<table>
<thead>
<tr>
<th>Title</th>
<th>Optically excited near-surface phonons of TiO2 (110) observed by fourth-order coherent Raman spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Nomoto, Tomonori / Sasahara, Akira / Onishi, Hiroshi</td>
</tr>
<tr>
<td>Citation</td>
<td>Journal of Chemical Physics, 131(8):084703</td>
</tr>
<tr>
<td>Issue date</td>
<td>2009-08-24</td>
</tr>
<tr>
<td>Resource Type</td>
<td>Journal Article / 学術雑誌論文</td>
</tr>
<tr>
<td>Resource Version</td>
<td>publisher</td>
</tr>
<tr>
<td>DOI</td>
<td>10.1063/1.3207947</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://www.lib.kobe-u.ac.jp/handle_kernel/90000955">http://www.lib.kobe-u.ac.jp/handle_kernel/90000955</a></td>
</tr>
</tbody>
</table>

Create Date: 2017-04-19
Optically excited near-surface phonons of TiO$_2$ (110) observed by fourth-order coherent Raman spectroscopy

Tomonori Nomoto (野本知理),$^{1,2,a)}$ Akira Sasahara (篠原亮),$^{2,3,b)}$ and Hiroshi Onishi (大西洋)$^{3)}$

$^1$Molecular Photonscience Research Center, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan
$^2$Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, Honmachi, Kawaguchi 332-0012, Japan
$^3$Department of Chemistry, Graduate School of Science, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

(Received 18 May 2009; accepted 30 July 2009; published online 24 August 2009)

We observed the fourth-order and third-order optical responses in the time domain on a TiO$_2$ (110) surface covered with trimethyl acetates. Coherent vibrations assignable to near-surface phonon modes were present at 179, 191, 359, 440, 507, 609, and 823 cm$^{-1}$ in the fourth-order responses. The amplitude and phase of each mode were determined with different azimuths and polarizations of pump and probe light pulses. Vibrational assignments and possible mechanisms to excite the vibrations were discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3207947]

I. INTRODUCTION

Interfaces have different characteristics from the bulk substrates. The loss of the translational symmetry of the crystal causes the depth dependent distribution of vibrational resonance as observed as surface phonon modes. Adsorbed species further affect the surface modes. However, in many cases, the optical responses of an interface are overridden by responses of the bulk because the spatial resolution is limited by the wavelength of the light probe. For reducing the bulk contribution to the signal, several interface-sensitive methods have been developed. For vibrational spectroscopy, high-resolution electron energy loss spectroscopy,$^3$ infrared reflection absorption spectroscopy,$^3$ helium atom scattering,$^4$ and sum frequency generation$^5,6$ are frequently used.

Fourth-order coherent Raman (FR) spectroscopy, which has been developed recently, is a new alternative of interface-selective vibrational spectroscopy.$^7,8,10,12,14,16$ It is an even-order nonlinear optical spectroscopy sensitive to interfaces on centrosymmetric substrates. A merit of FR spectroscopy is that the FR process does not require an infrared light source. The infrared-free measurement of FR spectroscopy enables observation of interfaces buried in media with intense infrared absorption such as water. FR spectra were reported on vacuum-solid,$^7,8$ air-solid,$^{10,15}$ solid-solid,$^9$ air-liquid,$^{12,14,16}$ liquid-liquid,$^{11}$ and liquid-solid interfaces.$^{16,17}$ Another merit of FR spectroscopy is sensitivity to low-frequency vibrations. Using time-domain detection of impulsively excited vibrational coherences with 20 fs pulses, vibrations below 1000 cm$^{-1}$ are observable.

We have examined the fourth-order optical response of a TiO$_2$ (110) surface covered with an organic compound$^{10,15}$ to simulate TiO$_2$-based photocatalysts operated in the air.

