

## Study on Formation Process of N-Doped Anatase TiO<sub>2</sub> (001) with Ambient Pressure X-Ray Photoelectron Spectroscopy

Yuji Monya<sup>1,\*</sup>, Masaaki Yoshida<sup>1</sup>, Ryo Toyoshima<sup>1</sup>, Masato Emori<sup>2</sup>, Kenichi Ozawa<sup>3</sup>, Hiroshi Sakama<sup>2</sup>, Hitoshi Abe<sup>4</sup>, Kenta Amemiya<sup>4</sup>, Kazuhiko Mase<sup>4</sup> and Hiroshi Kondoh<sup>1</sup>

<sup>1</sup>Keio University, Yokohama 223-8522, Japan

<sup>2</sup>Sophia University, Tokyo 102-8554, Japan

<sup>3</sup>Tokyo Institute of Technology, Tokyo 152-8551, Japan

<sup>4</sup>Institute of Materials Structure Science, Tsukuba 305-0801, Japan

### 1 Introduction

To utilize solar energy efficiently, visible-light-response photocatalyst has been extensively studied [1-3]. Nitrogen (N) doping under NH<sub>3</sub> atmosphere into TiO<sub>2</sub> is an efficient way to give rise to visible-light-response [2,3]. Although there have been a number of studies on N-doped TiO<sub>2</sub>, neither its formation process nor structure is still unclear. To understand the formation process, we measured XPS spectra during the N-doping process into an anatase TiO<sub>2</sub> single-crystal thin film at 800 K under 1.0 Torr of NH<sub>3</sub> with Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS).

### 2 Experiment

All the experiments were performed with the AP-XPS apparatus at the soft x-ray beamline, BL-13. An anatase TiO<sub>2</sub>(001)/LaAlO<sub>3</sub>(100) single crystal was heated up to 800 K under 1.0 Torr of NH<sub>3</sub> atmosphere to prepare an N-doped anatase TiO<sub>2</sub> sample. During the doping process, Ti 2p, N 1s and valence band (VB) regions of XP spectra were measured to monitor the formation process of the N-doped TiO<sub>2</sub>. All the binding energies for XP spectra were calibrated with the Fermi edge of a Au substrate that was attached to the sample.

### 3 Results and Discussion

Figure 1 shows XP spectra of (a) VB and (b) N 1s regions, measured before, during and after the doping. Under 1.0 Torr of NH<sub>3</sub> atmosphere, the VB maximum (VBM) shifted drastically toward the lower binding energy side with increasing temperature to 800 K. However, the VBM shifted back to the higher binding energy side after 90 min while the sample was kept at 800 K in NH<sub>3</sub>. The final position of the VBM is lower by 0.4 eV than the original position. This transient large shift might be attributed to a significant surface roughening in the beginning of doping and a resultant over-doping of nitrogen near the surface region. Prolonged annealing at 800 K in NH<sub>3</sub> restores the surface atomic order and may eliminate the over-doped area. Note that a small hump at around 0.4 eV is attributed to a Ti<sup>3+</sup> species due to oxygen vacancies in the lattice. These oxygen vacancy disappears during the doping at elevated temperatures.

N 1s XP spectra measured at the same time with the VB region show four peaks. The peak at around 401 eV is

attributed to NH<sub>3</sub> gas because it was observed most intensely in NH<sub>3</sub> atmosphere at r.t., while another peak at around 406 eV is attributed to gas phase N<sub>2</sub> which arises from thermal decomposition of NH<sub>3</sub> gas (it was confirmed by MASS measurement). These gas peaks were shifted depending on the work function of the surface. On the other hand, the two peaks at 400.5 and 398.5 eV are related to surface and/or subsurface species and unchanged in binding energy. The 400.5 eV peak is attributed to chemisorbed NH<sub>3</sub> because it was observed after the first exposure of NH<sub>3</sub> at r.t. and there should be no decomposition in this condition (There is no other peaks). Besides, after reaching 800 K, another peak appears at 398.5 eV and its appearance accompanied a significant shift of the VBM. Therefore, this peak can be related to a doped N (d-N) species which are responsible for the shift of the VBM. According to DFT calculations, the d-N peak is attributed to subsurface N and/or NH species which substitute the lattice O atoms. The *in-situ* observation of the doping process is useful to understand which nitrogen species induces the VBM shift.

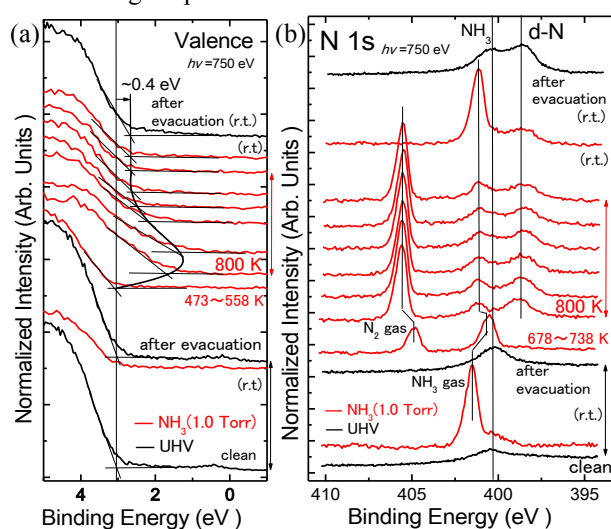


Fig. 1: XP spectra of valence band and N 1s regions.

### References

- [1] R. Asahi *et al.* *Science*, **293**, 269 (2001).
- [2] O. Diwald *et al.* *J. Phys. Chem. B*, **108**, 6004 (2004).
- [3] Z. Zhang *et al.* *J. Catal.*, **276**, 201 (2010).

\* monya@chem.keio.ac.jp