition [11, 12], by the Peierls structural distortion [13–15], or by a cooperative Mott-Peierls mechanism are the most favored models for VO$_2$ MIT [16]. While the structurally induced effects on the electronic properties of the materials, in particular at low dimensions and high strain, are well known, [17–20] a clear correlation among lattice, orbital, and electronic degrees of freedom and MIT feature is still missing.

In this structure, each metal site is surrounded by slightly distorted oxygen octahedral and the crystal field splits the degenerate 3d manifold into 3 $t_{2g}$ and 2 $e_g$ levels. The small orthorhombic distortion further splits the 3 $t_{2g}$ levels in one singly degenerate $a_{1g}$ and two $e_{g}$ levels. According to the
Goodenough model [14]. V 3d and O 2p orbitals hybridize forming bonds of σ and π symmetry. Their unoccupied levels are identified as π*(e_g^* character) and σ*(e_g^* character). The a1g orbital is populated by unpaired 3d electrons and is called d_{1g}. The dimerization of vanadium atoms in the insulating phase splits the d_{1g} originating empty d_{1g}*(with t_{2g} character). In the metallic phase, the d_{1g} is oriented along the c_\perp axis and along the V–V dimer in the insulating phase. This bond is strictly related with the unidimensional V–V dimer chain formation in the monoclinic insulating phase [21], while the π* has an isotropic behavior within the lattice [22]. Across the MIT, the π* and d_{1g} collapse to the Fermi level (FL) upon being both populated. This mechanism closes the band gap. Moreover, since π*, d_{1g} and σ* have mostly a 3d character; changes on the electronic structure can be followed by monitoring the absorption spectroscopy intensity at the V L_{2,3} edges (V 2p - -> 3d) [8]. Here we present the results obtained on three different single crystalline strained films of VO_2/TiO_2 (001) with thickness 8, 16, and 32 nm, probing simultaneously the structural and orbital contribution to the MIT using the V L_{2,3} edge XANES (X-ray Absorption Near Edge Structure) spectroscopy [23], which is a good probe of strongly correlated electronic systems [24] and of strain control of functionality of quantum materials [25–28].

### 2 Methods

Films of VO_2 having a thickness of 8, 16, and 32 nm were deposited on a clean substrate of TiO_2 (001) by the RF plasma–assisted oxide-MBE instrument working with a base pressure better than 4 × 10^{-9} mbar. At the constant growth rate of 0.1 Å/s, the thickness was controlled by adjusting the deposition time in a range from several unit cells to tens of nanometers. During the deposition process, the substrate has been kept at the temperature of 550 °C. The interfacial cross-section has been investigated with the high-resolution scanning transmission electron microscope (STEM). High angle annular dark field (HAADF) STEM images were taken on the JEM ARM200F with a probe aberration corrector, while the diffraction pattern was acquired on the JEM 2100 TEM. The complete details of the epitaxial film preparation are reported elsewhere [23, 29].

The XANES experiments have been performed at the ANCHOR end-station of the ALOISA beamline [30] at Elettra synchrotron radiation facility. Electrons were collected at normal emission by the PSP Vacuum 120-mm mm electron analyzer with 2D delay line detector. The photon beam was linearly polarized in the scattering plane and impinged the sample at the magic angle (35°). Measurements were performed at constant pass energy (E_p = 20 eV).

### 3 Results

To discern the spectral changes observed in the XANES spectra of these films, it is necessary to understand the strain-induced modification of the VO_2 crystal structure. The TiO_2 substrate has the tetragonal (rutille) lattice structure as the metallic VO_2. Most of the considerations in the next are referred to the rutille phase of VO_2 except where specified otherwise. Since the TiO_2 substrate is oriented along the (001) surface, the lattice mismatch will affect the a and b structural parameters of the vanadium oxide films. The in-plane lattice mismatch can be calculated as:

$$M = \frac{a_s - a_f}{a_f} \times 100\%$$  

(1)

where a_s and a_f are the lattice parameters of the substrate and of the sample, respectively. Between rutile TiO_2 (a = b = 4.58 Å) and bulk VO_2 (a = b = 4.55 Å), the lattice mismatch M is 0.66%. Then, to match the substrate lattice during the early stage of the epitaxial growth, a VO_2 film will undergo a tensile strain, which results in the increase of both a_s and b_r and the consequent elastic compression of c_r [22, 23, 31]. Increasing the thickness of the VO_2 film, the distortions induced by the lattice of the substrate fades and the lattice constants relax to the bulk VO_2 values. For the sample analyzed in this work, the critical thickness for which the sample can be considered bulk-like is ~ 25 nm [23].

