Characterization of structural dynamics of \( \text{VO}_2 \) thin film on \( c-\text{Al}_2\text{O}_3 \) using in-air time-resolved x-ray diffraction

Masaki Hada*

Department of Nuclear Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan

Kunio Okimura

Faculty of Engineering, Tokai University, Hiratsuka, Kanagawa 259-1292, Japan

Jiro Matsuo†

Quantum Science and Engineering Center, Kyoto University, Uji, Kyoto 611-0011, Japan

(Received 6 September 2010; published 5 October 2010)

The lattice motion and displacement of atoms in the unit cell in vanadium dioxide (\( \text{VO}_2 \)) grown on \( c-\text{Al}_2\text{O}_3 \) were characterized by static and time-resolved x-ray diffraction (XRD) measurements. The monoclinic-tetragonal phase transition of the \( \text{VO}_2 \) unit cell and the twist motion of vanadium atoms in the unit cell were observed. The time-resolved XRD measurements were performed in air using a tabletop high-repetition femtosecond laser. The results obtained from the time-resolved XRD measurements suggested that the unit cell of the low-temperature monoclinic \( \text{VO}_2 \) transformed into the high-temperature tetragonal phase extremely rapidly (within 25 ps); however, the atoms in the unit cell fluctuated or vibrated about the center of the tetragonal coordinates, which abated within \( \sim 100 \) ps. Thus, the time-resolved XRD measurements of the Bragg angle, intensity, and width of the diffraction lines simultaneously revealed the phase transition of \( \text{VO}_2 \) and the atomic motion in the unit cell.

DOI: 10.1103/PhysRevB.82.153401

PACS number(s): 61.66.–f, 61.05.C--, 63.70.+h

Recently, time-resolved crystallography (x-ray diffraction\(^{1-5} \) and electron diffraction\(^{6-9} \)) has attracted considerable attention for its use in molecular-dynamical studies where it has been used to reveal chemical processes such as phase transitions and coherent phonon vibration in condensed matter. Vanadium dioxide (\( \text{VO}_2 \)) is a representative material that undergoes a metal-insulator phase transition, which occurs at a temperature of \( \sim 340 \) K.\(^{10} \) Several papers on optical,\(^{11-13} \) terahertz,\(^{14,15} \) and soft x-ray\(^{16} \) spectroscopic pump-probe measurements of the phase transition in \( \text{VO}_2 \) have been reported and a few reports on time-resolved crystallography revealed the intriguing nature of the structural dynamics of the phase transition in \( \text{VO}_2 \). A phase transition was observed in a bulk sample by the changes in intensity of x-ray diffraction lines from around the (011) plane\(^{11} \) and in a thin-film sample by the changes in intensity of several electron-diffraction spots.\(^{18} \) In this study, we performed time-resolved x-ray diffraction (XRD) measurements of the photo-induced phase transition in an epitaxial \( \text{VO}_2 \) thin film on \( c-\text{Al}_2\text{O}_3 \). The analysis based on complicated XRD data enabled the separation of the motion in the \( \text{VO}_2 \) film, the lattice unit cells and the atoms in the unit cell, enabling us to directly observe not only the phase transition of the unit cell but also the displacement of atoms in the unit cell at a picosecond time scale. A series of direct structural observations reveals the transition states of the phase-transition materials and it is expected that in the future the mechanism of the photo-induced nonequilibrium process will be clarified.

A highly (010) oriented \( \text{VO}_2 \) film (280 nm thickness) was epitaxially grown on a \( c-\text{Al}_2\text{O}_3 \) (0001) substrate at a temperature of 673 K.\(^{19,20} \) Static out-of-plane and in-plane XRD measurements with \( \text{Cu} K\alpha \) x-ray radiation (\( \lambda=0.154 \) nm) were performed at temperatures of 293 K (low-temperature phase) and 343 K (high-temperature phase) using an x-ray diffractometer. The monoclinic and tetragonal \( \text{VO}_2 \) structures reside in the space groups of \( P2_1/c \) (No. 14) (Ref. 21) and \( P4_2/mnm \) (No. 136),\(^{22} \) respectively. Figure 1 shows the lattice parameters and atomic coordinates determined from the static XRD lines of (020), (040), (200), (022), and (40–2). The lattice parameters were calculated from the Bragg equation and the Bragg angle obtained from results of static XRD measurements. The atomic coordinates in the unit cell were calculated on the basis of Ref. 23 by the computer simulation using CRYSTALMAKER 8.2 with the relative integral intensity of each diffraction line.\(^{24,25} \) The simulation software calculates the Bragg angle and the relative intensity of the diffraction lines from the Bragg equation and Eqs. (1)–(3). These lattice parameters were slightly destorted (0.1–0.5 % for each axis) from those reported for \( \text{VO}_2 \) powder\(^{21-23} \) because of the effect of tension from the substrate.

