Interplay between electronic correlations and coherent structural dynamics during the monoclinic insulator-to-rutile metal phase transition in VO$_2$

H Dachraoui$^1$, N Müller$^1$, G Obermeier$^2$, C Oberer$^1$, S Horn$^2$ and U Heinzmann$^1$

$^1$Molecular and Surface Physics, Faculty of Physics, Bielefeld University, Germany
$^2$Experimental Physics II, Institute of Physics, University of Augsburg, Germany

E-mail: dachraoui@physik.uni-bielefeld.de

Received 22 July 2011, in final form 16 September 2011
Published 13 October 2011
Online at stacks.iop.org/JPhysCM/23/435402

Abstract

We report direct observations of the structural and electronic dynamics of the photoinduced insulator–metal transition in VO$_2$, by means of time-resolved photoemission spectroscopy. These observations provide new insights into the processes involved in this transition. Slightly above the threshold of the photoinduced phase transition, the different response times of the electrons and the lattice reveal the electronic nature of the band gap collapse. At high excitation densities, we find that the phase transition is induced nonthermally in an ultrashort time scale. Moreover, we identify different V 3p dynamics indicating the existence of different structural pathways. These results represent a clear demonstration of the potential of time-resolved core level photoelectron spectroscopy to study ultrafast dynamics in condensed matter.

1. Introduction

Materials exhibiting photoinduced transitions from an insulating to a metallic phase (IMT) are attractive candidates for ultrafast electrooptic applications because of the significant changes in the resistivity and extremely fast optical switching upon the transition [1, 2]. Vanadium dioxide (VO$_2$) is one example of these complex solids with strongly correlated electron systems: it undergoes an insulator–metal transition when heated above 340 K [3]. The IMT is characterized by a crystal structure change from the low-temperature monoclinic phase (M1) to the high-temperature tetragonal phase (R). On cooling, the monoclinic distortion of the R phase involves a pairing of vanadium ions along the rutile c-axis and a structural twist.

Two major mechanisms have been proposed to describe the phase transition in VO$_2$: Peierls [4] and Mott–Hubbard mechanisms [5, 6]. While a Mott insulator is caused by the breakdown of a strongly correlated critical electron Coulomb interaction, the electronic gap of a Peierls insulator arises from a periodic distortion of the lattice. Time-resolved studies of the photoinduced phase transition in VO$_2$ have promised insight into its origin and its technological potential. Ultrafast optical [9, 8], x-ray diffraction [10, 11], x-ray absorption [12] and terahertz [13] experiments on this compound have demonstrated that both electron–electron correlations and structural arrangements are needed for the collapse of the band gap.

However, the exact electron–lattice interplay across the photoinduced IMT is still a subject of considerable debate and of particular significance is the question of whether this transition is driven directly by the excited electrons or by the subsequent structural arrangements of the lattice. A conclusive answer to this question requires tools that probe the lattice and the electronic structure, and capture the whole evolution including all nonequilibrium intermediate states on the relevant time scales. Time-resolved photoemission spectroscopy offers the promise of exactly...
this kind of measurement [14]. In this paper, we present the first time-resolved core level photoemission study of the photoinduced phase transition in VO$_2$. We use EUV pulses to follow the temporal evolution of the V 3p core level and the hybridized V d–O p electronic bands near the Fermi level after an impulsive near infrared excitation. We show that the breakdown of the electronic energy gap arises from a purely electronic process. Analyzing the V 3p response as a function of pump fluence we identify different V 3p dynamics indicating the existence of two structural pathways. Moreover, the transition from monoclinic to rutile structure is induced in either sub-picosecond or picosecond time scale. We propose a qualitative model explaining the dynamics.