In the tetragonal unit cell, the vanadium atoms occupy the positions (0, 0, 0) and (½, ½,½). Each vanadium atom is surrounded by oxygen octahedra with two different V–O bond lengths. Metal and oxygen atoms separated by the apical distance share the same z value along c_r. The equatorial distance that separates the vanadium atom and the four neighboring oxygen atoms is \(z = z_{metal} \pm \frac{1}{2}\) (see Fig. 1). The two apical oxygen atoms are located at ± (u, u, 0), while the four equatorial oxygen atoms are in the positions ± (±(u-½), ½(u-½); ½) where \(u = 0.3001\) at 360 K [13, 32], although V–O bond lengths are influenced by strain-induced modifications in the lattice parameters. Looking at the apical distance, this is described by:

$$J_{Apical} = J_A = \sqrt{u_1^2 a_r^2 + u_2^2 b_r^2} = \sqrt{2u_1^2 a_r^2} = \sqrt{2}ua_r$$  

(2)

and the apical V–O bond increases linearly with the \(a_r\) length. On the other hand, the equatorial bond length includes the three lattice parameters:

$$J_{Equatorial} = J_E = \sqrt{\left(u_1 - \frac{1}{2}\right)^2 a_r^2 + \left(u_2 - \frac{1}{2}\right)^2 b_r^2 + \frac{1}{4} c_r^2}$$

$$= \sqrt{2 \left(u_1 - \frac{1}{2}\right)^2 a_r^2 + \frac{1}{4} c_r^2}$$  

(3)

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Combining Eqs. 2 and 3, we may recognize that $J_A$ increases with the strain, while $J_E$ is almost independent since the increase in $c_r$ is compensated by the decrease of $c_r$. Moreover, increasing the apical V–O distance, the superposition between oxygen and vanadium orbitals decreases, and as a consequence, the 3d-2p hybridization.

Actually, the $\pi^*$ orbital, which points toward other vanadium atoms and is oriented toward the oxygen corners of the octahedron, is the most affected bond [22]. Moreover, the decrease of the V–O hybridization reduces the bonding–antibonding energy separation, hence the energy of $\pi^*$ orbital lowers. The $d^*\parallel$ experiences the opposite situation. The decrease of $c_r$ increases the overlap among orbitals within the unidimensional V–V chains, shifting to high energy the $d^*\parallel$ orbital. Indeed, the strain increases the $\pi^*$-$d^*\parallel$ splitting reversing the orbital population at the FL.

In the insulating phase, the V–O hybridization is stronger and, as a consequence, the $\pi^*$ and $d^*\parallel$ orbital are further separated, with the second appearing at higher energy respect to the former.

The V L edges XANES spectra for the metallic and insulating phase are compared in Fig. 2.

The interpretation of the L edge shape is not straightforward. However, the L$_2$ edge exhibits more defined features with respect to the L$_2$-one. In general, the L$_3$ and L$_2$ spectra differ because of the multiplet effects in the final state [33]. In this particular case, these are negligible, whereas the presence of a strong Coster–Kronig decay (V L$_3$M$_4$M$_5$) [34] severely reduce the lifetime of the excited state $2p^{1/2}$, thus broadening the XANES line shape and making hard to recognize different adjacent features. As a consequence, we will focus our attention to the L$_3$ edge.