II. EXPERIMENTAL

A TiO$_2$ (110) surface was prepared in an ultrahigh vacuum chamber. A one-side polished TiO$_2$ (110) crystal (10 $\times$ 10 $\times$ 0.5 mm$^3$, Shinkosha, Japan) was Ar$^+$-ion sputtered at room temperature and annealed at 1000 K in a vacuum of 1 $\times$ 10$^{-7}$ Pa. The sputter-annealed surface was reduced to be blue in color and presented the (1 $\times$ 1) pattern in low-energy electron diffraction. The TiO$_2$ surface was then exposed to trimethyl acetic acid (CH$_3$)$_3$COOH) vapor at 2 $\times$ 10$^{-5}$ Pa for 60 s at room temperature. A (2 $\times$ 1) pattern was observed on the exposed surface as evidence of a long-range ordered monolayer of trimethyl acetate (TMA). The TMA monolayer terminated with a hydrophobic functional group offers surface stability in the air.$^6,10$ The TMA-covered TiO$_2$ (110) was removed from the vacuum for FR measurements.

Our measurement system is shown in Fig. 1(a). The light source was a noncollinear optical parametric amplifier (NOPA: TOPAS-white, Quantamix) pumped by a Ti:sapphire regenerative amplifier (Hurricane, Spectra Physics, 1 kHz repetition rate). The output of the NOPA (620 nm) was separated into pump and probe pulses. A zero-order quartz half-wave plate was inserted into the pump light path for adjusting the polarization. An optical delay was inserted into the...
focused on the TiO2 surface by a concave mirror. The second harmonic light generated by the probe pulses was fil-
tered with two filters (U330 filter with coating, Asahi Spectra) and detected by a photomultiplier tube (PMT) (H5784-
03, Hamamatsu Photonics). The SH generation of TiO2 surfaces is well studied.18 The reflection of the fundamental probe pulses was simultaneously detected by a photodiode (PD1: S1336-4BQ, Hamamatsu Photonics) coupled with current preamplifiers (LI-76, NF Corporation). PMT and PD1 outputs were integrated by a boxcar integrator (SR245, Stanford Research System) and analog-to-digital converted pulse by pulse (PCI-6251, National Instruments). The pump pulses were modulated at 500 Hz with a synchronous me-
chanical chopper (3501, New Focus), and the signals with pump-on and pump-off were separately accumulated. The pump pulses reflected from VND were monitored by another photodiode (PD2) for determining whether the pump was on or off. The center wavelength of the pulses was 620 nm, and the time width was 25 fs as the cross correlation between the pump and probe pulses on the sample surface. The incident angle of both the pump and probe pulses was 55° from the surface normal with a crossing angle of 2°. Sample orientations were [001] and [110], where (110) and (001) planes bisect the crossing angle of pump and probe pulses. Probe pulses were p-polarized for all measurements, while s and p-polarized pulses were used as pump pulses with each sample orientation [Fig. 1(b)]. The time delay was scanned from −0.3 to 3 ps at a 6 fs step for the [001] and [110] orientations with p-polarized pump excitation ([001]pp and [110]pp each) and from −0.3 to 1.5 ps at a 6 fs step for the [001] and [110] orientations with s-polarized pump excitation ([001]sp and [110]sp). 108 000, 344 000, 238 000, and 206 000 pulses were integrated to obtain the SH and funda-

III. RESULTS

A. Separation of the fourth-order responses from the time-resolved second harmonic intensity

The time profile of the SH intensity of probe pulses for the TMA covered TiO2 (110) of the [001]pp setup is shown in Fig. 2(a). I(2ω)/I0(2ω) is the pumped SH intensity relative to the pump-free SH intensity. The electric field of the observed SH is the summation of the periodically modulated field $E_{\text{mod}}(2\omega, t_d)$ and the nonperiodically modulated field $E_{\text{non}}(2\omega, t_d)$: Because the periodic modulations are generated from pump-induced vibrational coherences, $E_{\text{mod}}$ is ex-
prescribed as the sum of periodic oscillations as

$$E_{\text{mod}}(2\omega, t_d) \propto \chi^{(4)}(t_d)$$

$$\propto \sum_n A_n \exp(i(\omega_n t_d + \varphi_n))\exp(-t_d/T_n),$$  

(1)

where $A_n$, $\omega_n$, $\varphi_n$, $T_n$, and $t_d$ are the amplitude, frequency, phase, dephasing time of each vibrational mode, and time delay of the probe pulse. $\chi^{(4)}$ is the fourth-order response of the interface. The intensity of observed SH is

$$I(2\omega, t_d) \propto |E_{\text{non}}(2\omega, t_d) + E_{\text{mod}}(2\omega, t_d)|^2,$$  