The static XRD measurement also revealed structure changes in \( \text{VO}_2 \) before and after the transition. The intensity of the diffraction line (\( I \)) can be defined as

![FIG. 1. The lattice parameters and positions of vanadium atoms in the unit cell of the epitaxially grown \( \text{VO}_2 \) thin film.](image-url)
Laue function, crystal-structure factor, atomic-scattering factor, the diffraction line depends on the Laue function
reference, in which $V_1$ and $V_2$ moved.
These results agreed with the relative magnitudes in
dinates shown in Fig. 1. There are four vanadium atoms in a
the atomic positions can be estimated from the atomic coor-
dimensions of the atomic positions in the unit cell. The change in
the crystal structure factor
contrast, the intensity of the diffraction line strongly depends
more specifically, it depends on the size of the unit cell. In
0.09° toward a lower angle in the high-temperature phase as
The typical XRD spectra at time delays of $-50, 25, 100,$
and 250 ps are shown in Fig. 3. As shown in the figure, the
Bragg angle of the diffraction lines was higher for the negative
time delay and it shifted toward a markedly lower angle
as a function of delay time. As shown
FWHM
$17$ and $18$ refs. 17 and 18) and much lower
than the single-shot damage threshold (63 $\text{mJ/cm}^2$).$17$

The typical XRD spectra at time delays of $-50, 25, 100,$
and 250 ps are shown in Fig. 3. As shown in the figure, the
Bragg angle of the diffraction lines was higher for the negative
delay time and it shifted toward a markedly lower angle
at 250 ps. The integral intensity of the diffraction lines was
doubled by through the transition. These changes corre-
sponded well to those observed in the static XRD measure-
ments. The time-resolved XRD measurements enabled us to
obtain information on the disequilibrium state of VO$_2$, i.e.,
the diffraction lines at 25 ps. Figures 4(a)–4(c), which were
derived from Fig. 3, show the changes in the Bragg angle,
integral intensity and full width at half maximum (FWHM)
of the diffraction lines as a function of delay time. As shown
in Figs. 4(a) and 4(b), the Bragg angle of the diffraction lines
shifted toward a lower angle within 25 ps; on the other hand,
With this assumption, the FWHM of the diffraction lines increased by a factor of 2–3 in the first 25 ps then gradually decreased during the following 100 ps; Fig. 4(c)]. The change in the Bragg angle of the diffraction lines suggests that the VO$_2$ monoclinic unit cell transformed into a tetragonal unit cell extremely rapidly (within 25 ps). To analyze the changes in the intensity and FWHM of the diffraction lines, the fluctuation or vibration might be the similar nature observed in the spectroscopic methods.\textsuperscript{13–16} The transition state would be a very complex state involving "phase transition," "photoexcited layer propagation," and "fluctuation or vibration." Cavalleri \textit{et al.}\textsuperscript{17} and Baum \textit{et al.}\textsuperscript{18} showed that the phase transition in VO$_2$ mainly occurs within ~12 ps and by less than 500 fs, respectively, which are consistent with this phase transition time scale of less than 25 ps. Here, it is worth mentioning that in this study the Bragg angle, intensity, and FWHM of the diffraction lines from the (020) plane of the VO$_2$ thin film were measured by stimulatory time-resolved XRD using a tabletop system. The change in Bragg angle occurred at an ultrafast time scale (~10 ps) in short time (less than 25 ps). If the fluctuation in the unit cell was driven by the displaced atoms, which caused the increase in the FWHM of the diffraction lines, the intensity of the diffraction lines should be decreased simultaneously because the atomic fluctuation reduces the intensity of the diffraction lines according to Eq. (3). As shown in Fig. 3 shows, the peak intensity of the diffraction lines at 25 ps was reduced by about half. The fluctuations of the unit cell and atoms in the unit cell are thought to gradually abate by thermal coupling in ~100 ps, which should lead to a decrease in the FWHM of the diffraction lines and an increase in their peak intensity. The fluctuation or vibration might be the similar nature observed in the spectroscopic methods.\textsuperscript{13–16} The transition state would be a very complex state involving "phase transition," "photoexcited layer propagation," and "fluctuation or vibration." Cavalleri \textit{et al.}\textsuperscript{17} and Baum \textit{et al.}\textsuperscript{18} showed that the phase transition in VO$_2$ mainly occurs within ~12 ps and by less than 500 fs, respectively, which are consistent with this phase transition time scale of less than 25 ps. Here, it is worth mentioning that in this study the Bragg angle, intensity, and FWHM of the diffraction lines from the (020) plane of the VO$_2$ thin film were measured by stimulatory time-resolved XRD, which revealed the fluctuation or vibration of the VO$_2$ lattice and the atoms in the unit cell. The time-resolved electron-diffraction measurements revealed a change in the intensity of several diffraction spots with a very high time resolution; however, the displacement of the unit cell of VO$_2$ was ~1.0 pm, therefore the change in the FWHM of the diffraction lines can be calculated to be ~0.03°. The change in Bragg angle of ~0.03° corresponded to ~180 μm on the multichannel plate at the camera length of 300 mm, which is difficult to resolve with electron diffraction measurements because the electron beam size was ~200 μm.\textsuperscript{31} However, the change in Bragg angle of about ~0.1° can be easily resolved with x-ray diffraction measurements. In conclusion, the transition state of a photoexcited VO$_2$ thin film, which appeared only in the extremely fast time scale, was investigated by time-resolved XRD using a tabletop system. The fluctuation or vibration has been observed only in the spectroscopic methods; however, it was observed using more direct XRD measurement with the changes in the intensity and FWHM of the diffraction lines. The photoexcited monoclinic
VO₂ was transmitted into a tetragonal structure rapidly; however, the atoms in the unit cell and the unit cell itself fluctuated or vibrated around the center of the tetragonal coordinates. The atomic fluctuation was coupled with an isotropic thermal phonon and abated in ~100 ps. The photoexcited layer propagation would be a competitive process in this time scale. The results also suggest that the tabletop time-resolved XRD system is a promising tool for laboratory-based molecular-dynamics studies on materials, chemical, and biological systems.

This work was partially supported by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency (JST). The author would like to thank R. Manory of editassociates.com for help with preparing this material for publication.

---

9 hadamasaki@nucleng.kyoto-u.ac.jp
1 matsuo@nucleng.kyoto-u.ac.jp