

Soft X-Ray Resonant Emission Spectra of Ti_2O_3 .

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INTRODUCTION

Recently, soft X-ray emission spectra (SXES) of TiO_2 were observed [1]. The TiO_2 has no Ti 3d electron nominally and has wide band gap of about 3 eV. It is known that the Ti 3d state in the TiO_2 is strongly mixed to the O 2p-state [2]. In the resonant SXES measurements of TiO_2 , a Raman peak corresponding to charge-transition excitation from O 2p-valence band to Ti 3d-conduction band was observed. The Raman peak is elucidated by the strong hybridization [1].

In this study, resonant SXES of Ti_2O_3 is observed. It is known that the Ti_2O_3 is typical Mott-Hubbard type semiconductor that has narrow band gap (< 0.1 eV)[3]. The Ti_2O_3 has one Ti 3d electron nominally and the Ti 3d band is located at about 1 eV. Recently, resonant photoemission (PES) spectra of Ti_2O_3 were observed [4]. The results suggest that the Ti 3d state in the Ti_2O_3 is strongly mixed to the O 2p state.

EXPERIMENTAL

The resonant SXES spectra were measured at the undulator beam line 8.0.1 of Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). The spectra were observed using a spectrometer that has grazing-incidence monochromator and multichannel detector. A 1500 lines/mm spherical grating with 10-m radius was used. A Ti 3d \rightarrow 2p-fluorescence peak of Ti metal was observed for energy calibration of the emission spectra. The overall energy resolution in the measurements was about 1.0 eV at excitation energy of 450 eV.

A single-crystal Ti_2O_3 was made by the floating-zone method in an Ar- H_2 gas atmosphere. The sample temperature is room temperature at which the Ti_2O_3 is semiconductor phase having narrow gap.

RESULTS AND DISCUSSIONS

Figure 1 shows Ti 2p XAS spectrum of Ti_2O_3 , which is observed by total fluorescence yield method. Ti 2p-resonant emission spectra are observed in the Ti 2p-absorption edge. The excitation energy used in SXES measurements are shown by vertical bars.

Figure 2 shows resonant SXES spectra of Ti_2O_3 observed at the Ti 2p-absorption edge. A strong fluorescence peak is observed at about 451 eV. This peak is assigned to Ti 3d state that is hybridized to O 2p-valence band. On the other hand, two fluorescence peaks are observed

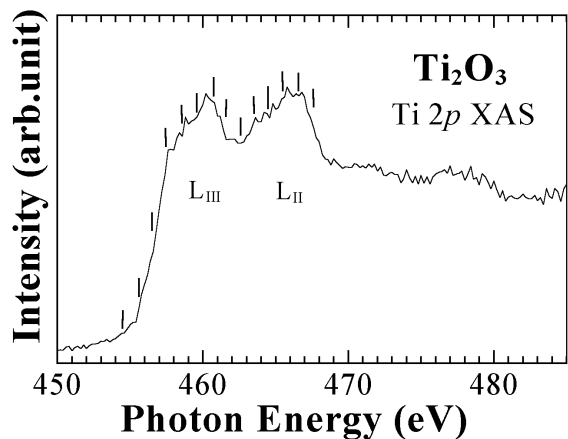


Figure 1. Ti 2p XAS spectrum of Ti_2O_3 . Vertical bars denote excitation energy of resonant emission measurements.

weakly at 456 and 458 eV in the spectra excited by the energy between 465.6 and 468.6 eV. These peaks are assigned to localized Ti 3*d* state.

Figure 3 shows Raman spectra of Ti₂O₃. In the Fig. 3, the emission spectra in Fig. 2 are plotted against energy shift from excitation energy. Vertical broken line at 0 eV indicates an elastic scattering. An elastic scattering peak is observed in the spectrum excited by 457.6 eV. The other two broken lines indicate Raman scattering peaks. Two Raman peaks are observed at about 1.0 and 7.0 eV. The peak at 7.0 eV is assigned to an excitation from O 2*p*-valence band to Ti 3*d*-conduction band. This result is similar to that of TiO₂ [1]. On the other hand, the peak at 1.0 eV is assigned to an excitation from Ti 3*d* states in valence band to that in conduction band.

