Title	Photo-induced lattice softening of excited-state VO2
Author(s)	Hada, Masaki; Okimura, Kunio; Matsuo, Jiro
Citation	APPLIED PHYSICS LETTERS (2011), 99(5)
Issue Date	2011-08-01
URL	http://hdl.handle.net/2433/160635
Right	Copyright 2011 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in APPLIED PHYSICS LETTERS 99, 051903 (2011) and may be found at http://link.aip.org/link/?apl/99/051903
Type	Journal Article
Textversion	publisher

AIP | Applied Physics Letters

Photo-induced lattice softening of excited-state VO2

Masaki Hada, Kunio Okimura, and Jiro Matsuo

Citation: Appl. Phys. Lett. **99**, 051903 (2011); doi: 10.1063/1.3621900
View online: http://dx.doi.org/10.1063/1.3621900
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i5
Published by the American Institute of Physics.

Photo-induced lattice softening of excited-state VO_2

Masaki Hada,[1,a),b)] Kunio Okimura,[2] and Jiro Matsuo[1,c)]
[1]*Quantum Science and Engineering Center, Kyoto University, Uji 611-0011, Japan*
[2]*Faculty of Engineering, Tokai University, Hiratsuka, Kanagawa 259-1292, Japan*

(Received 6 June 2011; accepted 14 July 2011; published online 1 August 2011)

In this letter, we demonstrated the photoexcitation of metallic phase vanadium dioxide (VO_2) with time-resolved x-ray diffraction measurements. Through the photoexcitation, the metallic phase VO_2 transitioned to the similar transient state, which was presented in the insulator to metal phase transition in the time-scale of ~10 ps. This transient state was accessed only by the photoexcitation and not through further thermal excitation. The presence of the transient state could be an important factor in any further application of the phase transition phenomena. © *2011 American Institute of Physics*. [doi:10.1063/1.3621900]

The metal–insulator transition in vanadium dioxide (VO_2) has potential applications for switching devices, actuators, and memories and has received considerable attention in fundamental studies on phase transitions.[1,2] Recent progress in femtosecond time-resolved techniques enabled the observation of phase transition phenomena by inducing a photonic excitation in the femtoseconds-to-picoseconds time-scale. Several studies on time-resolved optical,[3] teraherz,[4] soft x-ray spectroscopic,[5] and crystallographic[6,7] measurements have revealed the dynamics of phase transitions in these materials. In particular, ultrafast time-resolved x-ray diffraction (XRD) and electron diffraction enables direct observation of atomic motion during the phase transition. We used time-resolved XRD to observe the photo-induced structural phase transition in an epitaxially grown VO_2 thin film.

At the critical temperature (T_c) of ~340 K,[8] VO_2 undergoes a metal-to-insulator transition. This change in electrical properties is accompanied by a structural transition from a monoclinic phase (the M-phase) below T_c to a metallic rutile phase (the R-phase) above T_c. Previous studies have indicated an intermediate or transient state of VO_2 between the M and R phases. This is considered to be a deformed monoclinic[9] or vibronic excited state.[10,11] VO_2 is photoexcited to the transient state within 1–10 ps; the M-phase lattice rapidly transforms into the R-phase structure. However, the atoms in the unit cell and, the unit cell itself, become disordered or vibrate around the center of the rutile coordinates, and the excited state is abated by coupling with an isotropic thermal phonon within ~100 ps. In this paper, we report the observation of a similar transient state formed by photoexcitation of the thermally excited R-phase VO_2 in the time scale of ~10 ps.

A highly (010)-oriented VO_2 film (280 nm thick) was epitaxially grown on a c-Al_2O_3 (0001) substrate at a temperature of 673 K.[12,13] The lattice parameters of VO_2 in the M and R phases were measured using static XRD with Cu Kα X-ray radiation ($\lambda = 0.154$ nm) and were found to be $a = 0.5759$ nm, $b = 0.4518$ nm, $c = 0.5363$ nm, $\beta = 122.3°$ (space group: $P2_1/C$),[14] and $a = b = 0.4528$ nm, $c = 0.2860$ nm (space group: $P4_2/mnm$),[15] respectively. The Bragg angles of the (020) plane in the M and R phases were 39.86° and 39.77°, respectively. The integrated intensity increased by a factor of 1.3–1.6 in the phase transition. The critical heating temperature was 339 K.

