Research Article

Characteristics and Photocatalytic Properties of TiO₂ Thin Film Prepared by Sputter Deposition and Post-N⁺ Ion Implantation

Haider A. Shukur,¹ Mitsunobu Sato,² Isao Nakamura,³ and Ichiro Takano¹

¹Department of Electrical Engineering, Faculty of Engineering, Kogakuin University, 2665-1, Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan

²Division of Basic Liberal Arts, Kogakuin University, 2665-1, Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan

³Tokyo Metropolitan Industrial Technology Research Institute, 3-13-10, Nishigaoka, Kitaku, Tokyo 115-8586, Japan

Correspondence should be addressed to Haider A. Shukur, cd09001@ns.kogakuin.ac.jp

Received 30 June 2011; Revised 5 September 2011; Accepted 12 September 2011

Academic Editor: Koumei Baba

Copyright © 2012 Haider A. Shukur et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

TiO₂ thin films of a rutile, an anatase, and a mixture type with anatase and rutile were fabricated by a magnetron sputtering method. The fabricated films were irradiated by N⁺ ions with several doses using the Freeman ion source. Atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV-VIS spectrophotometer were employed to investigate morphology, structure, chemical state, and optical characteristics, respectively. Photocatalytic activity was evaluated by degradation of a methylene blue solution using UV and visible light. TiO₂ thin films with each structure irradiated by N⁺ ions showed the different N concentration in the same N⁺ ion dose and the chemical state of XPS results suggested that an O atom in TiO₂ lattice replaced by an N atom. Therefore the photocatalytic activity of TiO₂ thin films was improved under visible light. The maximum photocatalytic activity of TiO₂ thin films with each structure was indicated at N concentration of 2.1% for a rutile type, of 1.0% for an anatase type, and of 3.8% for a mixture type under the condition of 2.5×10^{15} ions/cm² in N⁺ ion dose.

1. Introduction

Titanium dioxide (TiO₂) has been known as a photocatalyst which is already used in various practical applications, such as degradation of environmental pollutants and self-cleaning of glass. Furthermore, the surface of TiO₂ exhibits high hydrophilicity under ultraviolet (UV) light irradiation [1, 2]. TiO₂ shows relatively high reactivity and chemical stability under UV light whose energy exceeds a band gap of 3.2 eV for the anatase crystalline phase and 3.0 eV for the rutile crystalline phase, however, UV energy accounts for only the small fraction (~5%) of the sun's energy compared to the visible light region (45%). It is the significant current to find the material with the lower band gap which can give high activity in the visible light region. Many methods have been tried to achieve this purpose. Those methods were such as incorporating metal atoms (Cr, Fe, Ni, V, or Ta) into the lattice of TiO₂ [3, 4] and doping anionic species (C, P, S, N, or F) into the TiO₂ matrix [5]. Among the doping of anionic

species, it has been reported that the N doping activated TiO₂ in both regions of visible and UV light [6, 7]. The N doping has been mainly performed by using a chemical process such as the sol-gel [8] or a physical process such as the PLD [9]. The enhancement of the photocatalytic property of N-doped TiO₂ in visible light has been researched from the different view about its mechanism [10–13].

Recently, some researchers have used N⁺ ion implantation method [14, 15] because of its advantages which were to be able to treat at a low temperature or to be able to easily control a doping layer [16]. Thus, the ion implantation alternated with the high-temperature diffusion method. In the case of N⁺ ion implantation into the TiO₂ thin film, this method can create oxygen vacancies to increase TiO₂ activity [17] and can make TiO₂ response to visible light when N is substituted for O in the TiO₂ lattice. Improvement of photocatalytic properties of the implanted TiO₂ thin film in a visible light is due to the chemical and microstructure changes of TiO₂. Most of studies about N⁺ ion-implanted

☆ Anatase

(a)

◇ Rutile

(b)

☆ Anatase

◇ Rutile

(c)

FIGURE 1: XRD patterns and FE-SEM cross-sectional images of the A-, R-, and M-TiO₂ thin film.

