Preparation of N-Doped TiO_x Films as Photocatalyst Using Reactive Sputtering with Dry Air

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Pale yellow N-doped TiO_x films on the glass substrate were prepared by RF magnetron reactive sputtering of Ti target in a mixed gas of argon and dry air. The characteristics of the N-doped TiO_x films were studied by SEM, XRD, UV-Vis spectrophotometer and XPS. The photocatalytic ability was evaluated by degradation of NO gas. The air flow ratio has a significant effect on the produced phase and the bonding states of Ti, O and N, resulting in the variation of the optical property and photocatalytic ability. The large amount of N atoms doped and oxygen deficiency are detrimental for photocatalysis, and N bonding states may not be the major contributing factor for the photocatalysis. It is suggested that the coexistence of N₂ gas with O₂ gas shifts the TiO₂ formation boundary towards the low oxygen concentration, which leads to various N (N oxide) doping states on N-doped TiO_x film. [doi:10.2320/matertrans.M2009063]

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1. Introduction

Recently, it is found that N (nitrogen)-doped TiO₂ (titanium dioxide) photocatalyst is activated under visible light irradiation as well as under ultraviolet irradiation.¹⁾ To realize a more efficient utilization of solar irradiation, many studies have been focused on the N-doped TiO₂ powders produced by various routes.²⁻⁴⁾ Various methods for preparing thin films of N-doped TiO₂ by gas condensation techniques have also been reported in recent years, such as reactive DC magnetron sputtering using Ti target in N₂/O₂ mixture gases,⁵⁾ pulsed laser deposition using TiN target in N₂/O₂ mixture gases,⁶⁾ and sputtering using TiO₂ target in N₂ gas.⁷⁾ Among those techniques, RF magnetron reactive sputtering is the most widely used method for thin film preparation and is advantageous for producing uniform, well-crystallized, and large-area films. The film thickness, crystal structure, composition, microstructure and defect structure are determined by many factors such as sputtering power, substrate temperature, partial pressures of sputtering gas, sputtering time, and distance from target to substrate.^{8,9)} However, many studies for N-doped TiO₂ film have focused only on the nitrogen flow ratio.^{5,6,10)}

Meanwhile, many researches have reported the relation between the nitrogen doping and the oxygen deficiency in TiO₂.¹¹⁻¹³⁾ On the basis of their results, the oxygen flow ratio is also important. For the non-doped TiO₂, the oxygen concentration has been considered as one of the most important factors for efficient photocatalysis because oxygen vacancies in TiO₂ may produce charge transfer states that can contribute to the photocatalytic activity.¹⁴⁾

The purpose of the present work is to prepare the N-doped TiO₂ films using RF magnetron reactive sputtering of Ti target in a mixture of Ar gas and dry air, with the set N₂/O₂ ratio, especially in the range of lower oxygen concentrations than the reported ones,^{5,15-19)} and to investigate the effect of air flow ratio (oxygen ratio) variation on the formation of

anatase TiO₂ and the physical properties in conjunction with the photocatalytic properties.

2. Experimental

Depositions were performed using an RF magnetron reactive sputtering apparatus. A titanium disk (99.9% purity) of 75 mm in diameter was used as a target and a glass plate (28 × 48 × 1 mm) as a substrate. Prior to sputtering deposition, the surface of the glass plate was rubbed with SiC abrasion paper (mesh No. 80). A mixture of Ar gas and dry air (N₂ : O₂ = 79 : 21(vol%)) (or O₂ gas for comparison) was used as the sputtering gas. The RF input power, sputtering time, and substrate temperature were fixed at 300 W, 3 h, and 473 K, respectively. The background pressure in the chamber was 1.0 × 10⁻³ Pa. The flow ratios of Ar and dry air were controlled by mass flow controllers. The distance between the substrate and the target was fixed at 70 mm. The conditions of working pressure and gas flow ratio, i.e. air flow ratio (AFR), oxygen ratio, and nitrogen ratio for each sample are shown in Table 1, where $f(\text{Ar})$, $f(\text{O}_2)$, and $f(\text{N}_2)$ are the individual flow rates of the gases.