(2)

where $\varphi_{\text{non}}$ represents the relative phase between $E_{\text{mod}}(2\omega, t_d)$ and the local oscillator $E_{\text{non}}(2\omega, t_d)$. When $|E_{\text{mod}}(2\omega, t_d)| \gg |E_{\text{non}}(2\omega, t_d)|$, the modulation amplitude is proportional to the heterodyned oscillatory component, which is

$$E_{\text{non}}(2\omega, t_d)E_{\text{mod}}(2\omega, t_d)\exp(i\varphi_{\text{non}})$$

$$\propto \sum_n A_n \exp(i(\omega_n t_d + \varphi_n + \varphi_{\text{non}}))\exp(-t_d/T_n).$$  

(3)

On one-photon resonant dye solution interfaces, cosine-type oscillation with $\varphi_n+\varphi_{\text{non}}=0°$ is reported.11,12

For obtaining the oscillatory component of the FR sig-
nal, a nonoscillatory decay of the SH intensity was fitted by a mixed function composed of one Gaussian function, one or two Gaussian convoluted exponential functions, and the Gaussian convoluted step function. The last component repres-
ents slow decay over 100 ps. The mixed function repro-
duced the whole nonoscillatory SH time profile well. The obtained time constants of the exponential decay were 160 fs and 1.2 ps with a full width at half maximum (FWHM) of the Gaussian function, 25 fs. The oscillatory FR component to 30 ps, and a Gaussian window function with 1 ps half width at half maximum (HWHM) was multiplied to the data before Fourier transformation. Multiplying the window function corresponds to a convolu-
tion of the FT spectrum with a Gaussian function having a FWHM of 15 cm$^{-1}$. The resulting FT spectrum is shown in Fig. 2(c), and it is essentially the same as the previously reported spectra.10,15 The imaginary part represents sine
components of the oscillation ($\varphi_o + \varphi_{non}=90^\circ$) and the real part represents cosine components of the oscillation ($\varphi_o + \varphi_{non}=0^\circ$).

B. Spectral fitting to the obtained FT spectra

For obtaining the wave number and the phase of vibrational coherences, the spectrum was fitted using the Lorentzian functions

$$ S_{RS}(\omega) = \sum_v \frac{A_v}{(\omega - \omega_v)^2 + \Gamma_v^2} \exp(i\theta_v), $$

where $A_v$, $\omega_v$, $\Gamma_v$, and $\theta_v$ are the amplitude, center wave number, bandwidth, and phase of each mode. The phase is defined as $\theta_v = \varphi_o + \varphi_{non} + 90^\circ$. Five Lorentzian functions were used to reproduce the spectrum. Four are for substantial vibrations of 817, 440, 368, and 179 cm$^{-1}$, while one at 325 cm$^{-1}$ represents the artifact derived from the fitting residue in the time-domain profile. The zero phase ($\theta_v=0$) was initially assumed to minimize the number of fitting parameters. Three bands (817, 440, and 179 cm$^{-1}$) were fitted using $\theta_v=0$, whereas finite phases were necessary for the other two bands to reproduce the observed spectrum. The obtained fitting parameters are shown in Table I(a) and the simulated spectrum is in Fig. 2(c).

The vibrational coherence is also projected on the intensity of the probe light reflected by the surface. $\chi(3)$ governs this optical response. The time-domain profile of reflected probe pulses is shown in Fig. 2(d). $R/R_0$ is the reflection intensity relative to the pump-free intensity. The oscillatory component of $R/R_0$ [Fig. 2(e)] was FT to obtain a $\chi(3)$ spectrum [Fig. 2(f)]. One peak present at 201 cm$^{-1}$ was fitted using Eq. (4) with the parameters in Table II. Structures below 100 cm$^{-1}$ are considered to be artifacts.

