Near-surface low-frequency vibrations of TiO_2 (110) observed by fourth-order coherent Raman spectroscopy

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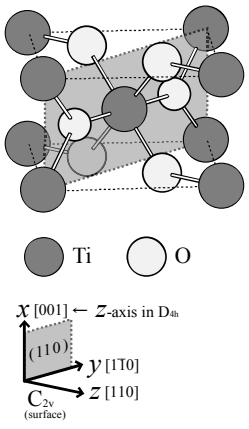
Interfaces have different characters from the bulk substrates. The translational symmetry of the crystal is lost to cause the depth dependence of the distribution of vibrational resonance and electronic states near the surface as observed as surface phonon modes or surface electronic states. Fourth-order coherent Raman (FR) spectroscopy, which have been developed recently[1-4], is a interface-selective vibrational spectroscopy. It is an even-order non-linear optical spectroscopy sensitive only at interfaces when the substrates are centro-symmetric media.

We observed FR spectra of a TiO_2 (110) rutile surface as an example of a typical photocatalyst. In the obtained $\chi^{(4)}$ spectra, we observed near-surface phonon modes of TiO_2. Some surface modes are different from those observed in bulk Raman spectra while others seem to correspond to the surface optical modes which were observed in HREELS. To relate the surface phonon modes to the bulk modes, azimuth and polarization dependences were observed and the observed phonon modes near the surface were assigned using selection rule of Raman process. As a result, vibrational assignment of near-surface phonon modes and excitation mechanisms of fourth-order coherent Raman spectroscopy of TiO_2 (110) are presented.

TABLE: Observed frequencies of TiO_2 phonon modes in $\chi^{(4)}$ spectra

Crystal azimuth, pump-probe polarization and observed frequency (cm^{-1})				Assignment and	Corresponding bulk mode
[001]p-p	[001]s-p	[1$\bar{1}$0]p-p	[1$\bar{1}$0]s-p	*k*-vector direction	and reported frequency (cm^{-1})
179	-	-	-	B_1 (TO), *in* (001)	A_{2u} (TO), 167
-	-	196	-	B_2 (TO), *in* (1$\bar{1}$0)	E_u (TO), 183
368	368	366	359	A_1 (LO), [110]	E_u (LO), 373
439	-	448	440	A_1 (LO), [110]	E_u (LO), 458
-	-	507	-	B_2 (TO), *in* (1$\bar{1}$0)	E_u (TO), 500
-	609	-	-	A_1, *in* (1$\bar{1}$0)	A_{1g}, 612
817	827	826	822	A_1, *in* (1$\bar{1}$0)	E_u (LO), 807 (or B_{2g}, 827)



The structure of rutile and axis for C_{2v} group

References
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