2. Experiment

A schematic overview of our experimental setup is shown in figure 1(A). The EUV and IR beams are generated using an amplified titanium–sapphire laser system that provides intense light pulses (10 mJ pulse energy), at a wavelength of 804 nm, with a repetition rate of 50 Hz and a pulse duration of τ = 50 fs. A monochromator based on Si:Mo multilayer mirrors of small bandwidth is used to spectrally select only the 63rd harmonic order at a photon energy of 95 eV (13 nm wavelength). The kinetic energy of the photoemitted electrons from the sample is energy-analyzed by a time-of-flight spectrometer (for details see [14]). Here it should be noted that the V 3p line shape is determined by the instrumental resolution (0.7 eV due to the TOF resolution and EUV bandwidth). Polycrystalline vanadium dioxide thin films (500 nm) on SiO$_2$ substrate were prepared by ion beam assisted deposition. The crystalline structure and stoichiometry of the films was measured by x-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX).

3. Results

Characteristic electron spectra of VO$_2$ thin films obtained with our system are shown in figure 1(C). The spectra recorded for EUV-probe excitation preceding the IR-pump pulse (black squares) and without IR-pump excitation (red circles) coincide, indicating that our measurements are not affected by a trivial charging-up effect. As described in [15], the VB structure consists of states strongly mixed between V 3d and O 2p orbitals. The V 3d part is dominant near the Fermi level (1–4 eV), and the O 2p part between 3 and 12 eV [16]. At a binding energy of about 39 eV we detect the V 3p core level to lower binding energy. (ii) A shift (0 ±0.05 eV) of the V 3p core level to lower binding energy. (iii) The small spectral weight of the O 2p band (around 3–8 eV). This transient change of the valence band shape, precisely the O 2p band (around 3–8 eV). This transient change confirms that the spectral changes across the IMT are due to intrinsic effects. (iii) The small spectral weight of the leading edge of the VB moves toward the Fermi level providing a direct picture of the collapse of the electronic gap in VO$_2$. (iv) Hot electrons are observed above the Fermi level. In this regime, the system is pushed to an extremely nonequilibrated hot electron metal phase. Already at 1 ps after

This energy is relatively large compared to the energy scale of the transition temperature $T_{IMT}$ (∼30 meV). This indicates that the monoclinic insulator-to-rutile metal phase transition cannot be described within the framework of a Mott mechanism.

Figure 3(A) displays V 3p and VB photoelectron spectra (PES), for various time delays between the IR-pump and the EUV-probe pulses and at a laser pump fluence of $F = 10$ mJ cm$^{-2}$. Negative time delay corresponds to the EUV-probe pulse preceding the IR-pump pulse. At a time delay of around 0 ps, the photoelectron spectrum is characterized by four new features. (i) A shift (0.71 ±0.05 eV) of the V 3p core level to lower binding energy. (ii) A pronounced change of the valence band shape, precisely the O 2p band (around 3–8 eV). This transient change confirms that the spectral changes across the IMT are due to intrinsic effects. (iii) The small spectral weight of the leading edge of the VB moves toward the Fermi level providing a direct picture of the collapse of the electronic gap in VO$_2$. (iv) Hot electrons are observed above the Fermi level. In this regime, the system is pushed to an extremely nonequilibrated hot electron metal phase. Already at 1 ps after
Figure 2. (A) The squares show the temperature dependence of the V 3p core level binding energy across the insulator–metal transition. The solid lines are guides to the eye. The IMT exhibits hysteretic behavior between the two thermodynamically stable structures. (B) Crystal structures of the monoclinic, low-temperature phase and the rutile, high-temperature phase.