C. Azimuth and polarization dependence of the FR responses for TiO$_2$ (110)

The raw SH intensity obtained on the TMA-covered surface of the [110]pp setup is shown in Fig. 2(g). The nonoscillatory component was fitted using a decay constant of 1.7 ps and a Gaussian FWHM of 29 fs. The oscillatory FR component and the FT spectrum are shown in Figs. 2(h) and 2(i). The obtained spectrum was fitted with the parameters in Table I(b). Six Lorentzian functions were required to fit [Table I(c)]. Five substantial bands (827, 507, 443, 365, and 191 cm$^{-1}$) were obtained. The obtained time profile of reflection of the probe pulses for the same sample is shown in Fig. 2(j). The oscillatory component of the reflection intensity and the $\chi(3)$ spectrum are shown in Figs. 2(k) and 2(l) with parameters in Table II. A peak at 607 cm$^{-1}$ was ob-
TABLE I. Fitting parameters of FR spectra of the TiO$_2$ (110) surface covered by TMA with irradiation azimuth to (a) [001] direction with $p$-pump and $p$-probe, (b) [001] direction with $s$-pump and $p$-probe, (c) [1$\bar{1}$0] direction with $p$-pump and $p$-probe, and (d) [1$\bar{1}$0] direction with $s$-pump and $p$-probe.

<table>
<thead>
<tr>
<th>$\omega_0/\text{cm}^{-1}$</th>
<th>$\Gamma_1/\text{cm}^{-1}$</th>
<th>$A_0$</th>
<th>$\theta_0/\text{deg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>817</td>
<td>28</td>
<td>1.4</td>
<td>0 (fixed)</td>
</tr>
<tr>
<td>440</td>
<td>13</td>
<td>0.3</td>
<td>0 (fixed)</td>
</tr>
<tr>
<td>368</td>
<td>9</td>
<td>0.4</td>
<td>15</td>
</tr>
<tr>
<td>179</td>
<td>18</td>
<td>1.3</td>
<td>0 (fixed)</td>
</tr>
<tr>
<td>Baseline</td>
<td>325</td>
<td>449</td>
<td>$-5.6$</td>
</tr>
<tr>
<td>570</td>
<td>201</td>
<td>8.6</td>
<td>31</td>
</tr>
<tr>
<td>609</td>
<td>26</td>
<td>0.2</td>
<td>58</td>
</tr>
<tr>
<td>368</td>
<td>13</td>
<td>0.1</td>
<td>46</td>
</tr>
<tr>
<td>Baseline</td>
<td>554</td>
<td>403</td>
<td>$-0.7$</td>
</tr>
<tr>
<td>827</td>
<td>28</td>
<td>$-4.2$</td>
<td>15</td>
</tr>
<tr>
<td>507</td>
<td>24</td>
<td>0.8</td>
<td>0 (fixed)</td>
</tr>
<tr>
<td>443</td>
<td>17</td>
<td>$-1.4$</td>
<td>33</td>
</tr>
<tr>
<td>365</td>
<td>10</td>
<td>$-0.8$</td>
<td>52</td>
</tr>
<tr>
<td>191</td>
<td>20</td>
<td>$-1.5$</td>
<td>21</td>
</tr>
<tr>
<td>Baseline</td>
<td>570</td>
<td>201</td>
<td>8.6</td>
</tr>
<tr>
<td>823</td>
<td>31</td>
<td>$-1.1$</td>
<td>50</td>
</tr>
<tr>
<td>440</td>
<td>12</td>
<td>$-0.2$</td>
<td>86</td>
</tr>
<tr>
<td>359</td>
<td>14</td>
<td>$-0.5$</td>
<td>110</td>
</tr>
<tr>
<td>Baseline</td>
<td>739</td>
<td>84</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The raw SH intensity obtained with the [001]sp setup is shown in Fig. 2(m). The nonoscillatory component was fitted using decay constants of 60 fs and 1.0 ps with a Gaussian FWHM of 28 fs. A Gaussian window function was multiplied with the oscillatory FR component and then FT. The oscillatory component of the SH intensity and the FT spectrum are shown in Figs. 2(o) and 2(p). The HWHM of the window function was tuned to be 0.5 ps. The SH response pumped with the $s$-polarized pulses was observed up to 1.5 ps. The time width of the window function is appropriate with the 1.5 ps response. As a result, the FT spectrum of Fig. 2(o) was convoluted with a Gaussian function with 30 cm$^{-1}$ FWHM. With the $p$-polarized pump pulses the SH response was traced up to 3 ps, while a wider window function was used.

