

Electronic Properties of Nb and N co-doped Anatase TiO₂ Thin Films

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1 Introduction

Anatase titanium dioxide (TiO₂) has been attracted much attention as a photocatalyst. However, anatase TiO₂ can be excited only by ultraviolet light because of its wide band gap (3.2 eV).^[1] For more efficient use of solar energy, it is necessary to extend the optical response of TiO₂ to the visible-light region. One of the effective methods synthesizing visible-light active photocatalyst is co-doping of the metal and the nonmetal elements. The compensation effect between the metal ions (act as donors) and the non-metal ions (act as acceptors) contribute to the high photocatalytic activity under the visible light.^[2,3]

In this research, niobium (Nb) and nitrogen (N)-doped anatase TiO₂ single-crystal films were fabricated by the vapor growth method that enables to control the dopant concentration accurately. The electronic properties of the films were investigated using the X-ray photoelectron spectroscopy (XPS) and the X-ray absorption fine structure (XAFS).

2 Experiment

The non-doped and the Nb-doped anatase TiO₂(001) thin films were fabricated on LaAlO₃(100) substrate using pulsed laser deposition (PLD). Sintered pellets composed of TiO₂ and Nb₂O₅ were used as the PLD targets. The prepared films were subsequently annealed in ammonia gas flow for 3 hours at 870 K and 970 K, respectively.

X-ray diffraction measurements have been conducted to investigate the structural properties of the prepared films. The 004 anatase diffraction peaks are clearly observed and shift toward lower diffraction angles in proportion to the concentration of niobium, following Vegard's law, indicating the formation of anatase solid solutions with niobium oxide.

3 Results and Discussion

Figure 1 shows N1s core level XPS spectra of the fabricated films with various Nb and N concentrations. For the films without Nb, two different peaks are observed around 400 eV. The peak at the binding energy of 400 eV is derived from the interstitial nitrogen (N_i) and that at 396.8 eV is due to the substitutional nitrogen (N_s), respectively.^[4] N 1s spectra indicate that the increase in nitrogen dopant concentration depends on the annealing temperature. Previous studies have reported that the N_s

leads to the band-gap narrowing and contributes to extend the optical response of TiO₂ to the visible light region, while the N_i acts as the recombination center and depresses the photocatalytic activity. For the Nb-doped TiO₂ samples, the N_s peak is clearly observed while the N_i peak is merely seen. The difference in N1s peaks of N-doped and Nb-N-doped TiO₂ are interpreted by the following mechanism.

1. TiO₂ has the valence band mainly derived from O 2p and the conduction band contributed from Ti 3d orbital.
2. Since the Nb impurity state forms the impurity band near the bottom of the conduction band, Nb incorporation leads to the forming of the degenerated conduction band. Nb ions exist as Nb⁵⁺ in the band and release the conduction electrons.
3. Incorporated nitrogen forms the partially occupied N 2p band just above the valence band. The electrons on the degenerated conduction band are trapped by the N 2p acceptor band for stabilization (compensation effect).

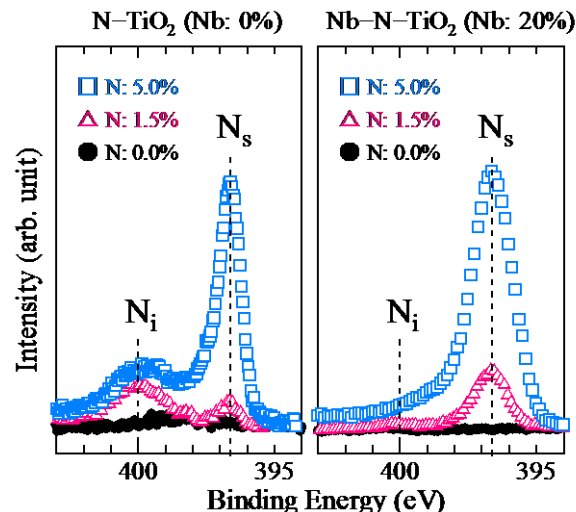


Fig. 1: N1s XPS spectra of the fabricated films with various Nb and N concentrations.

References

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