At the beginning of film preparation, a glass substrate was protected by a shutter and then a target was pre-sputtered in

Table 1 Sputtering deposition conditions for each sample.

Sample	Air flow ratio (AFR) $f(\text{air})/f(\text{Ar})$	Working pressure (Pa)	Oxygen ratio $f(\text{O}_2)/f(\text{Ar})$	Nitrogen ratio $f(\text{N}_2)/f(\text{Ar})$
O-1	—	0.74	0.050	—
A-0	0.063	0.70	0.013	0.049
A-1	0.086	0.72	0.018	0.069
A-2	0.125	0.75	0.026	0.099
A-3	0.136	0.76	0.029	0.109
A-4	0.150	0.76	0.032	0.119
A-5	0.163	0.77	0.034	0.128
A-6	0.175	0.78	0.037	0.138
A-7	0.188	0.78	0.039	0.148
A-8	0.200	0.80	0.042	0.158

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Fig. 1 Schematic apparatus for photocatalytic oxidation of NO gas.

Ar atmosphere for about 15 min in order to remove oxide layer and contaminant on the surface of the target, followed by the deposition process under the controlled gas flow. After the deposition, the substrate was slowly cooled in the chamber to room temperature under the flow of the gas mixture.

The crystal structure of the films was evaluated by X-ray diffraction (XRD) with Cu K_{α} radiation at 40 kV and 30 mA operated under the θ - 2θ mode (Rint 2100, Rigaku). Scanning electron microscope (SEM) was used for microstructural analysis (JSM-5800, JEOL). A UV-Vis spectrophotometer (Lambda 900, Perkin Elmer) was used to determine the UV-Vis transmission spectra from 340 nm to 700 nm. Chemical bonding states and concentration of each element at the film surface were analyzed by X-ray photoelectron spectroscopy (XPS) using monochromatic Mg K_{α} radiation (10 mA, 10 kV). The spectra were calibrated with C 1s, which exhibits the binding energy of 284.0 eV. The background pressure of the XPS system was less than 10^{-6} Pa. The depth profiles of the deposited film surface were obtained using Ar^{+} ion sputtering for 180 sec (with the acceleration voltage of 300 V and the assumed removal rate of 6.4 nm/min for SiO_2 standard). Before XPS measurement the film surface was cleaned in distilled water by an ultrasonic cleansing for 30 min and then dried in dry chamber for 6 h at 373 K.

The evaluation on photocatalytic activity of the film was performed by photocatalytic oxidation of NO gas using a

Fig. 2 SEM images of sample A-5; (a) cross-sectional and (b) surface morphology.

chemiluminescence detector (HORIBA APNA-360), as shown in Fig. 1. The film on glass substrate was put in the center of acrylic container ($200 \times 120 \times 10$ mm) with the inner volume of 79 ml. The air and NO gas (197.4 ppm, N_2 balance) were mixed to obtain the desired concentration (NO: 1.0 ppm) in a gas blender. After attaining the steady state of NO concentration through the by-pass line, the film in the main line was irradiated with a Xenon lamp (USHIO, UXL-500D-O, 500 W) from a distance of 700 mm through the quartz window for 5 min (300 s) at the beginning of the measurement, and then the NO gas was flown into a longitudinal direction of the container (main line) for 1200 s with light irradiation at a flow rate of 1.1 l/min. The UV light intensity at the film surface was 30 W/m^2 measured by a UV Monitor (EKO, CEK-MS211-I). For the visible light irradiation, the UV-filtered light (Koshin Kogaku Co., Ltd, >400 nm) was used.

3. Results

Figure 2 shows the cross-sectional and surface SEM images for the sample A-5 with the film thickness of approximately $1.7 \mu\text{m}$. The film has columnar structure with quite rough surface caused by the roughened substrate, but any crack was not observed. The other samples show similar

Fig. 3 UV-Vis transmission spectra of the films produced under various AFRs.

Fig. 4 X-ray diffraction spectra of the films deposited with various AFRs.

structure to sample A-5, and the thicknesses are approximately 1.7–1.8 μm (except for A-0 which shows about 2.0 μm) with sputtering deposition rate about 0.167 nm/sec.

