

Electronic Structures of Nb and N co-doped Anatase TiO₂

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1 Introduction

Titanium dioxide (TiO₂) has been attracted much attention as a photocatalyst for its high photocatalytic activity. However, TiO₂ can be excited only by ultraviolet light because of the wide band gap. For more efficient use of solar energy, the visible-light active photocatalyst is desired.

One of the effective methods synthesizing visible light active photocatalyst is co-doping of nonmetal and metal elements^[1]. High activity under visible light is expected because of the compensation effect^[2]. Compensation effect is the transfer of electron between non-metallic ions and metallic ions.

In previous studies, co-doping TiO₂ samples were mainly fabricated by liquid phase growth method. However, since a lot of impurities are contained in the products fabricated by this method, it was difficult to control the concentrations of non-metallic and metallic dopants accurately. In this research, nitrogen (N) and niobium (Nb) doped anatase TiO₂ were fabricated by vapour growth method that enables to control the dopant concentrations.

2 Experiment

The Nb -doped anatase TiO₂ thin films were fabricated by pulsed laser deposition (PLD) using the sintered pellet composed of titanium dioxide and niobium oxide with various Nb concentrations. Nb-N-doped anatase TiO₂ thin films were prepared by annealing Nb-doped TiO₂ samples in ammonia gas flow at 870 or 970K.

X-ray photoelectron spectroscopy (XPS) measurements were performed utilizing synchrotron radiation at Beam Line 3B and 11A of Photon Factory to examine the electronic structures of Nb-N-doped anatase TiO₂ thin films.

3 Results and Discussion

Figure 1 shows N1s XPS spectra of Nb-N-doped anatase TiO₂ thin films with various Nb and N concentrations. Two different peaks are observed around 400 eV. The peak at the binding energy of 400 eV is derived from interstitial nitrogen (N_i) and that at 396.8 eV is due to substitutional nitrogen (N_s). According to our previous study, the slope of the valence band edge became gentle and the states in the band gap just above balance band appeared by N doping. The states in the band gap just above balance band were successfully attributed to N_s^[3]. N 1s spectra in Fig.1 indicate that N_s concentration increases with the increase in annealing temperature. However, annealing above 870K in ammonia was shown to result in the formation of oxygen vacancies, which reduces the photocatalytic activities. In

fig.1(a), N_i is dominant in the film without Nb annealed at 870K in ammonia. In contrast, N_s becomes dominant in the film with Nb (9wt.%) annealed at 870K in ammonia. This suggests that the Nb doping promotes the substitutional incorporation of N atoms.

Figure 2 shows the valence band edge XPS spectra of Nb-N-doped anatase TiO₂ thin films with Nb 9wt.%. The states in the band gap just above balance band clearly appear at the annealing temperature of 870K.

In summary, Nb doping is shown to promote the generation of substitutional N atoms which increase the visible-light activities of anatase TiO₂ films.

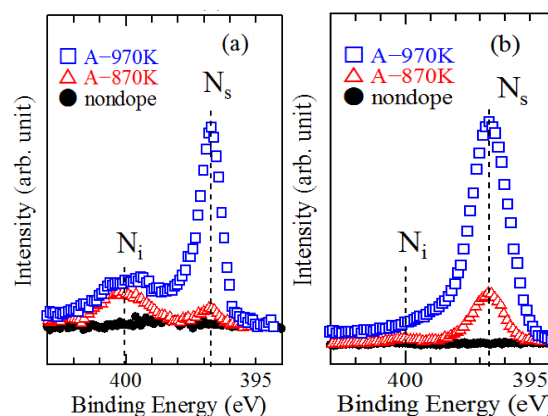


Fig. 1: N1s XPS spectra of anatase TiO₂ thin films (a) without Nb and (b) with Nb 9wt.%.

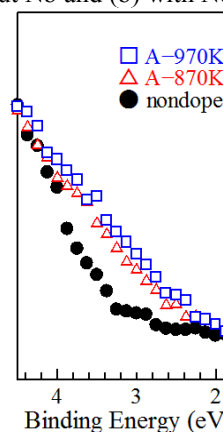


Fig. 2: Valence band edge XPS spectra of Nb-N-doped anatase TiO₂ thin films with Nb 9wt.%.

References

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