

Electronic Structure Study of Anatase (TiO₂) under UV irradiation by means of X-ray Raman Scattering

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1 Introduction

Titanium dioxide (TiO₂) occurs in nature as three different polymorphs; rutile, anatase, brookite. Among them, anatase shows larger photocatalytic activity, but the reason of such a difference is still unclear. Thus, electronic structure should be investigated to make clear the photocatalytic mechanism. We have reported X-ray Raman scattering (XRS) of Ti-oxides excited around Ti *K* absorption edge [1]. The XRS shows scattering by Ti $2p3d$ excitation under the excitation at pre-edge of Ti *K* absorption, as well as $2p4p$ excitation as normal XRS, where underline denote core-hole. Ti 3*d* state of titanium dioxide is split into e_g and t_{2g} by ligand field in O_h approximation, and the e_g state is known to be hybridized with O 2*p* state. In this study, we investigated electronic structure of anatase and rutile under UV irradiation by means of XRS.

2 Experiment

Commercially obtained single-crystal rutile(001) and epitaxially grown thin-film anatase(001) were used in this experiment. The anatase thin-film was made by pulsed laser deposition (PLD) on LaAlO₃(100). XRS spectra were observed using X-ray emission spectrometer (ESCARGOT) at beamline BL-7C. Scattered photon was analyzed using Ge(400) and detected by one-dimensional multi-channel proportional counter. The energy resolution of XRS measurements was about 1 eV for 5 keV photon. UV irradiator has maximum output of 3500 mW and wavelength of about 365 nm (about 3.4 eV). In this experiment, XRS spectra were excited at 4963.0 eV that is just below Ti *K* absorption edge where Ti 3*d* state was observed via quadrupole transition [1].

3 Results and Discussion

Figure 1 shows XRS spectra of anatase plotted against loss-energy (Raman shift). We have reported that P₁~P₄ correspond to excitation Ti $2p3d$ and P₅~P₇ correspond to excitation Ti $2p4p$ [1]. As UV-intensity were changed from 5 % to 30 % of maximum output successively, the P₁~P₄ shifted to the higher-energy side, then the P₁~P₄ returned to lower-energy side when irradiation was stopped. These results suggest that level of Ti 3*d* state is pushed up under UV irradiation, since the core Ti 2*p* state should not be changed.

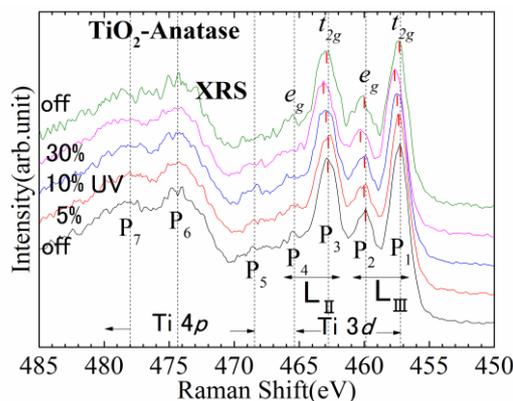


Fig.1 XRS spectra of anatase under UV irradiation. UV intensity was changed successively 5%, 10%, and 30% of maximum output of UV irradiator.

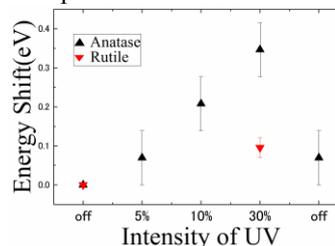


Fig.2 UV-intensity dependence of energy shift of XRS spectra of anatase and rutile.

Figure 2 shows UV-intensity dependence of energy shift of XRS. The energy shift increases with increasing intensity of UV irradiation. Though the energy shift did not return to zero when UV was offed, the energy shift was very small. Because of limited beam time, we could not observe irradiation effect for rutile except for 30 % intensity, where rutile shows a smaller energy shift than anatase. We have reported that anatase would have much Ti 3*d* electrons in e_g state than rutile [2]. If so, it is suggested that the 3*d* electrons in the e_g state possibly interact with that excited by UV irradiation, and then energy of $2p3d$ excitation would be larger.

References

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 [2] Y. Tezuka, et al., PF Activity Report, #138 (2011).

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