TiO₂ thin film [18] covered only an anatase type, while a few papers reported about N-doped rutile TiO₂, for example, the paper mentioned difference in the response compared to N-doped anatase TiO₂ [13].

In this work, TiO₂ thin films of a rutile, an anatase, and a mixture type with anatase and rutile were fabricated by the reactive magnetron sputtering method. The doping of N⁺ ions into TiO₂ thin films was performed using ion

beam irradiation with several N^+ ion doses. The chemical, structural, morphological, and photocatalytic properties were reported as a function of N^+ ion dose. It was expected that an N atom substituted for an O atom in the TiO_2 lattice so that the photocatalytic property of the TiO_2 thin film was improved under visible light.

2. Experimental Details

2.1. Preparation of Samples. The magnetron sputtering source and the Freeman type ion source of the multiprocess-coating system were used to fabricate TiO_2 thin films and to irradiate the TiO_2 thin film by N^+ ions, respectively. The corning glass (number 1737) substrate was fixed on the holder of the multiprocess-coating system and sputtered by Ar^+ ions for 10 min in order to clean the substrate. This cleaning was carried out in a separated chamber before the film fabrication process. The film deposition chamber was pumped up by a turbo molecular and a rotary pump to reach to the chamber pressure less than 1.3×10^{-5} Pa. The film fabrication process was carried out by introducing an Ar gas of 20 sccm in a flow rate near the Ti sputtering target and by applying an input power of 100 W. Simultaneously, an O_2 gas was introduced around the substrate at 1.5 or 2.3 sccm in a flow rate. The pressure of the film deposition chamber was kept at 8×10^{-2} Pa in a pressure and at 573 K in a substrate temperature through the film fabrication. The Ti-sputtering rates were measured by using a quartz crystal microbalance (QCM). Those were 0.025 nm/s for 1.5 sccm and 0.009 nm/s for 2.3 sccm in an O_2 gas flow rate, respectively. Because the different sputtering rates resulted due to the surface oxidation of a Ti target, the sputtering time was calculated from each deposition rate to obtain 200 nm in film thickness. The TiO_2 thin film fabricated at 2.3 sccm in an O_2 flow rate showed an anatase structure (A- TiO_2), while the sample with 1.5 sccm showed a mixture structure (M- TiO_2) of anatase and rutile. A rutile structure (R- TiO_2) was obtained by annealing a mixture structure under 700°C for 2 hours in the air.

The ion implantation was carried out by using Freeman type ion source. N^+ ions were separated by using a mass separator of 45 degree. The samples of A- TiO_2 , R- TiO_2 , and M- TiO_2 were irradiated under the constant ion energy of 15 kV at the constant current density of $40 \mu A/cm^2$. The different doses of 2.5×10^{15} , 5×10^{15} , and 7.5×10^{15} ions/cm² were controlled by the ion irradiation time. The ion implantation process was performed at a room temperature with a pressure less than 1×10^{-4} Pa and an incidence angle of 0 degree.

2.2. Film Characterization Measurement. The film structure was determined by X-ray diffraction (XRD: MAC Science High quality XG M18XCE) with $CuK\alpha$ (0.154 nm) radiation at an incident angle of 0.3° . The film composition was characterized by X-ray photoelectron spectroscopy (XPS: ULVAC-PHI, Inc.) with a focused monochromatic Al-K α X-ray source (1486.6 eV) and a maximum energy resolution of 0.48 eV at $Ag3d_{5/2}$. The chemical state and atomic

FIGURE 2: AFM top-view images of the unirradiated A-, R-, and M- TiO_2 thin film (a) and the irradiated A-, R-, and M- TiO_2 thin film with an N^+ ion dose of 5.0×10^{15} ions/cm² (b).