The time-resolved XRD measurements were performed in air using a laser plasma-induced x-ray source of Cu Kα_1 and Kα_2 radiations at 1 kHz, which were generated by focusing a millijoule femtosecond laser onto a rotating copper target in He ambient. The experimental setup is shown in detail in Ref. 11. The VO_2 sample was loaded onto a thermal heater which was maintained in the temperature range of 322–372 K. The VO_2 film was photoexcited using an 800-nm-wavelength femtosecond optical pulse. The area excited by the optical pulse had an ellipsoidal shape of 1.9×2.2 mm and was larger than the x-ray-probed area (0.8 mm horizontal and 1.5 mm vertical). The intensity of the pumping pulse was 8.5 mJ/cm^2 (~1.6×10^{21} carriers/cm^3), which was higher than the phase transition threshold (6–7 mJ/cm^2),[6,7] but much lower than the single-shot damage threshold (63 mJ/cm^2).[6]

Typical Kα_1 and Kα_2 XRD lines from VO_2 (020) planes at 322 K and 372 K were obtained in time delays from −50 to 300 ps (Figs. 1(a) and 1(b)). XRD lines in the negative delay time agreed well with the lines from the unperturbed M and R phases. For the positive delay times, the XRD lines showed a shift in the Bragg angle, increase or decrease in intensity, and broadening of the full width at half-maximum (FWHM). Figure 2 shows the changes in the integrated intensity of the diffraction lines as a function of delay time in the temperature range 322–372 K. The Bragg peak position, integrated intensity, and FWHM were derived from the double-peak Gaussian fitting curve. The states of VO_2 at these temperatures corresponded to the M (322 K) and R phases (341 and 372 K), respectively. Generally, the Bragg peak position of XRD lines depends on the Laue function, i.e., the size of the unit cell, and the integrated intensity depends on the positions or the ordering of the atoms in the unit cell. At all temperatures, the Bragg angles of the XRD shifted toward lower angles within about 25 ps. The integrated intensities of the XRD lines at 322 and 338 K decreased by 70%–80% in about 15 ps and gradually increased by about 1.1–1.4 times in ~100 ps (Fig. 2).

[a)]Electronic mail: masaki.hada@mpsd.cfel.de.
[b)]Present address: Max Planck Research Department for Structural Dynamics at the University of Hamburg, Center for Free Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany.
[c)]Electronic mail: matsuo@nucleng.kyoto-u.ac.jp.

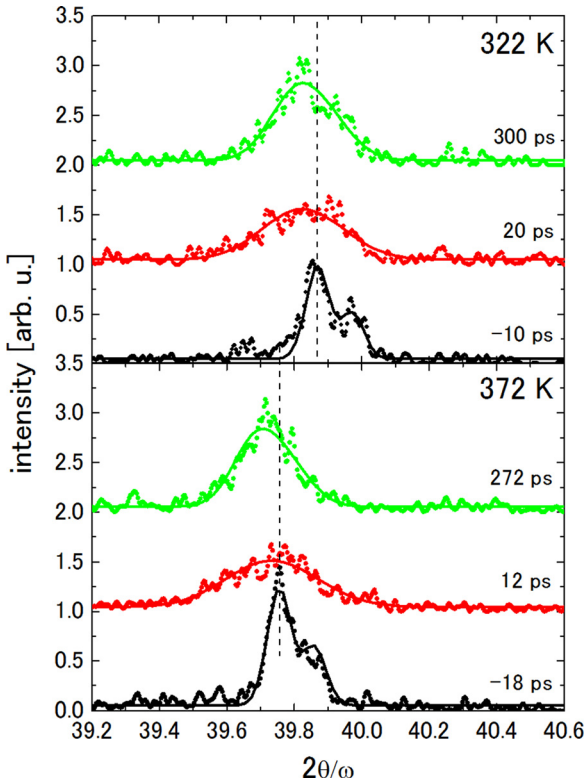

FIG. 1. (Color online) Typical spectra of time-resolved XRD lines from the (020) plane of VO_2 sample at (a) 322 K and (b) 372 K. The solid lines are double-peak Gaussian fitting curves. The vertical broken lines indicate the Bragg angles for a negative delay time.