Figure 3. (A) Photoelectron spectra acquired at different delays and for a laser fluence of $F = 10 \text{ mJ cm}^{-2}$. The data points show the detected V 3p peak and the hybridized V d–O p electronic bands with statistical errors after subtraction of the background. The dashed lines are the Gaussian fitting curves. The solid lines are guides to the eye. The arrow indicates the nonthermalized hot electrons. The vertical dashed lines indicate the position of the V 3p in the spectra recorded at 0.5 ps. (B) Illustration of the photoinduced Mott–Hubbard insulator–metal transition in VO$_2$. As expected from the theory [20], across the IMT V 3d spectral weight transfer from the incoherent Hubbard bands (at 1 and 4 eV) to the coherent band at the Fermi level leads to the collapse of the electronic gap.

the pump excitation the hot electron distribution thermalizes (via electron–electron collisions), establishing the valency of the equilibrium metallic phase. In addition, the V 3p core level moves back by 0.2 eV compared to the 0.5 ps spectrum. At subsequent delays, as illustrated in figure 1(A), right, the VB shape and spectral position of the 3p core level are similar to those of the previous case. Thus the V 3p transient shift and the VB change are longer living since the system thermalizes...
Figure 4. (A) Center of the vanadium V 3p line after fitting the spectra as a function of the pump probe delay for various fluences (5 mJ cm$^{-2}$, two different measurements). The error bars represent the 2σ confidence interval of the fit. (B), (C) Photoelectron spectra acquired at different delays: $F = 7$ mJ cm$^{-2}$ (B) and $F = 5$ mJ cm$^{-2}$ (C). The squares show the detected V 3p and VB. The dashed lines show the Gaussian fitting curve. The solid lines are guides to the eye. (D) Mott–Hubbard dynamics deduced by integration of the photoelectron spectrum change (obtained after subtraction of the spectrum recorded at a time delay of $-2$ ps) between 0 and 4 eV for two different measurements.

Figure 5. Illustration of the photoinduced nonequilibrium metal state (NMS) and of the possible transitional structures during the ultrafast phase transformation. The arrows show the directions of the displacements of the V ions. The V sublattice of the initial monoclinic (rutile) phase is depicted by dashed lines and filled circles (solid lines and open circles). (A) High excitation densities, the transition is characterized by stepwise atomic motions: femtosecond dilation of V–V (the purple arrow) followed by sub-picosecond rearrangements (the green arrow). (B) The situation at a laser fluence of $F = 7$ mJ cm$^{-2}$: nonequilibrium transition to the conducting state, accompanied by a sub-picosecond rearrangement of the atomic structure (the red arrow): direct structural transition. (C) Moderate excitation ($F = 5$ mJ cm$^{-2}$): the transition is characterized by picosecond direct transition (the primary excitation is different from the one in (B)).
into the equilibrium metallic state. The spectral shape of the VB (4–10 eV) across the IMT is consistent with previous static PES measurements [20].

As mentioned above, in the low binding-energy region (0–4 eV), one observes a small shift of the VB-edge toward the Fermi level pointing to the significant role played by Mott–Hubbard transition (MHT), as predicted by theory [20] and shown in figure 3(B). Furthermore, the spectral weight transfer in the energy region (5–8 eV) provides experimental hints for the charge transfer (CT) between the O 2p band and the upper Hubbard band. This observation is consistent with theoretical predictions [20] that the metallic state configuration has a mixed character (MH + CT) state.

An explanation of the observed V 3p shift in terms of CT between the O²⁻ anion and the V⁴⁺ cation is ruled out for the following reason: photoexcitation into the hybridized π band transiently diminishes the electron density in the valence shell of V⁴⁺, which would result in a shift of the V 3p core level toward higher binding energy. This is clearly not the case here.

Hence, we attribute this shift to an atomic motion [11]. These results reveal that at about 2 ps the system reaches a quasi-equilibrium rutile metal phase. The transient shift occurs before a thermal energy distribution of the lattice is established, indicating the nonthermal nature of this transition. Our observations are consistent with previous time-resolved terahertz [13], x-ray diffraction [10] and x-ray absorption [12] experiments on polycrystalline vanadium dioxide thin films. These measurements showed that rapid femtosecond ion motion leads to the high-temperature R phase. Although the nonequilibrium nature of the insulator–metal transition had been proposed previously, it is directly revealed by our VB measurements reported herein. We will return to this crucial point below. Further, these measurements enable us to show directly in the time domain that the band gap collapse is due to electron correlations rather than electron–phonon scattering.