concentration of Ti, O, N, and C were measured and referenced at the standard C peak. Depth profiles in the Ar^+ ion etching mode were obtained at 2 kV in a ion energy and $20 \mu A/cm^2$ in a ion current for the maximum 3 min. The surface morphology and the cross-section of samples were observed by an atomic force microscopy (AFM: Shimadzu SPM-9500) and a field-emission scanning electron microscope (FE-SEM: S-4800 Hitachi High-Technologies co.), respectively. The photocatalytic property of TiO_2 thin films was evaluated by decomposition of a methylene blue solution (MB, $C_{16}H_{18}ClN_3S$) of 10 ppm in a quartz cell with a size of $10 \times 10 \times 50$ mm. The sample with an area of 100 mm^2 was immersed in an MB solution of 3 mL. UV light was irradiated to the sample by using a commercial sterilization lamp (S.L.) with a main wavelength of 280 nm and a light intensity of 0.088 mW/cm^2 at 360 nm. Artificial sunlight lamp (A.L.) with a UV cut-off filter (under 350 nm) was also irradiated on the sample at a light intensity of 0.228 mW/cm^2 at 360 nm. After the light irradiation, the change of a decolorized MB solution was calculated by

FIGURE 3: XRD patterns of the unirradiated A-, R-, and M-TiO₂ thin film and the irradiated A-, R-, and M-TiO₂ thin film with an N⁺ ion dose of 2.5×10^{15} , 5.0×10^{15} , and 7.5×10^{15} ions/cm².

measuring the transmittance of the MB solution using a spectrophotometer (UV-2550, Shimadzu co.) at regular intervals.

3. Results and Discussion

3.1. Surface Morphology and Structure. Figure 1 shows XRD patterns and cross-sectional images of each TiO₂ thin film with different structure. The XRD pattern of the A-TiO₂ thin film showed the strong peak of anatase (101) without a rutile structure and that of the R-TiO₂ thin film showed the strong peak of rutile (110), while the M-TiO₂ thin film had the double strong peaks of anatase (101) and rutile (110). According to the cross-sectional images, the thickness of the A-TiO₂ thin film was 146 nm due to decrease of the sputtering rate by of the high O₂ gas flow rate at the film fabrication, while the thickness of the R-TiO₂ thin film and the M-TiO₂ thin film was 188 and 182 nm, respectively. Each TiO₂ thin film showed a columnar structure. The A-TiO₂ thin film had the grain size of about 40 nm because of the high crystalline. That of the R-TiO₂ and the M-TiO₂ thin film were 16.9–21.8 nm and 24.8–31 nm, respectively.

AFM images of a tapping mode clarified the roughness (Ra) and the morphology of each TiO₂ thin film with the different structure and post-N⁺ ion irradiation. Figure 2 shows the top views of A-, R-, and M-TiO₂ thin films (a) and those of films irradiated by N⁺ ions with a dose of 5×10^{15} ions/cm² (b). It was clear that the morphology of the A-TiO₂ thin film was different from the R- and the M-TiO₂ thin film. The morphology of the A-TiO₂ thin film was an aggregate of spherical particles with the number of 22–25

per 1.0 μm in the length. This spherical size corresponded to the grain size of 40–45.45 nm as observed in the cross-sectional images. The R- and the M-TiO₂ thin film shows small spherical grains and a large roughness compared with the A-TiO₂ thin film. These small grain sizes of 25–33.3 nm were calculated from spherical particle numbers of 30–40 per 1.0 μm and were slightly larger than the size indicated in the cross-section images of the R- and the M-TiO₂ thin film.

The roughness of N⁺ ion-irradiated TiO₂ thin films was larger than that of unirradiated TiO₂ thin films. The surface of each unirradiated TiO₂ thin film was roughed by sputtering of N⁺ ion irradiation. The surface of the N⁺ ion-irradiated R- and A-TiO₂ thin film showed a smaller grain size compared with the unirradiated thin film, while the surface of the M-TiO₂ thin film turned to a larger grain size by N⁺ ion irradiation. These surface changes of the irradiated TiO₂ thin film were influenced by an N⁺ ion dose and an ion projected range. It was considered that the increase of the grain size of the N⁺ ion-irradiated M-TiO₂ thin film was influenced by a high N concentration in the thin film.