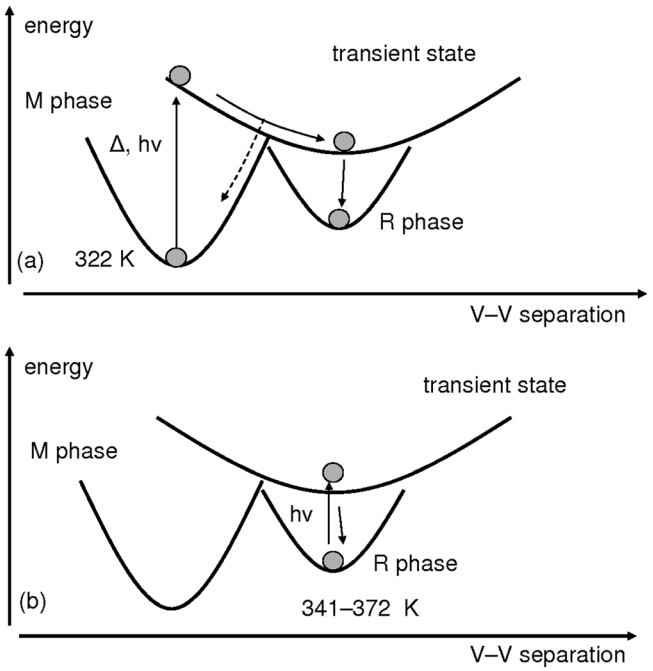

FIG. 3. Schematic diagrams of (a) the insulator-to-metal phase transition of VO_2: the M-phase transitions to R-phase by photo and thermal excitation through transient state (solid lines). When the excitation energy is lower than the phase transition threshold, VO_2 cannot transform from M-phase to R-phase (broken line); (b) photo-induced softening of the metal phase VO_2. The transient state can be accessed from R-phase by photoexcitation. The y-axes are energy and x-axes are the V–V separation of (010) lattice plane.

The changes in XRD lines at the temperatures of 322 and 338 K were indicative of the insulator-to-metal phase transition in VO_2; the Bragg angle was higher ($2\theta = 39.86$–$39.82°$) for the negative delay time and shifted toward a lower angle ($2\theta = 39.78$–$39.75°$) at 25 ps after photoexcitation. The integrated intensity of the XRD lines decreased in the delay time of ~15 ps and increased in ~100 ps. The decrease in integrated intensity in ~15 ps suggested the transient state of VO_2, i.e., disordering or fluctuation of the V atoms around the rutile coordinates would result in a reduced integrated intensity of the XRD lines. This transient state would gradually decay and transform into the R-phase in ~100 ps (Ref. 11). The schematic view of the metal–insulator phase transition of the VO_2 thin film (see Fig. 3(a)) was consistent with previously reported results.[9–11] It is noteworthy that the Bragg peak positions and integrated intensities of the XRD lines at 341 and 372 K showed a similar tendency as at 322 and 338 K. The integrated intensity of the XRD lines decreased by photoexcitation in ~15 ps to about 50%, almost the same as the films photoexcited at 322 and 338 K. The structure reverted to the R-phase again in ~100 ps. VO_2 was already in R-phase at the temperatures of 341 and 372 K and should not transform anymore; however, the decrease in integrated intensity suggested disordering or fluctuation of the V atoms around the rutile coordinates, i.e., the thermally excited VO_2 underwent a transformation into the transient state through photoexcitation. The transient state of VO_2 was not achieved by thermal excitation of the R-phase, but by the perturbation of the electron distribution and the electron–lattice interaction in the VO_2,[16] i.e., photoexcitation of a small fraction of electrons produced a large modification in the VO_2 lattice. In the schematic diagram of the photoexcitation of the thermally excited VO_2 film (Fig. 3(b)), the transient state of VO_2 appeared very unstable and the potential surface of the transient state has broadened.

