

Nitridation of TiO₂ Film by Reactive Sputtering for Visible Light Sensitization

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We realized the nitrogen doping in TiO₂ sputtered film without any oxygen defects that are thought to behave as the center of recombination, which results in the improvement of photocatalytic activity under visible light (wavelength>400nm) irradiation. Nitrogen-doped TiO₂ film was deposited on quartz substrate by Ar/N₂ mixture sputtering of TiO₂ ceramic target at a total gas pressure of 3.0 Pa without substrate heating, and annealed at 480 degree C in N₂ gas for 2 hours, consequently.

Key words: Nitrogen-doped TiO₂, Magnetron sputtering, Visible light sensitization, Oxygen defects

1. INTRODUCTION

Titanium dioxide (TiO₂) has been well known as a photocatalyst since the discovery of photoinduced water splitting at its electrodes [1]. When ultraviolet light with higher energy than the band-gap of TiO₂ is irradiated, inter-band transition can be induced resulting in the generation of electron and hole pairs. Such excited electrons and holes photogenerated in the TiO₂ photocatalysts have strong reduction and oxidation power, respectively, and they can diffuse to the TiO₂ surface and can drive a variety of reactions. These reactions are useful for the decomposition and mineralization of pollutants and undesirable compounds in the air and in waste water [2-7]. It is considered that the development of the photocatalysts showed photocatalytic activities under visible light irradiation to utilize sunlight or rays from artificial sources more effectively. So visible light sensitization of TiO₂ with a low non-radiative recombination rate in the material should be the key technology to make a breakthrough in the application of photocatalytic materials for versatile usage. For this aim, various methods have been investigated [8,9]. Visible light sensitization of TiO₂ photocatalyst can be caused by nitrogen doping or introduction of oxygen defects, as generally recognized [10-14]. But, oxygen defects act as the recombination center for the optically generated carriers. Nitrogen doping in high temperature TiO₂ sputtering causes oxygen defects partially. To improve the catalytic activity of visible light sensitive TiO₂, the oxygen-defect-free nitrogen doping had been one of the significant subjects.

It is thought that most useful style of photocatalyst is thin film on glass substrate, which has been synthesized mainly by wet processes such as the sol-gel method using titanium alkoxide. Compared with the conventional wet processes, sputter deposition is one of the most promising techniques for large area uniform

coatings with a high packing density and strong adhesion [15,16]. Nitrogen doping in TiO₂ film by reactive sputtering may be a hopeful candidate to produce a photocatalyst activated with visible light.

In this study, N-doped TiO₂ films were prepared by means of a sputtering method. In addition, these films scarcely had oxygen defects that are thought to behave as the center of recombination, which is responsible for decreasing photocatalytic activity.

2. EXPERIMENTAL

The N-doped TiO₂ films were deposited by rf magnetron sputtering (JEH-430RSC, JEOL) using a TiO₂ target (99.9%, Kojundo Chemical Laboratory Co.) on borosilicate glass substrates coated with fluorine-doped SnO₂ (Solaronix Co., 10ohm/sq, transparency 80%). The substrate temperature was at room temperature or 480 degrees C. Rf power was 300W. The nitrogen flow ratio [N₂ / (N₂+Ar)] was from 0 to 40%. Total gas pressure during the deposition was kept constant at 3.0Pa to keep the sputter damages to minimize, leading to vacancies in the crystal lattice. The deposition time was 105 min., resulting in a film thickness of 200nm.

Film thickness was measured by a surface texture measuring instrument (SURFCOM1400D, TOKYO SEIMITSU Co.). The crystal structures of the films were analyzed by X-ray diffraction (XRD, RINT-2000, Rigaku Co.) with 50 kV and 300mA. Raman spectroscopic analysis was applied to evaluate not only the crystal structure of the films, but also the oxygen deficiency. The micro-Raman measurements were performed at room temperature in backscattering geometry using a 514.5nm Ar ion laser. A spectrometer equipped with a SPEX1403 double monochromator (Jobin-Yvon Co.) was employed. The signal was detected by an LN/CCD-1340x100PB cooled CCD device (Roper Scientific Co.).

Photocatalytic activity of the N-doped TiO₂ film deposited on the substrate (20x20 mm²) was evaluated by measuring the decomposition rates of methylene blue (Wako Pure Chemical Industries, Ltd., 10 μmol dm⁻³) in aqueous solution (10 mL). Absorbance of methylene blue and transmittance of films were monitored by a UV/Vis spectrometer (JASCO V-550, JASCO Co.). A solar simulator (PEC-L 10, Peccell Technologies, Inc.) as the light source was used, and the short-wavelength components of the light (<400nm) were removed using a cutoff glass filter.

