Fabrication, N-doping Mechanism and Evaluation of N-doped TiO$_2$ Thin Films Based on Laser Ablation Method

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Abstract

The relation among the change of the crystal structure, the amount of doped N and the photocatalytic activity for the decomposition of methylene blue was studied. The N-doping was promoted by the change of the crystal structure from the rutile phase to the anatase phase. The photocatalytic activity for the decomposition of methylene blue was enhanced by an increase in the amount of anatase crystals and doped N.

1. Introduction

The earth is faced with difficult problems such as global warming and energy resources. It is important to create renewable energy resources such as hydrogen instead of using fossil fuels. Environmental pollution, for example, dioxin contamination is also regarded as a serious global problem.

Titanium (IV) oxide (TiO$_2$) is well known as an efficient photocatalyst which can produce hydrogen and decompose pollutants [1-4] using light. However, it is only activated under UV light because of its wide band gap. Therefore, the fabrication of visible light-responsive photocatalysts has received considerable attention because visible light occupies the main part of solar light. The development of the future generation of photocatalytic materials is important for the efficient use of solar light. There have been many reports [5-26] on the introduction of N atoms through substitutional doping into the TiO$_2$ lattice in place of O atoms, mainly to decrease the TiO$_2$ band gap (3.2 eV) and hence

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to improve the associated photocatalytic activity under visible light. Additionally, the state of doped nitrogen in the N-doped TiO_2 lattice was also discussed [27-29].

In 2004, Suda *et al.* [30, 31] reported the preparation of N-doped TiO_2 films from TiN and TiO_2 by the laser ablation method under mixed gases of N_2 and O_2. However, they had no discussion on the N-doping process and also no evaluation of the N-doped TiO_2 films. In this paper, we mainly studied the N-doping process into TiO_2 films by the laser ablation and the photocatalytic activity of the N-doped TiO_2 thin films.

2. Experimental

5.5 g of TiO_2 (Degussa P25) and 0.55 g of paraffin (Wako) were mixed to prevent cracking. It was pressed at 20 MPa for 1 h and calcined at 400 °C for 6 h to form a TiO_2 target. The second harmonics (532 nm) of a Nd:YAG pulse laser (Spectra-Physics Co., GCR-130-10) was used with a pulse width of 7 ns and a repetition rate of 10 Hz. The laser beam of cross section 0.8 cm^2 was focused onto an area of about 0.03 cm^2 using a quartz lens with a focal distance of 30 cm. To avoid the damage of the target by continuous irradiation of the laser beam, the target was rotated at 14 rpm during the deposition.

Irradiation of the target with a laser beam melted the target to form a plume. The ablated-particles were accumulated on the quartz substrate and the TiO_2 thin film was formed. The fluence of 2.8 J/(pulse cm^2) and the laser irradiation time of 12 min were used throughout the experiment. The distance between the substrate and the target was fixed at 3 cm. The experiments were carried out under the following conditions; the substrate temperatures are 298-873 K and the nitrogen gas pressures are 3.3-267 Pa. The non-doped TiO_2 thin film was also prepared as a reference by the laser ablation method under conditions of an O_2 pressure of 133 Pa and a substrate temperature of 873 K.

The prepared thin films were characterized by XRD (X-ray diffraction, Rigaku Rint-2000) and XPS (X-ray photoelectron spectroscopy, Shimadzu ESCA-1000).

The photocatalytic activity of the prepared thin films was evaluated by measuring the rate of the decomposition of methylene blue under light irradiation. The thin film was fixed on a stand and dipped into a 50 cm^3 beaker containing 1×10^{-5} mol / dm^3 methylene blue solution. This solution was irradiated under visible light from the top of the beaker. A xenon lamp (Ushio, 500 W) was used as a visible light source with an L42 cut-off filter. The rate of the decomposition of methylene blue was determined by measuring the change in the absorbance of methylene blue during irradiation using absorption spectroscopy (Shimadzu, MPS-2000).