The colors of the samples were varied from black-gray (A-0, 1), deep yellow (A-2, 3), to pale yellow (A-4 to A-8) with AFR, while non-doped TiO₂ film (O-1 sample) appears transparent. The optical transmission spectra of the samples are shown in Fig. 3. Compared with non-doped TiO₂ (O-1) the transmission band edge of the samples shifts toward the visible light regions as decreasing AFR (from A-8 to A-2). The A-0 and A-1 samples show almost no transmission due to the black-gray film color. It is noted that both A-2 and A-3 samples show a clear transmission/absorption edge around 430–440 nm.

Fig. 5 Unit cell volumes of the films from A-1 to A-8 vs AFR, calculated from (101) and (200) diffractions of anatase TiO₂ in XRD.

Fig. 6 N 1s spectra with XPS of the films prepared with various AFRs.

The X-ray diffraction patterns for the films are shown in Fig. 4. The polycrystalline anatase structure was observed for the samples from A-2 to A-8 and O-1, with small trace of rutile (110) peak. As for the A-0 and A-1 samples with low AFRs, the TiO and amorphous phases were obtained for the former, while the magneli and anatase phases were observed for the latter. The lattice parameters of the anatase phase in the samples from A-1 to A-8 and O-1 are determined with (101) and (200) diffractions peaks, and the corresponding unit cell volume is estimated, as shown in Fig. 5. They are largely decreased from A-2 to A-4 (the value of A-1 also exhibits similar to A-2), while the values are only slightly varied from A-4 to A-8 samples. The non-doped O-1 sample exhibits 0.13584 nm³, which is smaller than the standard TiO₂ (from JCPDS file No. 21-1272,²⁰ 0.13629 nm³), probably due to the residual stress during crystallization.^{21,22}

The N 1s spectra with XPS of A-1 to A-8 and O-1 samples are shown in Fig. 6. The peaks of N 1s are shifted with AFR to the higher binding energy from around 396.4 eV (A-1) to

Fig. 7 Depth profiles for N 1s spectra of the films prepared with various AFRs; (a) A-4, (b) A-5, (c) A-6.

401.5 eV (A-8), with the sample O-1 showing only background noise. Figure 7 shows the N 1s depth profiles of the A-4, 5, 6 samples in order to analyze the N bonding states at both the outermost surface and the inside. The A-4 sample exhibits two broad peaks around 395–397.8 eV and 399–401.5 eV (the range indicated with broken lines). The A-5 and A-6 samples exhibit broad peaks around 397.5–400.5 eV and around 399–401.5 eV, respectively. Further, the surface atomic concentrations (Ti, O, and N) of the films prepared with various AFRs are shown in Fig. 8, where the concentration of each element is estimated from the individual XPS peak area divided by atomic sensitivity factor (ASF). The

titanium and nitrogen concentrations gradually decrease with AFR (Fig. 8(a), (c)), while the oxygen concentration gradually increases (Fig. 8(b)).

The typical result of photocatalytic test is shown in Fig. 9(a). Compared with the blank test (no sample inside the container) both O-1 and A-5 samples clearly show the photocatalytic decomposition of the NO gas. The (outlet) concentration of NO gas is rapidly decreased with the light irradiation for both samples, and kept constant for the former, while slightly decreased and gradually increased for the latter. At the same time, both concentrations of NO₂ gas are rapidly increased with the irradiation, and kept constant for

Fig. 8 Variations of atomic concentration of the films prepared with various AFRs; (a) Ti 2p, (b) O 1s, (c) N 1s.

the former, while gradually increased for the latter. For the A-5 sample the amount of removed NO during light illumination for 1200 s was 0.31 μmol , and the generated NO₂ was 0.18 μmol , which was 58.1% of the removed NO. The rest of the removed NO (0.13 μmol) is inferred to be oxidized into NO₃⁻ or HNO₃ and then fixed on the film surface,^{23,24)} or directly decomposed into N₂, O₂, and N₂O.²⁵⁾ Figure 9(b) shows the amount of removed NO (Q_{NO}) and the amount of generated NO₂ (Q_{NO_2}) under the (UV + visible) light for various samples. The TiO, amorphous and magneli phases (sample A-0, A-1) show less photocatalytic ability than the anatase (A-2 to A-8, and O-1). The A-4, A-5 and A-6 samples exhibit the highest activity among the samples. On the other hand, the photocatalytic activity under visible light is significantly small, at least by an order of magnitude, the

Fig. 9 Photocatalytic activity of the samples under irradiation of (UV + visible) light; (a) photocatalytic oxidation of 1 ppm NO for O-1 and A-5 samples, (b) the amount of removed NO and generated NO₂ for all samples.