Figure 3 shows the XRD patterns of the unirradiated A-, R-, and M-TiO₂ thin film and the irradiated A-, R-, and M-TiO₂ thin film prepared with several N⁺ ion doses. The structure of the A-TiO₂ thin film declined with N⁺ ion irradiation as the drastic decrease of the anatase peak (101) showed, while the rutile peak (110) of the R-TiO₂ thin film showed no large change for N⁺ ion irradiation because of thermostability of a rutile type. It is generally known that the ion implantation method courses physical and thermal influence to a substrate. The lattice damage due to collisions between the ions and the lattice atoms stimulates recombination and the kinetic energy of implanted ions is

TABLE 1: O, Ti, and N atomic concentration of the A-, R-, and M-TiO₂ thin films under several N⁺ ion doses.

N ⁺ ion dose	A-TiO ₂ (%)			Atomic con. R-TiO ₂ (%)			M-TiO ₂ (%)		
	O	Ti	N	O	Ti	N	O	Ti	N
2.5×10^{15} ions/cm ²	75.8	22.1	2.1	68.5	30.5	1.0	73.6	22.7	3.8
5.0×10^{15} ions/cm ²	71.3	23.2	5.5	67.0	29.1	3.9	68.6	23.2	8.3
7.5×10^{15} ions/cm ²	67.6	21.9	10.5	64.1	30.6	5.3	63.2	22.0	14.9

FIGURE 4: XPS Ti2p and N1s spectra of unirradiated TiO₂ thin film and the irradiated A-, R-, and M-TiO₂ thin film with an N⁺ ion dose of 5.0×10^{15} ions/cm².

converted to thermal energy. N⁺ ion irradiation played a main role to change the structure from anatase to mixture [16]. In the XRD pattern of the A-TiO₂ thin film, the small rutile peak (110) started to appear with an N⁺ ion dose. Furthermore, in the case of the M-TiO₂ thin film the XRD pattern showed decrease of the anatase peak (101) with increasing of an N⁺ ion dose. The change of XRD patterns for each TiO₂ depended on thermostability of TiO₂ structure type.

3.2. Chemical State. Figure 4 shows XPS Ti2p and N1s spectra of the unirradiated TiO₂ thin film and the irradiated A-, R- and M-TiO₂ thin film with an N⁺ ion dose of 5.0×10^{15} ions/cm², respectively. These spectra were measured at the sample surface without an Ar⁺ ion etching process. N1s peaks of all N⁺ ion-irradiated TiO₂ thin films were detected at 399.1 eV in a binding energy. Since the peak of titanium nitride appeared at 396.0 eV according to the XPS catalog data, it was estimated that these peaks of 399.1 eV were caused by the Ti–O–N linkage assigned as an atomic β -N state. Therefore, these results suggested that the implanted N was incorporated into the TiO₂ lattice and substituted for O [19–22]. This was also proved by results of the Ti2p XPS spectra because the Ti2p peak decreased and slightly shifted to the high binding energy side by N⁺ ion irradiation as indicating that Ti–O bonding was accompanied by Ti–N

bonding [23], and, moreover, the O atomic concentration was decreased by increasing N⁺ ion dose as shown in Table 1, which showed the atomic concentrations of O, Ti, and N in the N⁺ ion irradiated A-, R-, and M-TiO₂ thin film with several N⁺ ion doses. N concentration in each thin film was proportional to N⁺ ion dose with an evidenced distinct difference according to the TiO₂ structure type. The M-TiO₂ thin film included a larger N concentration compared with the A- or R-TiO₂ thin film while the smaller N concentration was indicated at the R-TiO₂ thin film. The value of implanted N was influenced by a crystalline and a density of the TiO₂ thin film, since the density of the TiO₂ bulk was taken as 3.86 g cm⁻³ for a rutile type and was smaller by 8.7% for an anatase type [24]. It is well known that the deposited film had a lower density depending on the deposition parameters than the bulk material [25].

