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Consideration on the optimum implantation conditions of nitrogen for visible light responsive TiO_2 photocatalyst

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TiO_2 photocatalyst has attracted much attention due to its superior nature for environmental cleaning, but it works only under irradiation of light having the energy higher than UV. Recently, it was found that doping of nitrogen (N) into TiO_2 provided a visible light response [1]. In previous studies [2], it was found that photocatalytic activity under visible light illumination did not increase monotonically with the N dose, but exhibited a maximum at a certain N dose. It was also found that two types of chemical states for the implanted N were present depending on the local N concentration. One was a state in which N replaced the O site ($(N)_O$), characterized by the double–peak in N K XANES/ELNES and catalytically active. The other was a state in which possibly N–O- or N–N-like species occupied the O and/or interstitial sites, characterized by the single distinct peak and catalytically inactive (*cf*: depth resolved N K ELNES in Fig. 1 [2]).

To investigate the optimum concentration of implanted nitrogen for the visible light responsiveness, we employed an ion implantation technique for N incorporation into TiO_2. The depth distribution of the implanted N was calculated by the Monte Carlo simulation, TRIM code. And, to investigate the local N concentration as a function of depth from the surface, we experimentally quantified the implanted N with STEM-EELS for the cross-sectional samples. We estimated the local N concentration by measuring the intensity ratios among the N and O K- and Ti $L_{2,3}$-edge ELNESs in reference to those from TiO_2 and TiN standard samples with the known compositions. The estimated N concentration as a function of depth from the surface is shown in Fig. 2. Our previous study revealed that in the photocatalytically active sample the $(N)_O$ species was formed up to the depth from surface no deeper than 25 nm [2], as shown in Fig. 1. Comparing between the results above, the optimum N concentration, C_{crit} that maximizes the visible light responsiveness was estimated to be no larger than 1.8 at% (see Fig. 2).

We also tried to estimate the depth (d_{eff}) where the implanted N can effectively contribute to the photocatalytic reactions: by considering the relationship among C_{crit}, d_{eff} and the net number of photocatalytically active sites, N_{eff}, within the range < d_{eff}, we derived a formula $d_{eff} = C_{crit} / a_c$ after some algebraic manipulations, where a_c is the critical depth gradient of N concentration, a, when the N_{eff} curve as a function of a starts to be deviated from the straight line. Since N_{eff} is proportional to the photocatalytic reaction rate, which can be experimentally measured by decomposition of a methylene blue solution using N-implanted TiO_2 with several different N fluences. a for each N fluence was calculated from the results of TRIM simulations. Then we estimated a_c from the experimental $N_{eff}(a)$ curve to be no larger than 0.2 at%/nm. d_{eff} was eventually calculated to be *ca*. 9 nm by the formula. We have started preparing thickness-controlled nitrogen-doped TiO_2 films by a pulsed laser deposition (PLD) method to investigate the

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relation between the sample thickness and the photocatalytic activity, which is now in progress.

References
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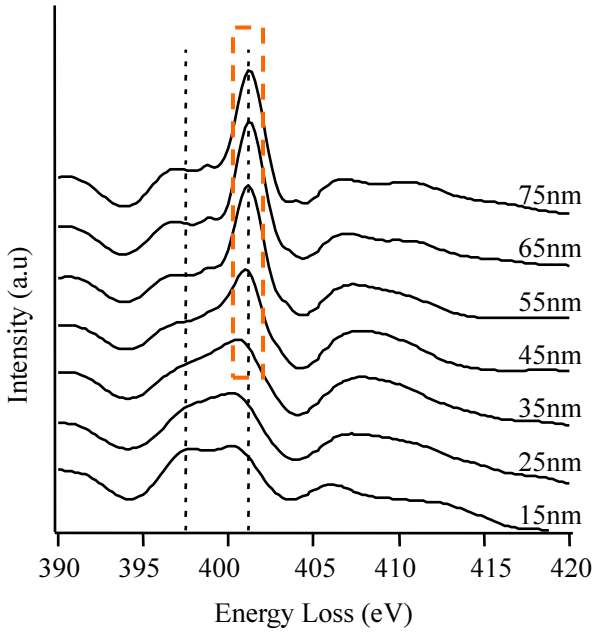

FIG. 1. Depth-resolved N K-edge ELNES of sample, N^+-implanted with fluence of 3×10^{21} m^{-2}. The single peak characteristic of inactive species, appearing for the depth > 25 nm, is framed by broken lines.

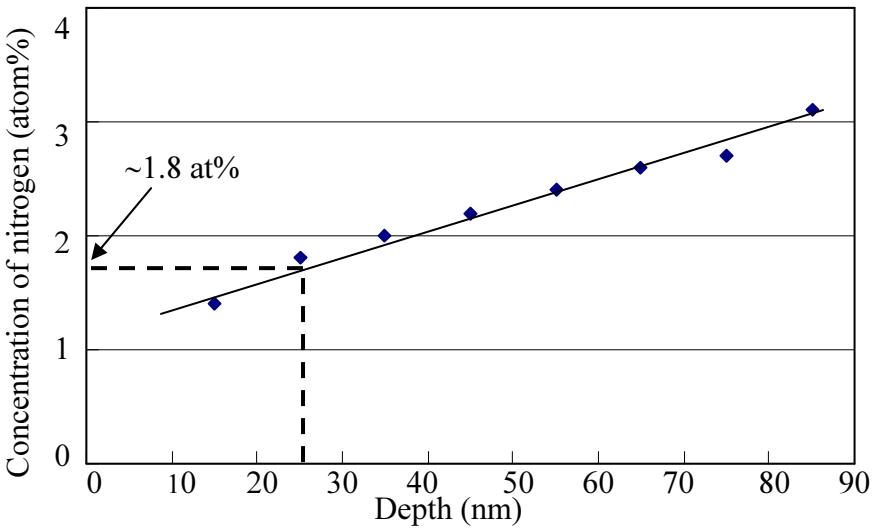

FIG. 2. Measured concentration (dots) of nitrogen as a function of depth from surface. The straight solid line is drawn as a guide for eyes.