3. RESULTS AND DISCUSSION

The films prepared under high temperature condition (480 degrees C) were crystalline, with features assignable to a mixed structure of the anatase and rutile crystalline phases, as determined by Raman spectroscopic analysis and XRD (data is not shown). From the XPS measurement, it was ascertained that the peak of XPS was located at 396eV assigned Ti-N bonding, that is, the O atoms were replaced by N atoms

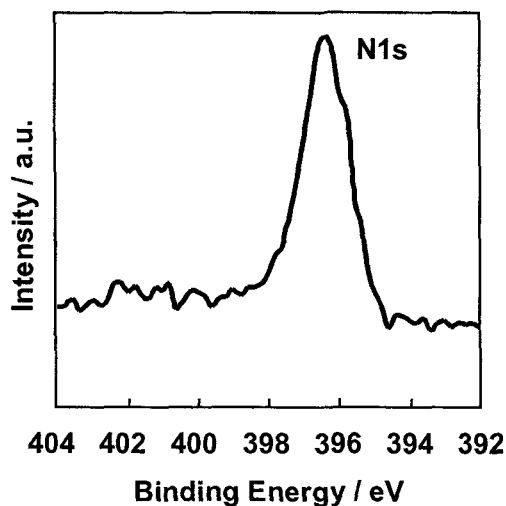


Fig. 1 XPS spectrum of N-doped TiO₂ film.

(Fig. 1). The films were yellowish and transparent. Transmission spectra of these films are shown in Fig. 2. Photoabsorption of N-doped TiO₂ films in the visible region is stronger than that of non-doped TiO₂ films that were prepared in a similar fashion by sputtering in Ar 100% gas. The reason for the decrease of transmittance with increase of the N₂ gas ratio was considered to be that the metal like compound (e.g. TiN) was produced at a high N₂ partial pressure condition. So the proportion of the reflectance of the film increased, and the transmittance consequently decreased. As a result of taking transmittance and reflectance into consideration, we adopted that the N₂ gas ratio was 20%.

As a shown in Fig. 3, however, there was hardly any difference among the activity of each of the photocatalysts under visible light irradiation at 400nm or higher. These results indicated that the photocatalytic activity of N-doped TiO₂ film in the visible region was caused by oxygen defects. It is well known that oxygen defects were produced in TiO₂ (non-dope) film prepared by magnetron sputtering under a high temperature

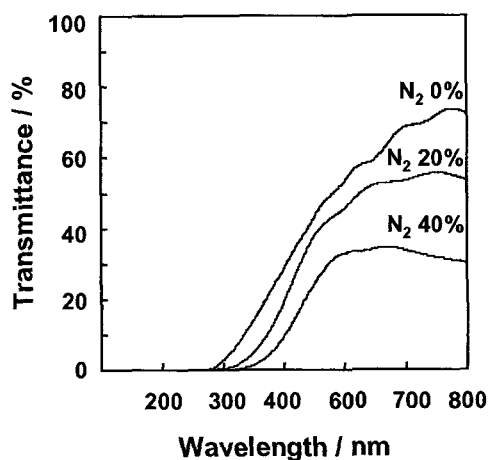


Fig. 2 Transmission spectra of N-doped and non-doped TiO₂ films. N₂ 0%, 20%, 40% represent the nitrogen flow ratio [N₂/(N₂+Ar)] at sputtering.

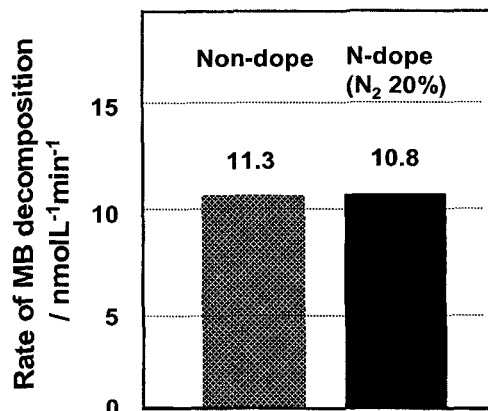


Fig. 3 Photocatalytic decomposition of methylene blue using N-doped TiO₂ or non-doped TiO₂ films under visible light (>400nm) irradiation.

condition [17]. It was considered that oxygen defects lead to photoabsorption and photocatalytic activity in the visible region.

In order to confirm the formation of oxygen defects, N-doped TiO₂ film was analyzed by means of Raman scattering. Figure 4(a) shows a Raman spectrum of N-doped TiO₂ film. The peaks of anatase and rutile were shifted from 143cm⁻¹ to 155cm⁻¹, and from 447cm⁻¹ to 424cm⁻¹, respectively. J.C.Parker *et al.* [18] reported the relation of Raman peaks and oxygen deficiency in TiO₂ particles. Based on their results, the examined material has about 10% oxygen deficiency. So it was considered that the photocatalytic activity of N-doped TiO₂ film prepared under this condition in the visible region is due to oxygen vacancies. Oxygen defects are thought to behave as the center of recombination, which is responsible for decreasing photocatalytic activity, therefore it is to be desired that N-doped TiO₂ film is prepared without oxygen defects.