Fig. 10 Photocatalytic oxidation of 1 ppm NO for O-1 and A-5 samples under irradiation of visible light.

example of which is shown in Fig. 10. The A-5 sample exhibits slight decrease of NO gas with almost no change of the NO₂ concentration, and the A-4, 6, 7, 8 samples show similar photocatalytic activity to the A-5 sample, where the amount of the NO_x removed ($Q_{\text{NO}_x} = Q_{\text{NO}} - Q_{\text{NO}_2}$) is between 0.012 and 0.021 μmol . The O-1 sample shows no change in either NO or NO₂ gas as expected, which are interestingly similar to the A-0, 1, 2, 3 samples.

Table 2 Oxygen ratios, nitrogen ratios, and formed phases for the present and reported researches on non-doped TiO₂ and N-doped TiO₂ film preparation.

Sputtering type		Oxygen ratio $f(\text{O}_2)/f(\text{Ar})$	Nitrogen ratio $f(\text{N}_2)/f(\text{Ar})$	Formed phases	References
This work	RF	0.050	—	TiO ₂ (anatase + rutile)	
		0.026 to 0.042	0.099 to 0.158	TiO ₂ (anatase + rutile)	
		0.018	0.069	Magneli + TiO ₂	
		0.013	0.049	TiO + Amorphous	
Reported researches (non-doped TiO ₂)	RF	Below 0.031	—	Ti + Amorphous	Takamura <i>et al.</i> ^{27)*}
		Above 0.075	—	Amorphous TiO ₂	
	RF	0.060	—	TiO	Bally <i>et al.</i> ^{28)**}
		0.100	—	Ti ₂ O ₃	
		0.120	—	TiO ₂ (anatase + rutile)	
	DC	Below 0.036	—	Metallic	Tavares <i>et al.</i> ²⁹⁾
				Sub-stoichiometric	
				Amorphous	
	DC	Above 0.044	—	stoichiometric TiO ₂	
				Amorphous	
Reported researches (N-doped TiO ₂)	DC	0.060	0.0017, 0.0067	TiO ₂ (rutile)	Lindgren <i>et al.</i> ⁵⁾
			0.013, 0.027	TiO ₂ (anatase)	
	RF	0.077	0.462	TiO ₂ (anatase)	Sakai <i>et al.</i> ¹⁵⁾
	RF	0.077	0.462	TiO ₂ (anatase)	Obata <i>et al.</i> ¹⁶⁾
	DC	0.150	0.05 to 0.2	TiO ₂ (anatase + rutile)	Wong <i>et al.</i> ¹⁷⁾
			0.3	TiN	
	DC	0.250	0.006 to 0.063	TiO ₂ (anatase + rutile)	Prabakar <i>et al.</i> ¹⁸⁾
	DC	1.000	0.2 to 0.8	TiO ₂ (anatase + rutile)	Chiu <i>et al.</i> ¹⁹⁾

*Thin film prepared by Takamura *et al.*²⁷⁾ has a thickness of only ~65 nm.

**Thin film prepared by Bally *et al.*²⁸⁾ was deposited at low working pressures (0.10 Pa) where the mean free paths of the sputtered particles are very high and they reach the substrate with high kinetic energy resulting in the metallic nature (non-stoichiometric)³⁰⁾ even with high oxygen ratio (0.100).