The shape of the L$_3$ edge is not commensurate with the shape of the O K edge spectrum available in literature [35, 36] despite they should exhibit the same features as a consequence of the V3d–O2p hybridization. This can be understood taking into account other effects: in the L$_3$ and L$_2$ XANES, there is a transfer of spectral weight away from threshold (L$_3$ maximum intensity 518.4 eV), the apparent reduction of the spin-orbit splitting (6.4 eV from XANES spectra, 7.3 eV from XPS [37]), and the deviation from the statistic intensity ratio $I(L_3)/I(L_2) \approx 2$. All features can be explained considering the strong interaction between the 2p core hole ($2p^1$) and the 3d electrons in the final state. In vanadium oxides, $2p$–3d interaction is of the same order of magnitude of the spin-orbit splitting, with a severe redistribution of the spectral weight of the entire spectrum [36–38]. The main shape occurs in the spectral region 514–518.5 eV where the $\pi^*$, $d^*\parallel$ and $\sigma^*$
orbitals are present \cite{21, 22, 39}. Precisely, $\pi^*$ and $d^\|$ are not distinguishable but are located in the range 514–516.5 eV while $\sigma^*$ is centered at 518.4 eV \cite{21}. However, in the insulating phase, when the strain increases, the $\pi^*-d^\|$ features become more evident because of the increasing $\sigma^*-d^\|$ splitting. To highlight the changes across the MIT, the difference spectra calculated using Eq. 4 are showed in Fig. 3.

$$I_{\text{ins}} - I_{\text{met}} \propto u\text{DOS}_{\text{ins}} - u\text{DOS}_{\text{met}}$$ (4)

Two main contributions can be identified at ~515 and 517.5 eV. The high-energy contribution associated to the $\sigma^*$ orbital shifts toward low photon energy due to the rearrangements of vanadium atoms within the oxygen octahedron. The low energy contribution can be assigned to the $\pi^*-d^\|$ rearrangement going from the insulating to the metallic phase (Fig. 4). Actually, the spectral difference is dominated by the $\sigma^*$ signal whose low energy-tail may probably affect the line shape of the $\pi^*-d^\|$ feature. Nevertheless, by integrating the difference spectra in the range 512–518.4 eV, a clear trend as a function of thickness emerges. The thickness dependence of the integrated intensity is alike what reported in \cite{22}, pointing out that the different orbital strain dynamics are qualitatively similar in agreement with the theoretical band model reported in \cite{23} for VO2/TiO2 (001) strained and ultra-strained films.

4 Conclusion

In this work we investigated three different single crystalline strained VO2 films deposited over a rutile TiO2 (001) substrate.
The epitaxially grown VO₂ undergoes a tensile strain, which results in the increase of \( a_s \) and \( b_s \) to match the higher lattice constant of the substrate and in the elastic reduction of \( c_s \). These changes in the cell unit parameters affect the oxygen octahedron, which surrounds each vanadium atoms increasing the apical V–O bond length decreasing also the V 3d–O 2p hybridization. In the metallic phase of VO₂, the induced strain reduces the hybridization, upshifts the \( \Delta_f^\text{d} \) empty orbital, and downshifts \( \pi^\text{d} \), leading to an inversion of the \( \Delta_f^\text{d} / \pi^\text{d} \) occupation at the Fermi level. In the insulating phase, the \( \pi^\text{d} \) and \( \Delta_f^\text{d} \) orbital split increased respect to the bulk case. In order to probe the dynamical model of the orbital states, we have performed XANES measurements of the V L edges probing the Auger yield (464 eV). Across the phase transition, we point out that the major changes are observed in the \( \pi^\text{d} - \Delta_f^\text{d} \) region of the spectra with the intensity increasing simultaneously to the strain. A numerical integration in the spectral region most perturbed by the MIT is in a qualitative agreement with the theoretical models and previous measurements, confirming the reliability of XANES to probe the orbital strain dynamics across the MIT. Further theoretical and experimental investigations are necessary to improve our understanding of the interplay between orbital and lattice structure in VO₂ MIT.

**Compliance with Ethical Standards**

**Conflict of Interest** The authors declare that they have no conflict of interest.

**References**

1. Bianconi, A., Natoli, C.R.: Effect of the metal-insulator transition on vanadium K-photoabsortion spectrum in V₂O₃. Solid State Commun.27(11), 1177–1179 (1978). https://doi.org/10.1016/0038-1098(78)91137-7

2. Bianconi, A.: Multiplet splitting of final-state configurations in X-ray-absorption spectrum of metal VO₂: effect of core-hole-screening, electron correlation, and metal-insulator transition. Phys. Rev. B. 26, 2741(1982). https://doi.org/10.1103/PhysRevB.26.2741

3. Stizza, S., Mancini, G., Benfatto, M., Natoli, C.R., Garcia, J., Bianconi, A.: Structure of oriented V₂O₃ gel studied by polarized X-ray-absorption spectroscopy at the vanadium K edge. Phys. Rev. B. 40, 12229 (1989). https://doi.org/10.1103/PhysRevB.40.12229