In order to check how far the IMT in VO₂ is affected by the population distribution of electrons within the conduction bands, we repeated our measurement for different excitation fluences. Figure 4(A) displays the ultrafast dynamics of the V 3p core level shift, for different pump fluences of 5, 7, and 15 mJ cm⁻² including the 10 mJ cm⁻² measurement. A 5 mJ cm⁻² threshold was obtained by comparing the measured spectra recorded for IR-pump excitation preceding the pulse EUV probe with EUV-only spectra. The threshold is here defined as the minimum fluence required to induce the phase transition. It is well known that the photoinduced phase transition threshold is sensitive to particle size, sample quality, and the initial temperature of the material. The threshold for a thinner layer of material is likely to be lower than the 6 mJ cm⁻² measured in crystalline vanadium dioxide; our fluence and sample condition are similar to those of Kübler et al [13].

The spectral position of V 3p is determined using a Gaussian fit as presented in figure 4(A). At high excitation (≥10 mJ cm⁻²), a strong shift of about 0.7 eV relative to the unperturbed system is present at short times and then recovers partially to the new equilibrium value of 0.47 eV with a time constant of about ~0.5 ps. Above 10 mJ cm⁻² the shift of the V 3p core level is independent of the excitation level.

What is the nature of the observed fast shift of 0.7 eV? We know that the thermal induced core level shifts by about 0.5 eV when going from the insulator to the metal phase. In addition the shift occurs in the first 10 fs and cannot be attributed to the rutile phase transition [11, 10]. From these results of the ultrafast valence band and core level dynamics, the following picture is provided (figure 5(A)). For excitations above a critical fluence a high carrier density is produced. As a result the electronic configuration of the V–V homopolar bonds acquires a strongly repulsive character, causing them to break along the bond direction at a time scale of ~100 fs. The impulsive depairing of the vanadium ions results in strong perturbation of the potential energy surface, which is monitored by the instantaneous 0.7 eV shift of the V 3p core level (first step). As a second step, the change in electronic structure results in a force on the lattice. The lattice responds and the atoms move toward the rutile structure. A metastable rutile phase is formed, which is described in terms of the 0.4 eV shift of the core level. Thus in this case, the phase transition is driven by an impulsive change in the potential energy surface. If we ignore the differences in transition times, the indirect pathway in this regime is consistent with the stepwise atomic motions observed in previous time-resolved diffraction measurements, where the V–V bond dilation is the initial step [11].

For $F = 7 \text{ mJ cm}^{-2}$ (figure 4(B)), the shift of the V 3p exhibits a sub-ps rise time (~0.2 ps). In this regime, the rutile phase occurs also too fast to be accounted for by inertial motion, consistent with a repulsive potential picture. Moreover, the results shown for the observed shift of the V 3p core level indicate a direct atomic motion toward the rutile phase, in contrast to the high excitation case where a stepwise atomic motion is observed (V–V separation followed by a structural arrangement). This interpretation is depicted schematically in figure 5(B). Further, we find no evidence of a high density of hot electrons, indicating that the situation is not similar to the nonthermal melting of several semiconductors [21, 22], in which the transition requires critical carrier density. Owing to the low excitation level, we recognize the sudden change of the lattice potential to MHT.

