

Electronic Properties of N-doped Anatase TiO<sub>2</sub> Films

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## 1 Introduction

Titanium dioxide (TiO<sub>2</sub>) has been attracted much attention as a photocatalyst. However, it can be excited only by ultraviolet light, because of the wide band gap (3.0 - 3.2 eV). For more efficient use of solar energy in photocatalytic reactions, it is necessary to extend the optical response of TiO<sub>2</sub> to the visible light region. One of the effective methods synthesizing visible light active photocatalyst is doping of nonmetal element. Since the report by Asahi et al., N-doped TiO<sub>2</sub> with visible-light activity has been recognized as a appropriate approach because the band gap narrowing is obtained by N2p localized state just above O2p valence band<sup>[1]</sup>.

According to previous research, the localized state is due to interstitial nitrogen(N<sub>i</sub>)<sup>[2]</sup>. On the other hand, however, some groups persist that the substitutional nitrogen(N<sub>s</sub>) is effective for band gap narrowing while N<sub>i</sub> produces deep-level defects in the gap<sup>[3]</sup>. Therefore, the most effective approach of it is still controversial.

In the present study, we fabricated N-doped anatase TiO<sub>2</sub> thin films by various methods, and examined the electronic structures by X-ray photoelectron spectroscopy (XPS).

## 2 Experiment

N-doped anatase(001) thin films were epitaxially grown using pulsed laser deposition with a KrF excimer laser ( $\lambda = 248$  nm) on LaAlO<sub>3</sub>(100), whose in-plane lattice constants are matched to those of anatase TiO<sub>2</sub><sup>[4]</sup>. Sintered pellets composed of TiO<sub>2</sub> and TiN were used as PLD targets.

As the other method for fabricating N-doped anatase, sol-gel method was employed. A precursor TiO<sub>2</sub> solution was prepared from a mixture of titanium tetra-n-butoxide monomer and 2-methoxyethanol. CH<sub>4</sub>N<sub>2</sub>O powder was added to the solution as N source. The solution was deposited on Si(100) substrate by a syringe, and the samples were rotated at 3000 rpm for 50 seconds using a spin-coater. The films were subsequently annealed in the air.

The *in situ* preparation to remove surface contamination involved cycles of Ar<sup>+</sup> sputtering (2.5kV, 0.5 $\mu$ A).

The XPS measurements were performed utilizing synchrotron radiation at Beam Line 3B and 13A of the Photon Factory, High Energy Accelerator Research Organization (KEK). A hemispherical electron energy analyzer (HA45, VSW) was used to acquire the spectra with a typical overall energy resolution of c.a. 0.25 eV. The binding energy of the spectra was referenced to the Fermi energy, which was determined from the spectra of the Ta sample holder.

## 3 Results and Discussion

Figure 1 shows the N1s and valence band spectra of N-doped anatase prepared by (a)PLD, and (b)sol-gel method, respectively. Two different peaks are observed around E<sub>bin</sub> = 400 eV. It has been reported that the peak at 400 eV and 397 eV were attributed to N<sub>i</sub> and N<sub>s</sub>, respectively. Figure 1(a) indicates that the nitrogen is merely doped into the interstitial site and the band gap narrowing is hardly observed for N-doped anatase prepared by PLD method. On the other hand, in Fig. 1(b), the N<sub>s</sub> peaks are clearly observed, leading to the band gap narrowing for N-doped anatase prepared by sol-gel method.

From these results, we concluded that the N<sub>s</sub> contributes the band gap narrowing and that sol-gel method is effective for N doping because CH<sub>4</sub>N<sub>2</sub>O produces oxygen vacancies in the TiO<sub>2</sub> lattice by reduction, and also acts as nitrogen source.

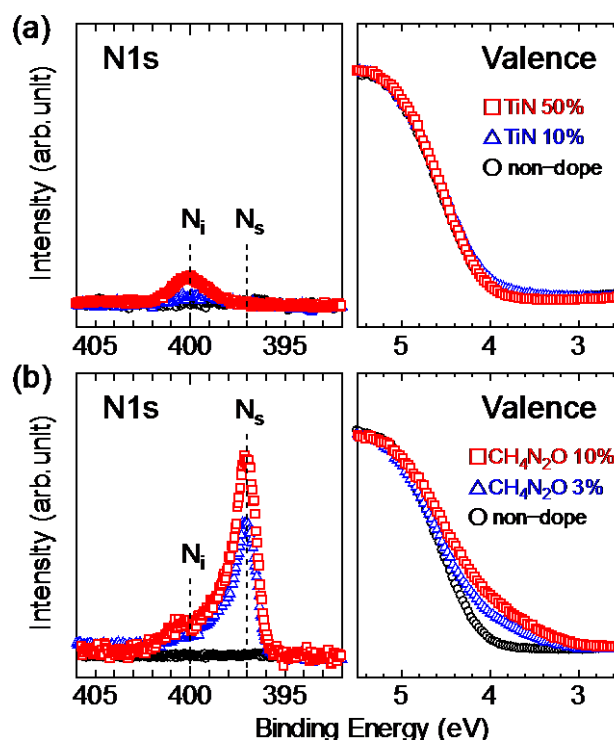


Fig. 1: N1s and valence band region XPS spectra of anatase prepared by (a) PLD, and (b) sol-gel method.

## References

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