3.   Results and Discussion

Fig. 1 shows the absorption spectra of (a) the TiO_2 thin film prepared at 600 °C under O_2 gas of 133.3 Pa (1 Torr) and (b) the yellowish N-doped TiO_2 thin film prepared at 600 °C under N_2 gas of 133.3 Pa (1 Torr). The nitrogen substitutional doping of TiO_2 is thought to be a method for narrowing the band gap by changing the valence band structure without any change in the position of conduction band [14].
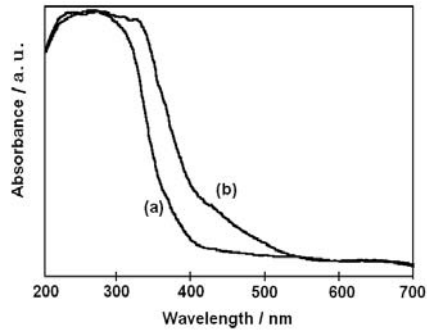
Fig. 1. Absorption spectra of (a) the white thin film and (b) the yellowish thin film under conditions of (a) O_2 133.3 Pa (1 Torr) and (b) N_2 133.3 Pa (1 Torr) (substrate temperature: 600 °C).

XRD spectra of the N-doped thin films indicate a decrease in the anatase phase with decreasing N_2 gas pressure as shown in Fig. 2. The intensity in the rutile phase in turn increases with decreasing N_2 gas pressure.
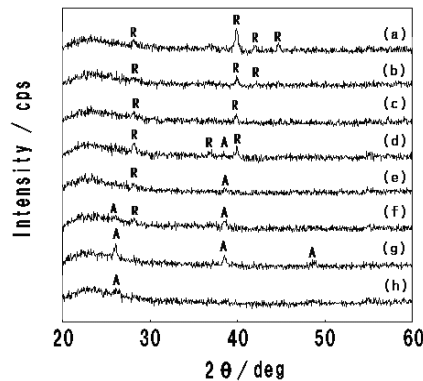

Fig. 2. XRD patterns of the thin films prepared under various nitrogen pressures ((a) 3.3 Pa, (b) 6.7 Pa, (c) 13 Pa, (d) 27 Pa, (e) 67 Pa, (f) 133 Pa, (g) 200 Pa, (h) 267 Pa). A and R denote anatase phase and rutile phase, respectively.

Fig. 3 shows the relation among the relative amount of doped N and the sum of the integrated intensity of all anatase peaks and that of rutile peaks as a function of N_2 gas pressure at a substrate temperature of 873 K. The rutile phase decreased, while the anatase phase appeared around 20 Pa and then increased with increasing N_2-gas pressure. Kitazawa *et al.* [32] reported the effect of O_2 gas pressure on the production of the rutile and the anatase using the laser ablation method. It can be explained as follows. The clustering of the ablated particles occurs during flight and then the crystal growth is induced on a heated substrate. With increasing gas pressure, the clustering of the laser-ablated particles progresses and their velocity decreases, resulting in the prevention of the crystal growth of the rutile and promotion of the anatase due to lack of the thermal

energy. Such an explanation can be adopted also in our case of N_2 gas atmosphere. The relative amount of anatase calculated using AA/(AA+AR) (AA and AR are the total area of all anatase and rutile peaks, respectively) at an N_2-gas pressure of 133 Pa (99%) was higher than that of an O_2-gas pressure of 133 Pa (80%) at a substrate temperature of 873 K.
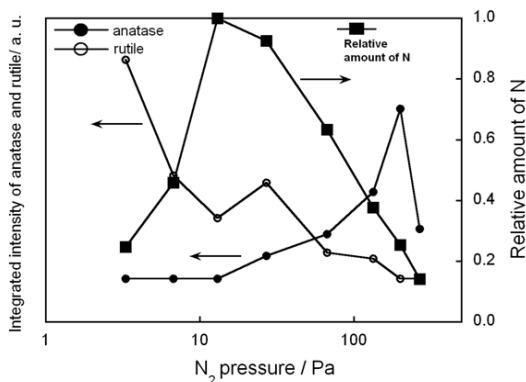

Fig. 3. The relation among the relative amount of doped N, the integrated intensity of all anatase peaks and that of rutile peaks as a function of N_2 gas pressure at a substrate temperature of 873 K.