To avoid the formation of oxygen defects in the N-doped TiO₂ films, the substrate temperature was

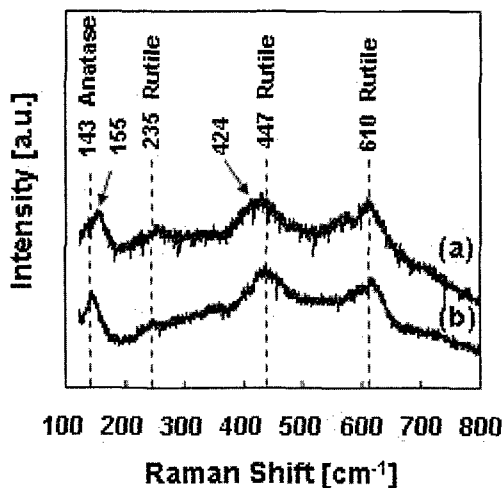


Fig. 4 Raman spectra of N-doped TiO₂ films deposited at 480degrees C (a), and room temperature (b).

changed from 480 degrees C to room temperature. The nitrogen flow ratio [$N_2/(N_2+Ar)$] and total gas pressure during the deposition were not changed. Under this condition, it was found that the deposited layer was amorphous by measuring the XRD spectra. So after the deposition, the substrate with the deposited layer was annealed at 480 degrees C in N₂ gas for 2 hours. Non-doped TiO₂ films were prepared in a similar fashion by sputtering in Ar 100% gas and subsequently annealed at 480 degrees C in N₂ gas for 2 hours to compare the N-doped TiO₂ films with non-doped TiO₂ films with respect to photocatalytic activity.

Fig. 5 shows photocatalytic activities of N-doped TiO₂ films and non-doped TiO₂ films. In this procedure, non-doped TiO₂ films were not yellowish and had little ability to decompose methylene blue under visible light irradiation. This indicates that non-doped TiO₂ films prepared in this method were not doped of N and hardly had oxygen defects. They exhibited very little activity compared with the blank, however, it was considered

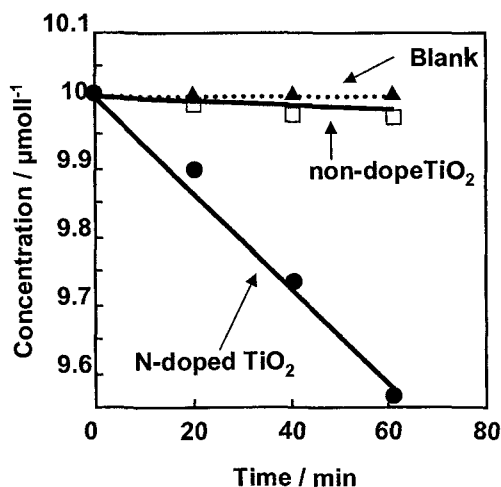


Fig. 5 Photocatalytic activities of N-doped TiO₂ or non-doped TiO₂ films under visible light (>400nm) irradiation.

that the very little activity was due to the oxygen deficiency resulting from the partially reduction by N atoms, because under this condition the atmosphere was reductive, so O atoms were reduced with N atoms partly and produced the oxygen deficiency. This very little activity vanished in the case of annealing at 480 degrees C in air instead of N₂ for 2 hours. The results revealed that the oxygen deficiency was formed very slightly in this condition, but the amount of it was basically negligible. On the other hand, N-doped TiO₂ films have photocatalytic activity under visible light irradiation. The reaction rate of this condition (approximately 8 nmolL⁻¹min⁻¹) was lower than that of the high temperature sputtering condition (10.8 nmolL⁻¹min⁻¹). The reason is that the reaction rate of the high temperature sputtering condition was the total of N-doped effect and the oxygen deficiency effect. In this condition, the oxygen deficiency effect was gone so the reaction rate was decreased. At the present time, we have considered that films having no oxygen defects are better even if photocatalytic activity was lower. Because the advantage of high crystallinity leading to a long carrier life is greater than behaving as the center of recombination, that is, the high crystalline (no oxygen defects) material has potential for photocatalytic reaction. Because of the reduction of photocatalytic activity of non-doped TiO₂ films, it was presumed that N-doped TiO₂ films scarcely had oxygen defects (Fig. 4(b)). So it was considered that their photocatalytic activity under visible light irradiation was based on the band-gap narrowing that resulted from the substitutional doping of N for O in the TiO₂ crystal.

3. CONCLUSION

N₂ annealing of sputtered TiO₂ film is the effective method of nitrogen doping without oxygen defects introduction and results in the improvement of its photocatalytic activity. It is expected that film without oxygen defects, thought to behave as the center of recombination, may enable the activity to improve by optimizing the preparation condition.

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