3.3. Photocatalytic Property. The photocatalytic property was investigated by decomposition of an MB solution. The MB solution exhibited an initial transmittance of 2.0% and a main absorption wavelength of 664 nm. Figure 5 shows the light transmittance change of 664 nm as the decomposition rate of the MB solution after 6 hours for the unirradiated A-, R-, M-TiO₂ thin film and those N⁺ ion irradiated thin films. The transmittance under S.L. of the unirradiated TiO₂ thin film showed larger activity than those of all N⁺ ion-irradiated TiO₂ thin films. It was clear that the effect of N⁺ ion irradiation under S.L. did not show because the defect of the TiO₂ lattice by the ion beam collision was generated and the effect of N⁺ ion dose for UV light was not originally anticipated. On the other hand, all N⁺ ion irradiated TiO₂ thin films showed increase of the transmittance under A.L. with N⁺ ion irradiation, however, the transmittance decreased by an excess of an N⁺ ion dose. From these results, the maximum photocatalytic activity of the A-, R-, and M-TiO₂ thin film was indicated at an N⁺ ion dose of 2.5×10^{15} ions/cm².

4. Conclusions

Three different structures of anatase, rutile, and mixture as TiO₂ thin films were prepared by the reactive magnetron sputtering method. N⁺ ion beam with several doses was irradiated to TiO₂ thin films with three different structures in a room temperature. Structural, morphological, chemical, and photocatalytic properties were investigated about unirradiated and N⁺ ion irradiated thin films. The anatase (101) peak was weakened by N⁺ ion irradiation, while the rutile

FIGURE 5: Transmittance changes of the methylene blue solution under sterilization lamp (S.L.) as UV light and artificial lamp (A.L.) as visible light for the unirradiated A-, R-, and M-TiO₂ thin film and the irradiated A-, R-, and M-TiO₂ thin film with an N⁺ ion dose of 2.5×10^{15} , 5.0×10^{15} , and 7.5×10^{15} ions/cm².

(110) peak had no large change against N⁺ ion irradiation. N1s spectra of all N⁺ ion irradiated A-, R-, and M-TiO₂ thin films had the peaks at 399.1 eV corresponding to Ti-O-N bonding; however, N concentration for each structure showed a different value in spite of the irradiation with the same N⁺ ion dose. It became clear that N⁺ ion implantation rate was different by TiO₂ structure type. Incorporation of N into the TiO₂ lattice by substituting for O was confirmed by XPS results and played the great role to improve the photocatalytic activity of the TiO₂ thin film under visible light.

References

- [1] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [2] R. Wang, K. Hashimoto, A. Fujishima et al., "Light-induced amphiphilic surfaces," *Nature*, vol. 388, no. 6641, pp. 431–432, 1997.
- [3] M. Anpo and M. Takeuchi, "The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation," *Journal of Catalysis*, vol. 216, no. 1-2, pp. 505–516, 2003.