The obtained spectrum was Lorentzian fitted with the parameters in Table I(b). Four Lorentzian functions were required for fitting and three substantial bands were obtained at 827, 609, and 368 cm$^{-1}$. The raw $R/R_0$, modulated component, and $\chi^{(3)}$ spectrum are shown in Figs. 2(p)–2(r) with the parameters in Table II. A peak at 615 cm$^{-1}$ was observed in the imaginary part.

The raw SH intensity obtained with the [1$\bar{1}$0]sp setup is shown in Fig. 2(s). The oscillatory component was fitted using a decay constant of 2.3 ps and a Gaussian FWHM of 30 fs. The oscillatory FR component of the SH intensity and the FT spectrum are shown in Figs. 2(t) and 2(u). Four Lorentzian functions were required with the parameters in Table I(d). Three substantial bands (823, 440, and 359 cm$^{-1}$) were identified. The $\chi^{(3)}$ response of the surface is shown in Figs. 2(v)–2(x) and Table II. A peak at 614 cm$^{-1}$ was present in the imaginary part.

IV. DISCUSSION

We observed seven phonon modes of TiO$_2$ in the $\chi^{(4)}$ response and two in the $\chi^{(3)}$ spectra. The molecular vibrations of TMA monolayer covering the surface were not observed because no electronic resonance could contribute to $\chi^{(4)}$ process for TMA, which has no absorption in fundamental and SH wavelength. The different numbers of the observed phonons reflect the different selection rules of the $\chi^{(3)}$ and $\chi^{(4)}$ processes. Because $\chi^{(3)}$ response is bulk sensitive, the two $\chi^{(3)}$ modes at 610 and 200 cm$^{-1}$ represent bulk phonons. Lattice dynamics of bulk TiO$_2$ was reported by infrared, Raman, and neutron diffraction with phonon dispersion. Based on the vibrational studies of TiO$_2$ crystals, the mode at 610 cm$^{-1}$ was assigned to a bulk phonon of $A_{1g}$ symmetry. On the other hand, there is no fundamental tone of TiO$_2$ phonons at 200 cm$^{-1}$. An overtone or combination of lower-frequency phonons is a possible origin of this band.

A. Possible excitation mechanisms

It is established with $\chi^{(3)}$ responses that the phase of vibrational coherence is sensitive to the time feature of the driving force. When an impulsive force is present at the time origin, a sine-form coherence is generated. This is typically the case with impulsive stimulated Raman scattering (ISRS) off-resonant to electronic transitions. A cosine-form coherence appears when a steplike force is applied. This is the case in the ISRS process with an electronic resonance when the imaginary part of the Raman tensor dominates coherent phonon generation. There is also a transient depletion field screening (TDFS) and displace excitation of co-
hensive phonon (DECP) (Ref. 25) processes which result in 
cosine-form coherence when the lifetime of the excited 
electrons is much longer than the cycle of coherent phonons. 
In the TDFS and DECP processes, a pump pulse creates the real 
population of electrons in the conduction band and the ion-
to-ion potentials are deformed. Coherent phonons are gener-
ated in the crystal which start to oscillate around new equi-
librium positions. Totally symmetric phonon modes are 
excited in the DECP mechanism while LO phonon modes in 
the depletion layer are excited in the TDFS process by a 
transient change in the electrical surface field. The bandgap 
of rutile is larger than the pump photon energy used in our 
study. The electronic resonance between occupied midgap 
states and the conduction band is needed to enable the reso-
nant ISRS, TDFS, and DECP. The vacuum-prepared rutile 
wafers contain oxygen-atom vacancies accompanied by Ti3+ 
cations. The 4-electrons localized on the Ti3+ ions possibly 
provide occupied midgap states. The occupied midgap states 
derived from the Ti3+ ions also can contribute to the nonoscilla-
tory SH decay components. A trapping of photo-
evoked electrons and a transport of photoexcited holes can 
result in a change in SH efficiency after photoexcitation from 
occupied midgap states to conduction band.

B. Assignment of third-order response

The $\chi^{(3)}$ responses of the $A_{1g}$ phonon mode at 610 cm$^{-1}$ 
were successfully fitted with $\theta_4=0$ in the [001]sp, [110]sp, 
and [110]pp spectra. This indicates that the ISRS process 
excites that mode. The other band at 200 cm$^{-1}$ is rather co-
sinellike with $\theta_4=62$ suggesting some contribution of the 
electronic resonance.

