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Photo-induced lattice softening of excited-state VO$_2$

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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 $\sim$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 $\sim$340 K,[8] VO$_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 $\sim$100 ps. In this paper, we report the observation of a similar transient state formed by photoexcitation of the thermally excited R-phase VO$_2$ in the time scale of $\sim$10 ps.

A highly (010)-oriented VO$_2$ film (280 nm thick) was epitaxially grown on a c-Al$_2$O$_3$ (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 ($\sim 1.6 \times 10^{21}$ 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 $\sim$100 ps (Fig. 2).

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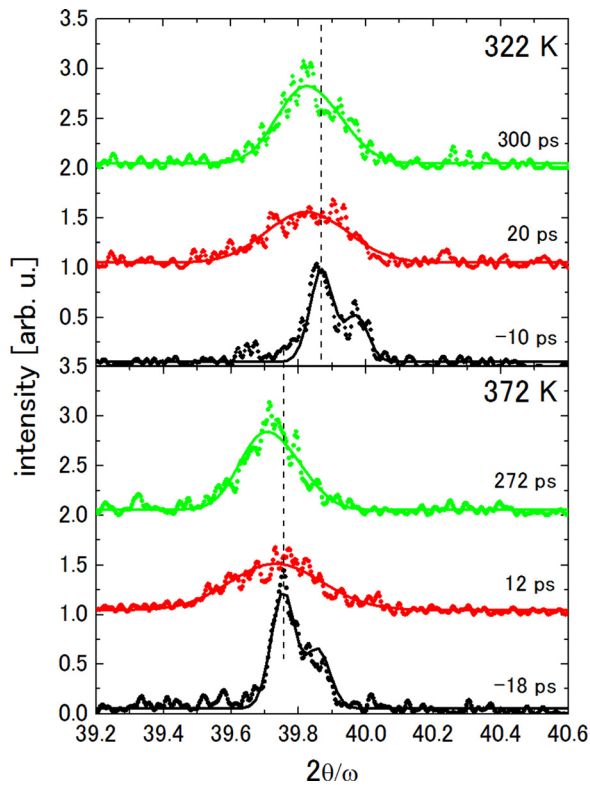c)Electronic mail: matsuo@nucleng.kyoto-u.ac.jp.

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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.

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–insula-
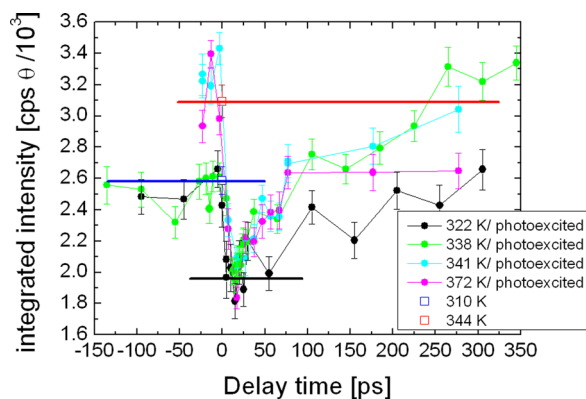

FIG. 2. (Color online) The change in integrated intensity of the (020) XRD lines in temperature range 322–372 K. The horizontal red, blue, and black lines show the integrated intensity of R-phase, M-phase and transient state, respectively.
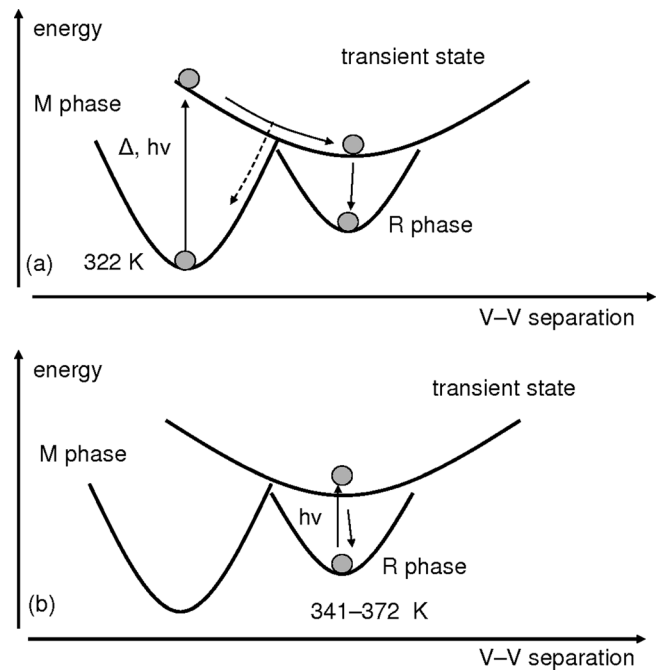

FIG. 3. Schematic diagrams of (a) the insulator-to-metal phase transition of VO$_2$: the M-phase transitions to R-phase by photo and thermal excitation through transient state (solid lines). When the excitation energy is lower than the phase transition threshold, VO$_2$ cannot transform from M-phase 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.

tor 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.

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.

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