4. Lu, Q., Bishop, S.R., Lee, D., Lee, S., Bluhm, H., Tuller, H.L., Lee, H.N., Yildiz, B.: Electrochemically triggered metal–insulator transition between VO₂ and V₂O₃. Adv. Funct. Mater. 28(34), 1803024 (2018). https://doi.org/10.1002/adfm.201803024

5. Singer, A., Ramirez, J.G., Valmianski, I., Cela, D., Hua, N., Kukreja, R., Wingert, J., Kovalchuk, O., Giovino, J.M., Sikorski, M., Chollet, M., Holt, M., Schuller, I.K., Shyryko, O.G.: Nonequilibrium phase precursors during a photoexcited insulator-to-metal transition in V₂O₃. Phys. Rev. Lett. 120, 207601 (2018). https://doi.org/10.1103/PhysRevLett.120.207601

6. Zhu, Y., Cai, Z., Chen, P., Zhang, Q., Highland, M.J., Jung, J.W., Walko, D.A., Dufresne, E.M., Jeong, J., Samant, M.G., Parkin, S.S.P., Freeland, J.W., Evans, P.G., Wen, H.: Mesoscopic structural phase progression in photo-excited VO₂ revealed by time-resolved X-ray diffraction microscopy. Sci. Rep. 6, 1 (2016). https://doi.org/10.1038/srep21999

7. Brahlek, M., Zhang, L., Lapano, J., Zhang, H.-T., Engel-Herbert, R., Shukla, N., Datta, S., Paik, H., Schom, D.G.: Opportunities in vanadium-based strongly correlated electron systems. MRS Commun. 7, 27–52 (2017). https://doi.org/10.1557/mrc.2017.2

8. Marcelli, A., Coreno, M., Stredansky, M., Xu, W., Zhou, C., Fan, L., Chu, W., Wei, S., Cossaro, A., Ricci, A., Bianconi, A., Delia, A.: Nanoscale phase separation and lattice complexity in VO₂: the metal–insulator transition investigated by XANES via Auger Electron yield at the vanadium L₂,₃-edge and resonant photoemission. Condens. Matter. 4(2), 38 (2017). https://doi.org/10.3390/condmat2040038

9. Gioacchino, D., Marcelli, A., Puri, A., Zhou, C., Fan, L., Zeitler, U., Bianconi, A.: Metastability phenomena in VO₂ thin films. Condens. Matter. 2(17), 10 (2017). https://doi.org/10.3390/condmat2010010

10. Morin, F.J.: Oxides which show a metal-to-insulator transition at the neel temperature. Phys. Rev. Lett. (1959). https://doi.org/10.1103/PhysRevLett.3.34

11. Mott, N.F.: The transition to the metallic state. Philos. Mag. (1961). https://doi.org/10.1080/14786436108243318

12. Zylbersztejn, A., Mott, N.F.: Metal-insulator transition in vanadium dioxide. Phys. Rev. B. (1975). https://doi.org/10.1103/PhysRevB.11.4383

13. Eyert, V.: The metal-insulator transitions of VO₂: a band theoretical approach. Ann. der Phys. (2002). https://doi.org/10.1002/1521-3889(200210)11:9<650::AID-ANDP650>3.0.CO;2-K

14. Goodenough, J.B.: The two components of the crystallographic transition in VO₂. J. Solid State Chem. (1971). https://doi.org/10.1016/0022-4596(71)90091-0

15. Cavalleri, A., Dekorsy, T., Chong, H.H.W., Kieffer, J.C., Schoenlein, R.W.: Evidence for a structurally-driven insulator-to-metal transition in VO₂: a view from the ultrafast timescale [2]. Phys. Rev. B - Condens. Matter Mater. Phys. (2004). https://doi.org/10.1103/PhysRevB.70.161102

16. Weber, C., O’Regan, D.D., Hine, N.D.M., Payne, M.C., Kotliar, G., Littlewood, P.B.: Vanadium dioxide: a Peierls-Mott insulator stable against disorder. Phys. Rev. Lett. (2012). https://doi.org/10.1103/PhysRevLett.108.256402