C. Assignment of fourth-order responses

Third-order response is bulk sensitive in rutile with cen-
trosymmetry. On the other hand, fourth-order response is in-
terface sensitive. Here, we estimate the thickness of the sur-
face layer observable by the $\chi^{(4)}$ response. The $\chi^{(4)}$ response 
is produced in a finite portion of the centrosymmetric TiO$_2$ 
medium because of the upward band bending from the bulk 
to the surface. The band bending of the surface depletion 
layer in TiO$_2$ was reported as electric field induced SH inten-
sity dependence in electrochemical treatment. The thick-
ness of the $\chi^{(4)}$-sensitive portion depends on the concentra-
tion of surface electronic states and donor states. The 
observable thickness is practically determined by the escape 
depth of the SH light. By considering the refractive index at 
the SH wavelength, $\kappa=2$ at 310 nm, the observable depth 
is estimated to be 10 nm.

Now we start to assign the seven $\chi^{(4)}$ bands. Rutile bulk 
structure is in $D_{4h}$ symmetry. When a rutile crystal is trun-
cated with a plane perpendicular to the [110] direction, the 
fourfold axis is lost to yield $C_{2v}$ symmetry. Table III shows 
the relationship of the irreducible representation in $D_{4h}$ 
and $C_{2v}$ symmetry groups. The corresponding Raman tensor 
components and pump light polarization in our experiments 
are listed together. Here, the $z$ axis is in the [110] direction 
with $x$ axis parallel to the [001] direction.

The lowest wave number band at 179 cm$^{-1}$ appeared 
only in the [001]pp spectrum with $\theta_4=0$. The zero phase 
suggests the ISRS mechanism in the coherent excitation. The 
irreducible representation only related to the [001]p Raman 
pump is $B_1$ on the surface according to Table III. When a 
bulk phonon is projected to a $B_1$ surface mode, the bulk 
mode should exhibit $A_{2u}$, $B_{2u}$, or $E_u$ symmetry. A transverse 
optical $A_{2u}$ mode [Fig. 3(a)] was found at 167 cm$^{-1}$ in bulk 
rutile with the closest wave number. We thus assign the $\chi^{(4)}$ 
band at 179 cm$^{-1}$ to the $A_{2u}$ (TO) phonon projected on the 
(110) surface. The wave number of the bulk mode shifts by 
+12 cm$^{-1}$ on the surface.

Two $\chi^{(4)}$ bands at 191 and 507 cm$^{-1}$ are assigned in a

![FIG. 3. Atomic displacements of the corresponding bulk phonon modes of the observed surface modes after Ref. 22. (a) $A_{1u}$ (TO: 167 cm$^{-1}$) mode that was observed as $B_1$ at 179 cm$^{-1}$; (b) One of $E_u$ (TO: 183 cm$^{-1}$) modes that corresponds to $B_1$ mode observed at 191 cm$^{-1}$; (c) One of $E_u$ (LO: 373 cm$^{-1}$) modes observed as $A_1$ mode at 359 cm$^{-1}$; (d) One of $E_u$ (LO: 458 cm$^{-1}$) modes observed as $A_1$ mode at 440 cm$^{-1}$; (e) One of $E_u$ (TO: 500 cm$^{-1}$) modes observed as $B_1$ mode at 507 cm$^{-1}$; (f) $A_{1u}$ (612 cm$^{-1}$) mode observed as $A_1$ mode at 609 cm$^{-1}$; (g) One of $E_u$ (LO: 807 cm$^{-1}$) modes.](image-url)
TABLE III. Correspondences of original irreducible representations of $D_{4h}$ (bulk TiO$_2$), irreducible representations of $C_{2v}$ [TiO$_2$ (110) surface], and possible pump polarizations.

