Chemical state analyses of nitrogen implanted titanium dioxide photocatalyst by means of XAFS, TEM and EELS

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Photocatalytic reactions at the surface of titanium dioxide (TiO_2) under UV light irradiation have been attracting much attention due to their practical applications such as environmental cleaning. Recently, Asahi *et al.* reported that substitutional doping of nitrogen into TiO_2 contributed to narrowing of the band gap, thus providing a visible-light response [1]. Furthermore, previous investigations demonstrated that nitrogen doping generated new optical absorption bands in the visible-light region and the absorbance evolved with increasing nitrogen. On the other hand, absorbance may not be linearly proportional to the photocatalytic activity, and it is thus important to understand the chemical environment and optimum concentration of N most effective for the photocatalytic response. In the present investigation, depth-selective electronic state analysis was performed for a N^+-implanted TiO_2 catalyst by means of X-ray absorption spectroscopy (XAFS), electron energy-loss spectroscopy (EELS) and energy-filtering TEM (FETEM).

Fig.1 shows the N K-edge XANES spectra of the N^+-implanted TiO_2 samples and a TiN powder. Similar XANES features for (a) and (b) suggest that N in the sample implanted by 3×10^{21} m^{-2} (highest active photocatalyst) is in a chemical environment similar to that in TiN. More thorough observation suggested that double-peak around 400 eV in (b) shifted to the lower energy side compared with that of TiN, which was well reproduced by the theoretical prediction using FEFF code [2] when N occupies one of the O sites of TiO_2, as suggested in ref.[1]. On the other hand, the XANES spectrum of the sample implanted with the N^+ fluence of 5×10^{21} m^{-2} followed by heat-treatment (almost inactive to visible-light) shows a distinct single peak at around 401 eV (Fig. 1c). This peak was attributed to formation of N-O bond near the surface [2], which significantly suppresses the photocatalytic activity.

Fig.2 shows extracted depth-resolved profiles of the N K-edge ELNES of the samples implanted with the N^+ fluence of 3×10^{21} m^{-2}. The double-peak structure around 398-401 eV was again observed near the surface region, and a distinct single peak around 401 eV gradually grows with increasing the depth, which reflects the different chemical states of nitrogen, presumably depending on the local N concentration. The single peak around 401 eV for the deeper regions was observed both in XANES and ELNES over the entire implanted region of the catalytically inactive sample. Thus, we confirmed that substitution of N at O sites is essential for visible-light responsive photocatalytic activity. The single peak around 401 eV predominates from ~28 nm to deeper regions, and thus the local concentration of doped nitrogen, most effective for visible-light response was estimated to be less than 1 at%, the average N concentration up to 28 nm from the surface.

Finally, we succeeded to visualize the depth distributions of the two kinds of N states in the sample implanted with the N^+ fluence of 3×10^{21} m^{-2} (highest active photocatalyst) by applying the SMCR technique to the FETEM-SI images of the cross section TEM sample. The resolved spectra are shown in Figs. 3(a), and the corresponding depth distributions of the two components are shown in (b) and (c), respectively. The chemical state of component (1) (catalytically inactive N species) is clearly localized over deeper depth regions, whereas that of component (2) is distributed over the entire implanted region.

References
[1] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Science **293** (2001) 269.
[2] A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, Phys. Rev. B **58** (1998) 7565.

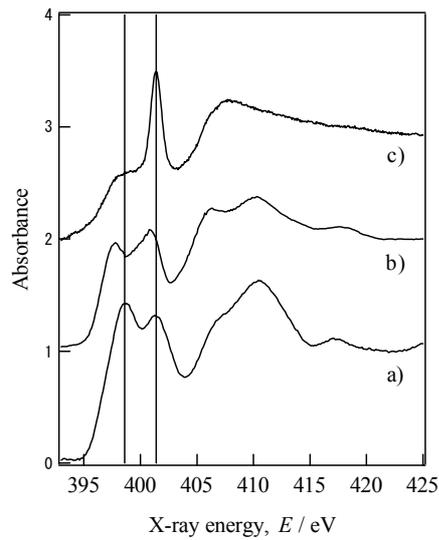FIG. 1. N K-edge XANES spectra of a TiN(a), N^+-implanted at 3 x 10^{21} m^{-2}(b) and 5 x 10^{21} m^{-2} followed by heating at 573 K for 2 h(c).
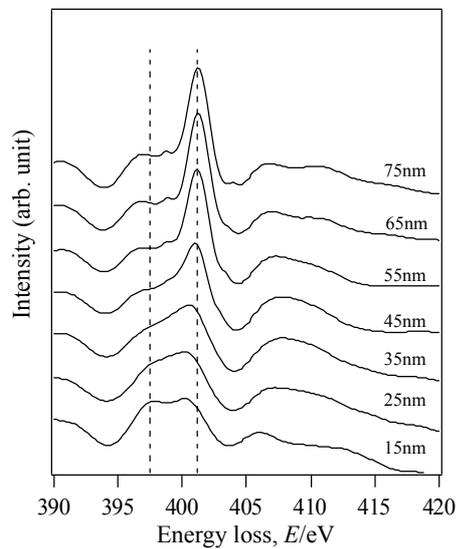

FIG. 2. Depth-resolved N K-edge ELNES of sample, N^+-implanted with fluence of 3 x 10^{21} m^{-2}.
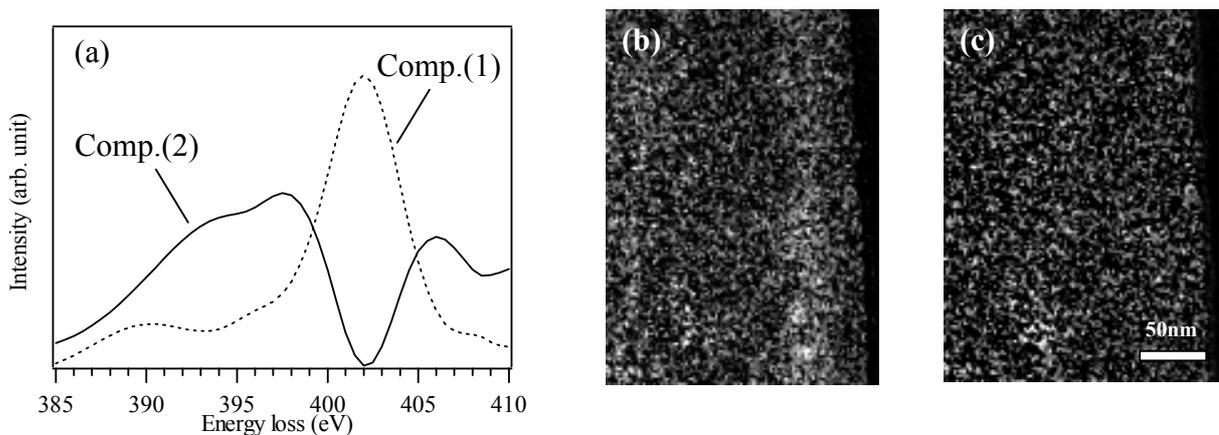

FIG. 3. (a) N K-edge ELNES profiles extracted from the EFTEM-SI image set of 3.0 x 10^{21} m^{-2} implanted sample. (b), (c) Corresponding depth distribution of each component (1) and (2).