- [4] S. T. Martin, H. Herrmann, W. Choi, and M. R. Hoffmann, "Time-resolved microwave conductivity. Part 1.—TiO₂ photoactivity and size quantization," *Journal of the Chemical Society, Faraday Transactions*, vol. 90, no. 21, pp. 3315–3322, 1994.
- [5] T. Ihara, M. Miyoshi, M. Ando, S. Sugihara, and Y. Iriyama, "Preparation of a visible-light-active TiO₂ photocatalyst by RF plasma treatment," *Journal of materials science*, vol. 36, no. 17, pp. 4201–4207, 2001.
- [6] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *Science*, vol. 293, no. 5528, pp. 269–271, 2001.
- [7] Y. Sakatani and H. Koike, Japan Patent P2001-72419A, 2001.
- [8] S. K. Zheng, T. M. Wang, W. C. Hao, and R. Shen, "Improvement of photocatalytic activity of TiO₂ thin film by Sn ion implantation," *Vacuum*, vol. 65, no. 2, pp. 155–159, 2002.
- [9] Y. Suda, H. Kawasaki, T. Ueda, and T. Ohshima, "Preparation of high quality nitrogen doped TiO₂ thin film as a photocatalyst using a pulsed laser deposition method," *Thin Solid Films*, vol. 453–454, pp. 162–166, 2004.
- [10] K. Yang, Y. Dai, B. Huang, and S. Han, "Theoretical study of N-doped TiO₂ rutile crystals," *Journal of Physical Chemistry B*, vol. 110, no. 47, pp. 24011–24014, 2006.
- [11] J. Graciani, L. J. Alvarez, J. A. Rodriguez, and J. F. Sanz, "N doping of rutile TiO₂ (110) surface. A theoretical DFT study," *Journal of Physical Chemistry C*, vol. 112, no. 7, pp. 2624–2631, 2008.
- [12] C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi, and E. Giamello, "Characterization of paramagnetic species in N-doped TiO₂ powders by EPR spectroscopy and DFT calculations," *Journal of Physical Chemistry B*, vol. 109, pp. 11414–11419, 2005.
- [13] S. Livraghi, A. M. Czoska, M. C. Paganini, and E. Giamello, "Preparation and spectroscopic characterization of visible light sensitized N doped TiO₂ (rutile)," *Journal of Solid State Chemistry*, vol. 182, no. 1, pp. 160–164, 2009.
- [14] R. Fernandes, N. Patel, R. Dholam, M. Adami, and A. Miotello, "Low energy ion-beam modification of TiO₂ photocatalyst thin film for visible light absorption," *Surface and Coatings Technology*, vol. 203, no. 17–18, pp. 2579–2583, 2009.
- [15] S. K. Zheng, T. M. Wang, W. C. Hao, and R. Shen, "Improvement of photocatalytic activity of TiO₂ thin film by Sn ion implantation," *Vacuum*, vol. 65, no. 2, pp. 155–159, 2002.
- [16] B. G. Streetman and S. Banerjee, *Solid State Electronics Devices*, Prentice Hall, Upper Saddle River, NJ, USA, 5th edition, 2000.
- [17] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, and K. Takeuchi, "Role of oxygen vacancy in the plasma-treated TiO₂ photocatalyst with visible light activity for NO removal," *Journal of Molecular Catalysis A*, vol. 161, no. 1–2, pp. 205–212, 2000.
- [18] P. Romero-Gomez, A. Palmero, F. Yubero, M. Vinnichenko, A. Kolitsch, and A. R. Gonzalez-Elipe, "Surface nanostructuring of TiO₂ thin films by ion beam irradiation," *Scripta Materialia*, vol. 60, no. 7, pp. 574–577, 2009.
- [19] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides," *Science*, vol. 293, no. 5528, pp. 269–271, 2001.
- [20] R. Knizikevicius, "Simulation of reactive sputter deposition of TiO₂ films," *Materials Science*, vol. 16, no. 3, pp. 202–204, 2010.
- [21] C. Burda, Y. Lou, X. Chen, A. C. S. Samia, J. Stout, and J. L. Gole, "Enhanced nitrogen doping in TiO₂ nanoparticles," *Nano Letters*, vol. 3, no. 8, pp. 1049–1051, 2003.
- [22] M. Xing, J. Zhang, and F. Chen, "New approaches to prepare nitrogen-doped TiO₂ photocatalysts and study on their photocatalytic activities in visible light," *Applied Catalysis B*, vol. 89, no. 3–4, pp. 563–569, 2009.
- [23] P. G. Wu, C. H. Ma, and J. K. Shang, "Effects of nitrogen doping on optical properties of TiO₂ thin films," *Applied Physics A*, vol. 81, no. 7, pp. 1411–1417, 2005.
- [24] N. Matsunami, M. Uebayashi, K. Hirooka, T. Shimura, and M. Tazawa, "N ion irradiation enhancement of photocatalytic activity of TiO₂," *Nuclear Instruments and Methods in Physics Research, Section B*, vol. 267, no. 8–9, pp. 1654–1657, 2009.
- [25] W. Wagner, F. Rauch, and K. Bange, "Concentration profiles of hydrogen in technical oxidic thin films and multilayer systems," *Fresenius' Zeitschrift für Analytische Chemie*, vol. 333, no. 4–5, pp. 478–480, 1989.