<table>
<thead>
<tr>
<th>Original point group $D_{4h}$</th>
<th>$C_{2v}$ transformation properties</th>
<th>Input pulse direction and pump polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}B_{1g}E_{u}$</td>
<td>$A_{1}$ $z[110]$ $x^2,y^2,z^2$</td>
<td>$[001]p(x^2), [001]p(y^2), [110]p(z^2), [110]p(x^2)$</td>
</tr>
<tr>
<td>$A_{1g}B_{1g}E_{u}$</td>
<td>$A_{2}$ $xy$</td>
<td>$[001]p(xz)$</td>
</tr>
<tr>
<td>$A_{2g}B_{2g}E_{u}$</td>
<td>$B_{1}$ $[001]$ $xz$</td>
<td>$[110]p(xz)$</td>
</tr>
<tr>
<td>$A_{2g}B_{2g}E_{u}$</td>
<td>$B_{2}$ $\gamma[110]$ $yz$</td>
<td></td>
</tr>
</tbody>
</table>

similar way. Each mode is related to one of degenerated $E_u$ (TO) mode with $B_2$ symmetry on the surface [Figs. 3(b) and 3(e)]. They are pumped by the ISRS mechanism and the wave number shifts from the bulk to the surface were +8 and +7 cm$^{-1}$, respectively.

A $\chi^{(4)}$ response at 609 cm$^{-1}$ appeared in the [001]sp spectrum. It is related to an $A_{1g}$ bulk phonon at 612 cm$^{-1}$ [Fig. 3(f)] because of the correspondence of wave numbers and the excitation symmetry. This bulk mode is responsible for the $\chi^{(3)}$ response at 610 cm$^{-1}$. The nonzero phase of the $\chi^{(4)}$ response suggests an electronic excitation contributing the coherent excitation. The $A_{1g}$ mode is projected to an $A_1$ mode on the surface and the $A_1$ mode excitation is allowed with the [001]s, [001]p, [110]s, and [110]p pump polarizations. The band actually appeared in the [001]sp spectrum, while being absent in the other three spectra for an unknown reason.

Three $\chi^{(4)}$ bands appeared in the [001]pp spectrum at 368, 440, and 817 cm$^{-1}$. They are present also in the [001]sp, [110]pp, and [110]sp spectra with one exception of the 440 cm$^{-1}$ band in the [001]sp spectrum. The perfect and nearly perfect appearances with the different azimuths and polarizations suggest $A_1$ symmetry of the three surface phonon modes. The corresponding bulk modes are $A_{15g}$, $B_{1g}$, or $E_u$ as seen in Table III. According to Table II of Ref. 22, two $E_u$ (LO) phonons are present at 373 and 458 cm$^{-1}$. We assigned the $\chi^{(4)}$ band at 368 and 440 cm$^{-1}$ to the two $E_u$ (LO) modes with wave number shifts of $-5$ and $-18$ cm$^{-1}$, respectively [Figs. 3(c) and 3(d)].

The last $\chi^{(4)}$ band exhibited wave numbers ranging from 817 to 827 cm$^{-1}$ in the four spectra. In our previous paper the $\chi^{(4)}$ band was assigned to the $B_{2g}$ mode due to close wave numbers. However, $B_{2g}$ is not corresponding to $A_1$ symmetry. On the other hand, the $E_u$ (LO) mode of 807 cm$^{-1}$ [Fig. 3(g)] presents an intense hyper-Raman band at 822 cm$^{-1}$ (Ref. 30) and corresponding to $A_1$ symmetry. Hence we now propose a contribution of the $E_u$ (LO) mode as the origin of the $\chi^{(4)}$ band at 817–827 cm$^{-1}$. In a viewpoint of the hyper-Raman process, which is the probe process of the measurement, $A_1$ and $B_1$ symmetries are symmetrically allowed in the results of [001] azimuth while $A_1$ and $B_2$ symmetries are allowed in the results of [110] azimuth when $p$-polarized probe pulses were used. Selective observation of the $B_1$ and $B_2$ modes may be possible by

TABLE IV. Frequency and assignment of phonon modes observed in (a) fourth-order spectra and (b) third-order spectra.

(a) Fourth-order Raman

<table>
<thead>
<tr>
<th>Crystal orientation, input polarization, and observed frequency (cm$^{-1}$)</th>
<th>Assignment and k-vector direction</th>
<th>Corresponding bulk mode and reported frequency$^a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>179</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>...</td>
<td>191</td>
<td>...</td>
</tr>
<tr>
<td>368</td>
<td>368</td>
<td>365</td>
</tr>
<tr>
<td>440</td>
<td>...</td>
<td>443</td>
</tr>
<tr>
<td>...</td>
<td>507</td>
<td>...</td>
</tr>
<tr>
<td>817</td>
<td>827</td>
<td>827</td>
</tr>
</tbody>
</table>

(b) Third-order Raman

<table>
<thead>
<tr>
<th>Crystal orientation, input polarization, and observed frequency (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>201</td>
<td>...</td>
</tr>
<tr>
<td>...</td>
<td>615</td>
</tr>
</tbody>
</table>

$^a$Reference 22.
using s-polarized probe pulses. However, on our TiO$_2$ wafers the SH intensity was small with the s-polarized probe pulses. It was difficult to examine the $B_1$ and $B_2$ modes.