Recently, we observed Ti 2*p*-resonant PES of Ti₂O₃, which shows strong resonance of Ti 3*d* state [4]. The resonant PES spectra were elucidated by the cluster model calculation. That result suggests the strong hybridization of Ti 3*d* and O 2*p* states. The resonant SXES spectra in this study also suggest the strong hybridization.

CONCLUSION

Resonant SXES of Ti₂O₃ was observed in this study. Raman scattering peaks of both charge-transition excitation and *d-d* transition excitation were observed. The results suggest the strong hybridization of Ti 3*d* and O 2*p* states.

REFERENCES

1. Y. Tezuka, S. Shin, A. Agui, M. Fujisawa, T. Ishii, J. Phys. Soc. Jpn., 65, 312 (1996).
2. K. Okada, and A. Kotani, J. Electron Spectrosc. Relat. Phenom., 62, 131 (1993).
3. K. E. Smith, and V. E. Henrich, Phys. Rev. B38, 5965 (1988).
4. Y. Tezuka, S. Shin, T. Uozumi and A. Kotani, J. Phys. Soc. Jpn., 66, 3153 (1997).

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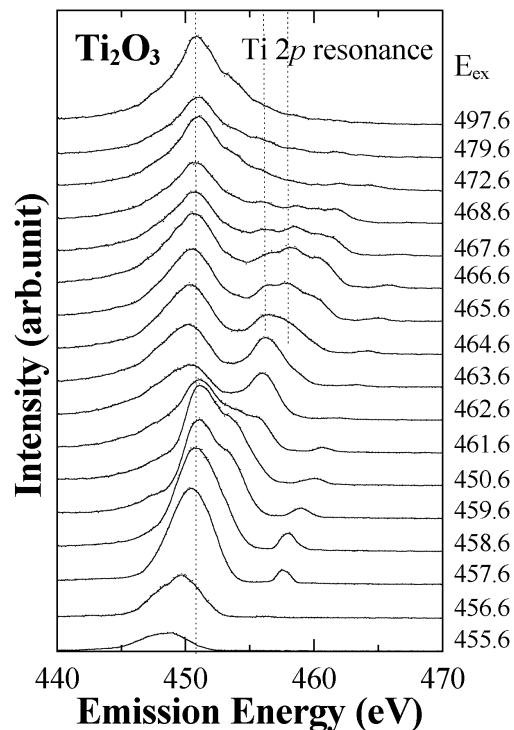


Figure 2 Ti 2*p*-resonant emission spectra of Ti₂O₃. Numbers beside the spectra indicate excitation energy. Vertical broken lines show Ti 3*d* → 2*p*-fluorescence energy.

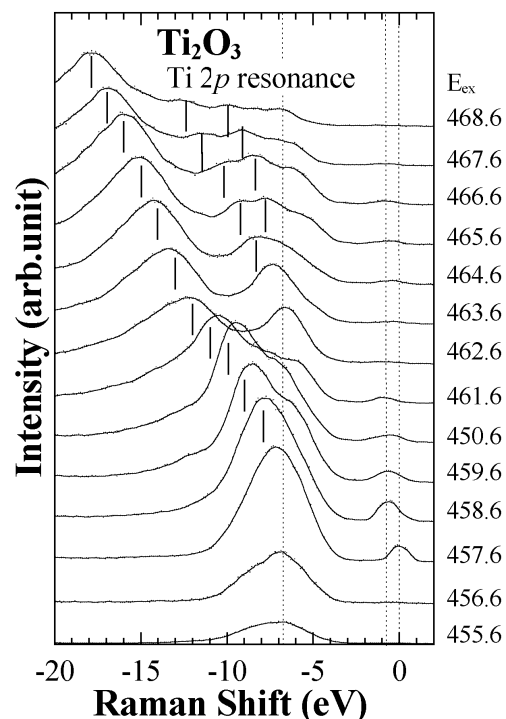


Figure 3. Resonant Raman spectra of Ti₂O₃. Vertical broken line at 0 eV indicates elastic peak, while the other broken lines indicate Raman peak. Vertical solid lines indicate fluorescence peak.