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Total Reflection Fluorescence XAFS Analysis of Self-assembled Monolayer Film of the Titania Nanosheets

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Introduction

Advanced analytical technique utilizing synchrotron radiation for the nanomaterials began to play an important role in *Nanotechnology* due to offering their broad experimental application. For example total reflection fluorescence X-ray absorption fine structure (TR-FXAFS) is an element specific method and applicable even to very low concentration, indifferent to the crystallinity of sample, providing structural information around absorber atom. These advantages are suitable for structural analysis of two dimensional nanomaterial, nanosheets, because it has no periodic structure in normal direction to the sheet.[1)] Here, we have examined structural change of titania nanosheets as a function of temperature by TR-FXAFS technique which permits considerable enhancement of the signal from such inorganic monolayer relative to a substrate contribution.[2)]

Experiments

A monolayer of the titania nanosheets obtained by delamination of a layered titanate, $H_{0.7}Ti_{1.825}\Upsilon_{0.175}O_4 \bullet H_2O$ (Υ= vacancy), into single layers[3)] can be deposited by electrostatic self-assembly onto quartz glass substrate coated with positively charged polymer.[4)] The resultant films were treated with heating at 600, 700, 800 and 900°C for 1h. TR-FXAFS spectra were obtained at the Photon Factory BL-9A, 12C equipped with Si(111) double-crystals and a 19 element Ge-Solid State Detector. Ti K-edge XAFS spectra were measured from 4660 to 5968 eV with an interval of 0.3 and 2.2 eV for XANES and EXAFS regions, respectively, at room temperature.

Results and Discussion

Figure 1 represents normalized Ti-K-edge XANES spectra for the as-grown and heated films. The titania nanosheets (a) showed pre-edge consisting of three or four peaks in which central peak is stronger than the others and white line peak related to tetravalent of titanium. There was little change in the XANES spectra up to 700°C (c), indicating absence of any structural change. Then, pre-edge structure characteristic for anatase (f) and a sharp white line peak at 4984 eV appeared overlapping with the profile of nanosheets at 800°C(d). Upon further heating at 900°C, the spectrum (d) was identifiable as a single phase of anatase by compared with the reference spectra(f). Consequently, it is found that the nanosheets started to transform into anatase at 800°C, and finished at 900°C. This behavior is distinct from the behavior of the bulk material and seems to be peculiar to two-dimensional nanoscopic system.

Furthermore, we have succeeded in acquisition of polarization-dependent XAFS spectra under s- and p-polarization from the monolayer with changing the geometrical location of the film against incident X-ray beam. The data analysis is now underway to reveal the three-dimensional framework of titania nanosheet.

The present study has demonstrated that the TR-FXAFS analysis is a powerful technique to trace the structural change of the nanosheets.

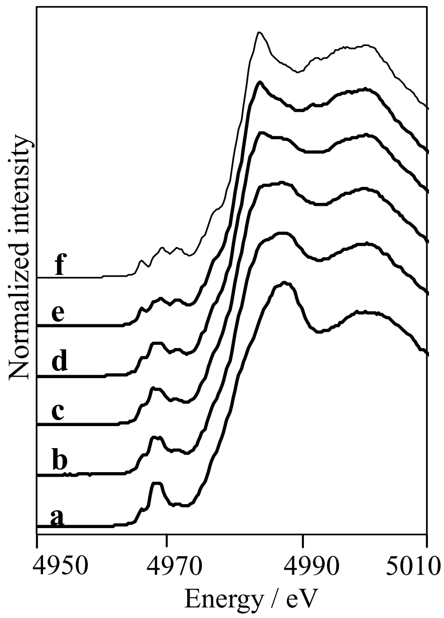

Figure 1. Normalized Ti-K XANES spectra for (a)as-grown film and for samples heated at (b) 600°C, (c) 700°C, (d) 800°C and (e) 900°C. The data for (f) anatase is shown as a reference.

References

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