The relative amount of doped N was estimated from the XPS data using the ratio A / A_{max}, where A is the integrated intensity of the XPS peaks of nitrogen doped in the TiO_2 lattices (the binding energy is ca. 397 eV) [30] and A_{max} is the maximum peak intensity of nitrogen under an N_2 gas-pressure of 13 Pa. The peaks around 406 eV of the binding energy correspond to nitrogen species in air [30], which are adsorbed on the TiO_2 surface and was almost constant at each N_2 gas pressure. It is found from Fig. 1 that the amount of doped N increases with increasing N_2-gas pressure up to around 20 Pa and decreases through the maximum. Notice that the pressure at which the formation of anatase phase starts corresponds to the maximum amount of doped N. It is clear that the N-doping easily occurs near the pressure at which the change of the crystal structure from the rutile to the anatase starts because of its instability. The films turned yellow only when the substrate temperature was higher than 773 K and the yellow of the films became deeper at higher temperatures. These results imply that the N-doping is accelerated by the thermal energy of the heated substrate. We suggest the N-doping process as follows. (I) N_2 molecules are adsorbed on the ablated TiO_2 particles (plume) in the gas phase during flight (some nitrogen in the gas are doped into the TiO_2 lattice, but it is not major), (II) the particles collide on the heated substrate, (III) the migration of the particles occurs on the heated substrate and (IV) nitrogen species are doped into the TiO_2 lattice at the same time as the migration.

Fig.4 shows the SEM image of the N-doped TiO_2 thin film prepared by the laser ablation method (N_2 1Torr, 600°C). From this image, we can see that the surface is rough. A large number of pores were also observed.
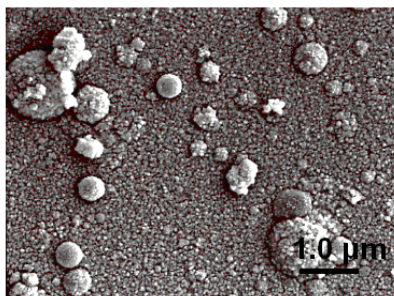
Fig. 4. The SEM image of the N-doped TiO_2 thin film (N_2: 133.8 Pa (1 Torr), substrate temperature: 600 °C).
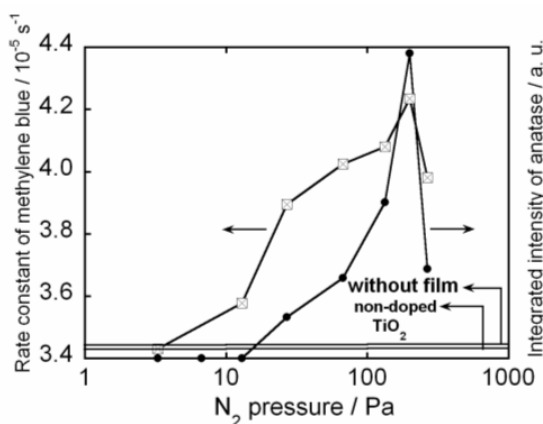

Fig. 5. The relation between the integrated intensities of all anatase peaks and the rate constant of the decomposition of methylene blue as a function of N_2 gas-pressure at substrate temperature of 873 K.

Fig. 5 shows the relation between the integrated intensities of all anatase peaks and the rate constant of the decomposition of methylene blue as a function of N_2-gas pressure. The rate constant k for the pseudo first order reaction was obtained from the initial linear portion using the relation (Eq. 1).

$$ln\ ([MB] / [MB]_0) = -kt, \tag{1}$$

where $[MB]_0$ is the initial concentration of methylene blue, $[MB]$ is the concentration of methylene blue after time t of photocatalytic decomposition. An increase in the rate of methylene blue decomposition can be noticed in the pressure range of 3.3-200 Pa and the rate was decreased at 267 Pa as shown in Fig. 2. These increase and decrease are explained by the increase and decrease of the amount of anatase phase, respectively. Moreover, the curve of the rate constant was convex upword at the region of 150-200 Pa as compared with that of the amount of the anatase phase. This difference implies that the

photocatalytic activity under visible light was enhanced by the increase of the amount of N doped in the TiO_2 lattice.

4.   Conclusion

In the present work, the N-doped TiO_2 thin films were fabricated by the laser ablation method and evaluated as a photocatalyst. We proposed the plausible mechanism of nitrogen doping by the laser ablation method. The elucidation of the mechanism will contribute to the development of more useful visible light-responsive photocatalyst thin films.

Acknowledgements

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