4. Discussions

The N doping often causes the shift in the transmission band-edge toward the visible light range and the cell-volume expansion (the N³⁻ anion (0.171 nm) is larger than the O²⁻ anion (0.132 nm)),^{11,26)} both of which are observed in our results. When considered from the atomic concentrations, the unit cell volumes and the optical properties, the A-2 and A-3 samples should contain high concentration of N atoms in the TiO₂ anatase phase with high oxygen deficiency. It is notable that the range of O₂/Ar gas flow ratio in the present sputtering condition is lower than other reported conditions for N-doped TiO₂ film productions,^{5,15–19)} as shown in Table 2. The $f(\text{O}_2)/f(\text{Ar})$ value of 0.026 may exhibit the minimum oxygen flow ratio that is necessary to produce anatase TiO₂ under the N₂ gas coexistence. Besides, compared with the reported researches on non-doped TiO₂ film,^{27–29)} the boundary of phase formation from TiO (or magneli) to TiO₂ may be shifted towards the low oxygen concentration. It seems that the $f(\text{O}_2 + \text{N}_2)/f(\text{Ar})$ gas flow ratio determines the boundary for the formation of anatase TiO₂ in the RF sputtering, and that the coexistence of N₂ gas contributes to stabilizing the anatase TiO₂ phase.

The A-2 to A-8 samples can contain various N doping states in TiO₂, which are extremely sensitive to the small variation in the oxygen ratio range of 0.026–0.042 (AFR: 0.125–0.200). Recently, Asahi *et al.* reported⁷⁾ the visible-light sensitization of the anatase phase by introduction of

N complex species in TiO₂, where they claim the binding energies between 396 eV and 400 eV correspond to the N atoms or other complex species such as NO or NO₂ at the substitutional and/or interstitial sites in the TiO₂ lattice. Based on their report the observed binding energies of N 1s peaks for the A-2 to A-8 samples may correspond to substitutional N (A-2, 3), substitutional N and interstitial NO (A-4), substitutional NO (A-5), substitutional NO₂ or interstitial NO (A-6), and adsorbed N₂ (or NO, NO₂) (A-7, 8), respectively. And, the contained substitutional/interstitial N or N oxide dopants exist at both the outermost surface and the inside (from the depth profile result).

As to the relation with the photocatalysis of the samples it is still difficult to determine the main contributing factor. The A-4, 5 samples exhibit more red-shift in the light absorption compared with A-6 sample, and the doped N amount slightly decreases as going from A-4 to A-6. Thus, although the A-4, 5, 6 samples exhibit similar photocatalytic ability, the reason and the mechanism could be quite different. One interesting point is that all the three samples contain 1.9–2.0 at%N, the amount of which could be important for the photocatalysis, but the binding energies and therefore the atomic bonding configurations are quite different.

The A-2 and A3 samples, which exhibit the clean and smooth red shift in the light absorption spectra, not only possess modest photocatalysis for NO degradation (under UV + visible light) but do not have any photocatalysis under visible light. It is thus suggested that a large quantity of N

atoms doped may provide active recombination centers for holes and electrons, degrading the photocatalysis.^{3,5,7,10} Also, although the bulk crystal structure of the deposited film exhibits the anatase TiO₂ phase, the outermost surface of the film could be quite different from the inside in that there would be residual surface stress, dangling bonds, chemically and physically adsorbed gases, variation in the constituent composition, more vacancies with oxygen deficiency, and so on.^{31,32} Further observation and analysis on the surface doping states involving the electronic bonding states, the atomic structure and electronic structure, and the composition near the surface is needed to explain the observed photocatalytic abilities and the underlying science.

5. Summary

The N-doped TiO_x films were prepared by RF magnetron reactive sputtering of Ti target in a mixed gas of Ar and dry air. By varying air flow ratios with the set O₂/N₂ gas composition, the lowest reported O₂ gas concentration is achieved in terms of TiO₂ phase formation. As decreasing the air flow ratio, the color of the film changes from pale-yellow to dark-yellow, even black-gray, and the light transmission band edge shifts toward the visible light regions due to the nitrogen (nitrogen oxide) doping. The air flow ratio has a significant effect on the produced phases and the bonding states of Ti, O and N, resulting in the variation of the optical property and photocatalytic ability. The large amount of N atoms doped and oxygen deficiency are detrimental for photocatalysis, and N bonding states may not be the major contributing factor for the photocatalysis. It is suggested that the coexistence of N₂ gas with O₂ gas shifts the TiO₂ formation boundary towards the low oxygen concentration, which leads to various nitrogen (nitrogen oxide) doping states on N-doped TiO_x film.

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