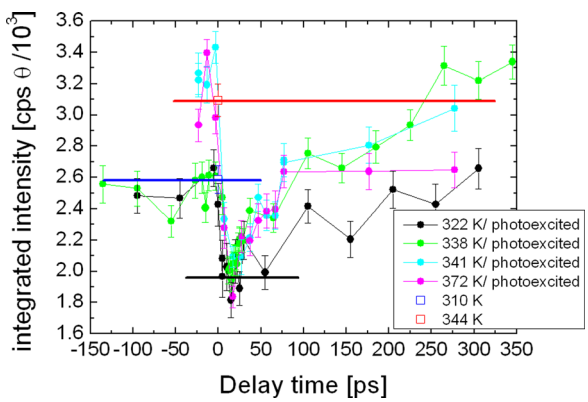

FIG. 2. (Color online) The change in integrated intensity of the (020) XRD lines in temperature range 322–372 K. The horizontal red, blue, and black lines show the integrated intensity of R-phase, M-phase and transient state, respectively.

In conclusion, using time-resolved XRD measurements, we investigated the transient state induced by weak photoexcitation in a VO_2 thin film. VO_2 transformed from the M to the R phase through the transient state within a time scale of a few picoseconds, and a similar transient state was obtained by photoexcitation of the thermally excited R-phase. The transient state of the VO_2 film was related to the electron–electron and electron–lattice interactions. The results also suggest that time-resolved XRD is a promising method for

exploring as-yet-unknown phenomena in various material systems. As a further application, it is interesting to note that because VO_2 can be structurally photo-modulated in the metallic phase, it can be used as an electronic switching device that is controlled optically on the 100 ps time-scale.

This work was partially supported by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency (JST). The authors would like to acknowledge the discussions with Y. Hontani, T. Seki, and T. Aoki at Kyoto University and H. Zia and D. Mazurenko at Max Planck Research Department of Structural Dynamics, and thank R. Manory of editassociates.com for helping in preparing this material for publication.

[1]S. Chen, H. Ma, X. Yi, H. Wang, X. Tao, M. Chen, X. Li, and C. Ke, Infrared Phys. Technol. **45**, 239 (2004).
[2]H. Coy, R. Cabrera, N. Sepúlveda, and F. E. Fernández, J. Appl. Phys. **108**, 113115 (2010).
[3]M. F. Becker, A. B. Buckman, R. M. Walser, T. Lépine, P. Georges, and A. Brun, Appl. Phys. Lett. **65**, 1507 (1994).
[4]C. Kübler, H. Ehrke, R. Huber, R. Lopez, A. Halabica, R. F. Haglund, Jr., and A. Leitenstorfer, Phys. Rev. Lett. **99**, 116401 (2007).
[5]A. Cavalleri, M. Rini, H. H. W. Chong, S. Fourmaux, T. E. Glover, P. A. Heimann, J. C. Kieffer, and R. W. Schoenlein, Phys. Rev. Lett. **95**, 067405 (2005).
[6]A. Cavalleri, Cs. Tóth, C. W. Siders, and J. A. Squier, Phys. Rev. Lett. **87**, 237401 (2001).
[7]P. Baum, D.-S. Yang, and A. H. Zewail, Science **318**, 788 (2007).
[8]F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[9]K. Okimura, J. Sakai, and S. Ramanathan, J. Appl. Phys. **107**, 063503 (2010).
[10]S. Lysenko, A. J. Rua, V. Vikhnin, J. Jimenez, F. Fernandez, and H. Liu, Appl. Surf. Sci. **252**, 5512 (2006).
[11]M. Hada, K. Okimura, and J. Matsuo, Phys. Rev. B **82**, 153401 (2010).
[12]K. Okimura and J. Sakai, Jpn. J. Appl. Phys. **48**, 045504 (2009).
[13]K. Okimura, N. Ezreena, Y. Sasakawa, and J. Sakai, Jpn. J. Appl. Phys. **48**, 065003 (2009).
[14]G. Andersson, Acta Chem. Scand. **10**, 623 (1956).
[15]S. Westman, Acta Chem. Scand. **15**, 217 (1961).
[16]A. Cavalleri, M. Rini, and R. W. Schoenlein, J. Phys. Soc. Jpn. **75**, 011004 (2006).