**D. Contribution of the non-ISRS mechanisms in LO modes**

The phase of the three $\chi^{(4)}$ bands at around 359, 440, and 823 cm$^{-1}$ is sensitive to the azimuths and polarizations. In the [001]pp spectrum, their phases were close to zero. Hence, a dominant contribution of the ISRS is expected to produce the $\chi^{(4)}$ response. On the other hand, those bands presented phases far from zero when pumped with s-polarized pulses. As we assigned the three modes at 359, 440, and 823 cm$^{-1}$ to $A_1$ derived from bulk $E_u$ (LO), the phonon vibrations in the three modes are the polar modes toward the surface normal [Figs. 3(c), 3(d), and 3(g)] and they can be sensitive to the depletion field. Hence a definite contribution of the TDFS mechanism was assumed in order to interpret the s-polarized pump results. For excitation of coherent phonons of TiO$_2$ in TDFS, we assumed photoexcitation from an occupied mid-gap state derived from the Ti$^{3+}$ to the conduction band.

The azimuths and polarization dependences of the phases can be explained by different ratios of excitation efficiencies in ISRS and non-ISRS mechanisms. It is natural that the amplitude of Raman tensor components is sensitive to polarizations. The fraction of the ISRS is dominant in the [001]pp spectrum, medium in the [110]pp spectrum, and small in the [001]sp and [110]sp spectra. The ISRS excitation together with TDFS has been reported in coherent phonon excitation in zinc-blende semiconductors.

The different bandwidths of 359, 440, and 823 cm$^{-1}$ bands suggest different excitation mechanisms. The bandwidth of 359 cm$^{-1}$ was narrower than those of the other modes. The displacements of Ti atoms are in the opposite direction to the displacements of the O atoms in the mode at 359 cm$^{-1}$, as illustrated in Fig. 3(c). When a depletion field appears at the surface, that mode can be efficiently excited.

With a homogeneous broadening assumption, the dephasing time of the 440 and 823 cm$^{-1}$ bands is 1 ps. The nonoscillatory decay of the raw SH intensity was fitted with time constants of 0.16 and 1.2 ps in Fig. 2. The two characteristic times agreed at 1 ps. The excited-state electron dynamics may possibly affect the lifetime of the coherent phonons at 440 and 823 cm$^{-1}$ via the DECP mechanism.

The assignments of the $\chi^{(3)}$ and $\chi^{(4)}$ responses are summarized in Table IV. The atom displacements in the corresponding bulk phonon modes are illustrated in Fig. 3 following a theoretical study by Lee et al. The $\chi^{(4)}$ response of a Raman-active mode of vibration is enhanced when the Raman transition is in resonance with a one-phonon electronic transition. This happened on an oxazin dye solution, where Raman-active bands were observed. On the other hand, the pump photon energy is out of resonance in the present study and infrared-active modes of the bulk crystal appeared in the $\chi^{(4)}$ responses as a result of two-phonon resonance of the probing hyper-Raman process. These results offer selective observation of $\chi^{(4)}$ responses originated from Raman-active and infrared-active modes by tuning the pump photon energy.

**V. SUMMARY**

The fourth-order optical responses of a wide-bandgap material, rutile TiO$_2$, were observed by a pump-and-probe method with different azimuths and polarizations of pump and probe light pulses. The observed responses were assigned to seven phonon modes present in the surface layer of 10 nm thickness. Possible contributions of the ISRS and TDFS are evaluated on each $\chi^{(4)}$ response. It was suggested that Raman-active and infrared active phonon modes can be selectively observed in a wide-bandgap material by tuning the pump photon energy.

**ACKNOWLEDGMENTS**

This work was supported by Grant-in-Aids for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (Grant Nos. 17GS0209 and 20850026).

---

(1964).