17. Rezvani, S.J., Perali, A., Fretto, M., De Leo, N., Flammia, L., Milosević, M., Nannarone, S., Pinto, N.: Substrate-induced proximity effect in superconducting niobium nanofilms. Condens. Matter. 4(1), 4 (2018). https://doi.org/10.3390/condmat4010004

18. Pinto, N., Rezvani, S.J., Perali, A., Flammia, L., Milosevic, M.V., Fretto, M., Cassiago, C., De Leo, N.: Dimensional crossover and incipient quantum size effects in superconducting niobium nanofilms. Sci. Rep. 8, 1 (2018). https://doi.org/10.1038/s41598-018-22983-6

19. Pinto, N., Rezvani, S.J., Favre, L., Berbezier, I., Fretto, M., Boarino, L.: Geometrically induced electron-electron interaction in semiconductor nanowires. Appl. Phys. Lett. (2016). https://doi.org/10.1063/1.4962893

20. Rezvani, S.J., Pinto, N., Enrico, E., D’Ortenzio, L., Chiadoni, A., Boarino, L.: Thermally activated tunneling in porous silicon nanowires with embedded Si quantum dots. J. Phys. D. Appl. Phys. (2016). https://doi.org/10.1088/0022-3727/49/10/105104

21. Lee, S., Meyer, T.L., Sohn, C., Lee, D., Hellings, N., Lee, D., Seo, H.N., Noh, T.W., Lee, H.N.: Electronic structure and insulating gap in epitaxial VO₂ polymorphs. APL Mater. (2015). https://doi.org/10.1063/1.4939004

22. Aetukuri, N.B., Gray, A.X., Drouard, M., Cossale, M., Gao, L., Reid, A.H., Kukreja, R., Oldagi, H., Jenkins, C.A., Arenholz, E., Roche, K.P., Dür, H.A., Samant, M.G., Parkin, S.S.P.: Control of the metal-insulator transition in vanadium dioxide by modifying
orbital occupancy. Nat. Phys. (2013). https://doi.org/10.1038/nphys2733

23. Fan, L.L., Chen, S., Luo, Z.L., Liu, Q.H., Wu, Y.F., Song, L., Ji, D.X., Wang, P., Chu, W.S., Gao, C., Zou, C.W., Wu, Z.Y.: Strain dynamics of ultrathin VO2 film grown on TiO2 (001) and the associated phase transition modulation. Nano Lett. (2014). https://doi.org/10.1021/nl501480f

24. Bianconi, A. Surface X-ray absorption spectroscopy: surface EXAFS and surface XANES. Applications of Surface Science, 6(3–4), 392–418. (1980). https://doi.org/10.1016/0378-5963(80)90024-0

25. Bianconi, A., De Santis, M., Flank, et al. Determination of the symmetry of the 3d9 Laz state by polarized Cu L3 XAS spectra of single crystal YBa2Cu3O≈6.9. Physica C: Superconductivity, 153, 1760–1761. (1988). https://doi.org/10.1016/0921-4534(88)90469-8

26. Agrestini, S., Di Castro, D., Sansone, M., et al.: High Tc superconductivity in a critical range of micro-strain and charge density in diborides. J. Phys. Condens. Matter. 13(50), 11689 (2001). https://doi.org/10.1088/0953-8984/13/50/328

27. Agrestini, S., Saini, N.L., Bianconi, G., Bianconi, A.: The strain of CuO2 lattice: the second variable for the phase diagram of cuprate perovskites. J. Phys. A Math. Gen. 36(35), 9133 (2003). https://doi.org/10.1088/0305-4470/36/35/302

28. Agrestini, S., Metallo, C., Filippi, M., et al.: Substitution of Sc for Mg in MgB2: effects on transition temperature and Kohn anomaly. Phys. Rev. B. 70(13), 134514 (2004). https://doi.org/10.1103/PhysRevB.70.134514

29. Costantini, R., Stredansky, M., Cvetko, D., Kladnik, G., Verdini, A., Sigalotti, P., Cilento, F., Salvador, F., De Luisa, A., Benedetti, D., Floreano, L., Morgante, A., Cossaro, A., Dell’Angela, M.: ANCHOR-SUNDYN: a novel endstation for time resolved spectroscopy at the ALOISA beamline. J. Electron Spectros. Relat. Phenomena. (2018). https://doi.org/10.1016/j.elspec.2018.09.005

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