Decreasing the laser fluence to 5 mJ cm⁻² (figure 4(C)), the V 3p core level energy begins to move progressively to lower binding energy and reaches a metastable metal state with a time constant of about ~0.8 ps, which is roughly estimated from an exponential fit function, while the VB dynamics shows no clear laser fluence dependence. Besides the ultrafast collapse of the M1 phase (figure 4(D)), immediately after the excitation a strong spectral change is observed at 3–10 eV. The onset of the VB change and V 3p shift exhibit different temporal behaviors. This decoupling represents clear evidence that the MHT and the metal rutile phase do not occur simultaneously. This indicates that the system becomes metallic from the disruption of electron...
correlations. The Mott–Hubbard nature of the band gap collapse in VO$_2$ which had been predicted by theory [20] but not confirmed by prior experiment has been supported now by the present experiment. Because of the relatively large time constant ($\sim$1 ps) and the intrinsic coupling between the structural and electronic degrees of freedom in VO$_2$ (where high electron–phonon coupling is expected), it is not clear in this regime whether the motion is driven by potential changes [12, 10, 13] or directly through electronic relaxation (via electron–phonon thermalization) [11] (see figure 5(C)). The current experimental data cannot resolve this issue, which represents an important question for future studies.

4. Conclusions

In conclusion, EUV spectroscopy enabled us to observe dramatic changes in the valence band and a core level shift across the insulator–metal transition of VO$_2$. These changes therefore establish that the monoclinic–rutile transition in VO$_2$ involves both electron–electron correlations and structural rearrangement. At moderate excitation fluences the different response times of electronic and lattice excitation show that the band gap collapse is due to Mott–Hubbard physics. For excitation above a critical fluence ($7 \text{ mJ cm}^{-2}$) our results show that the redistribution of the valence electron population alters the potential energy surface of the lattice and gives rise to a restoring force which drives the atomic motion, supporting a nonthermal picture. Moreover, in the high carrier density regime the observed sequence of structural transition with V–V bond dilation as the initial step indicates the existence of different structural pathways: direct and nondirect transition. The present data answer a standing question on the IMT in VO$_2$ and further demonstrate the potential of time-resolved electron spectroscopy to study light induced processes in complex materials.

Acknowledgments

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 613) and the discussion with V Eyert and W Pfeiffer.

References

[1] Cilento et al 2010 Appl. Phys. Lett. 96 021102
[2] Jin P, Yoshimura K and Tanemura S 1997 J. Vac. Sci. Technol. A 15 1113
[3] Morin F J 1959 Phys. Rev. Lett. 3 34
[4] Wentzcovitch R M, Schulz W W and Allen P B 1994 Phys. Rev. Lett. 72 3389
[5] Paquet D and Leroux-Hugon P 1980 Phys. Rev. B 22 5284
[6] Rice T M, Launois H and Pouget J P 1994 Phys. Rev. Lett. 73 3042
[7] Ladd L A and Paul W 1969 Solid State Commun. 7 425
[8] Kim H-T, Lee Y W, Kim B-J, Chae B-G, Yun S J, Kang K-Y, Han K-J, Lee K-J and Lim Y-S 2006 Phys. Rev. Lett. 97 266401
[9] Becker M F et al 1994 Appl. Phys. Lett. 65 1507
[10] Cavalleri A et al 2001 Phys. Rev. Lett. 87 237401
[11] Baum P, Yang D S and Zewail A H 2007 Science 318 788
[12] Cavalleri A et al 2005 Phys. Rev. Lett. 95 067405
[13] Kübler C et al 2007 Phys. Rev. Lett. 99 116401
[14] Dachraoui H et al 2011 Phys. Rev. Lett. 106 107401
[15] Shin S et al 1990 Phys. Rev. B 41 4993
[16] Koethe T C et al 2006 Phys. Rev. Lett. 97 116402
[17] Cavalleri A, Dekorsy T, Chong H H W, Kieffer J C and Schoenlein R W 2004 Phys. Rev. B 70 161102
[18] Biermann S, Poteryaev A, Lichtenstein A I and Georges A 2005 Phys. Rev. Lett. 94 026404
[19] Suga S et al 2009 New J. Phys. 11 103015
[20] Eguchi R et al 2008 Phys. Rev. B 78 075115
[21] Rousse A et al 2001 Nature 410 65
[22] Lindenberg A M et al 2005 Science 308 392