Catalysis Today 164 (2011) 399–403

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Visible light response of nitrogen and sulfur co-doped TiO_2 photocatalysts fabricated by anodic oxidation

Yosuke Komai[a,*], Kenji Okitsu[a], Rokuro Nishimura[a], Naofumi Ohtsu[b], Goro Miyamoto[c], Tadashi Furuhara[c], Satoshi Semboshi[c], Yoshiteru Mizukoshi[d], Naoya Masahashi[d]

[a] *Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan*
[b] *Instrumental Analysis Center, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan*
[c] *Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan*
[d] *Osaka Center for Industrial Materials Research, Institute for Materials Research, Tohoku University, Sakai, Osaka 599-8531, Japan*

ARTICLE INFO

Article history:
Received 29 June 2010
Received in revised form 21 October 2010
Accepted 21 October 2010
Available online 3 December 2010

Keywords:
Photocatalysts
TiO_2
Anodic oxidation
Visible light response

ABSTRACT

N,S-codoped TiO_2 photocatalysts were successfully immobilized on the surface of plasma-nitrided pure Ti substrate by anodic oxidation in a sulfuric acid electrolyte and their photocatalytic activities were evaluated. The anodic TiO_2 photocatalysts effectively bleached methylene blue (MB) aqueous solution under visible light illumination. X-ray photoelectron spectroscopy (XPS) analysis clarified the presence of nitrogen and sulfur, and auger electron spectroscopy (AES) analysis revealed that sulfur was distributed over the anodic oxide. It is estimated that N,S-codoping in the anodic TiO_2 narrows the band gap of pristine TiO_2 and improves the photocatalytic activity under visible light illumination.

1. Introduction

Since the first study of Fujishima and Honda [1] in 1972, TiO_2 has been considered to be the most attractive photocatalyst due to its strong oxidizing power, broad functionality, chemical stability and non-toxicity. However, a major drawback of TiO_2 for practical application is that it can act as photocatalyst only under UV light due to a wide band gap of 3.2 eV for anatase and 3.0 eV for rutile. Therefore, TiO_2 can absorb UV right contained in solar light with only a few percent, leading to low photocatalytic efficiency. In order to expand its application under visible light, it is necessary to modify the electronic structure of the photocatalyst to respond to visible light. Over the past decade, visible light active TiO_2 has been prepared by several methods such as metal–ion doping [2,3], dye-sensitizing [4,5], or non-metal doping by incorporation of various dopants into TiO_2 lattice [6–10]. Among them, nitrogen doping is regarded as one of the most promising methods to narrow the band gap of TiO_2 and a number of methods have been employed to prepare N-doped TiO_2 such as sol–gel synthesis [11,12], oxidation of titanium nitride [10], annealing in NH_3 gas [6,13], and ion implantation [14,15].

In our group, we have employed anodic oxidation to fabricate TiO_2 thin layers on the surface of Ti and its alloys, and investigated their photocatalytic activities in relation to its crystallinity and microstructure [16–19]. Using this method [18], abrupt elements contained in the electrolyte can be doped into the oxide, which is advantageous in controlling the band structure of the oxide. Recently, we showed that the photocatalytic activity of rutile TiO_2 prepared by anodic oxidation in a sulfuric acid electrolyte bleached methylene blue (MB) aqueous solution under visible light with wavelengths longer than those corresponding to the band gap of pristine rutile TiO_2 [20]. We concluded that the enhanced photocatalytic activity under visible light illumination was due to the band gap narrowing by sulfur doping.

In the present study, a different approach for doping was explored by using plasma nitriding to the surface of Ti substrate used for following anodic oxidation. Plasma nitriding has been employed to improve surface hardness, corrosion and wear resistance of metallic materials, usually steel. In case of Ti and its alloys, TiN and/or Ti_2N layer formed on their surface provide surface hardening [21,22]. It is expected to control the concentration of nitrogen by selecting the mixture ratio of H_2 and N_2, thereby control the amounts of dopant in the anodic oxide. The object of this study is to examine the effects of N,S-codoping in the anodic TiO_2 on the photocatalytic activity under visible light illumination.

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* Corresponding author. Tel.: +81 0 72 254 6372; fax: +81 0 72 254 6375.
E-mail address: dm0704@mtr.osakafu-u.ac.jp (Y. Komai).

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doi:10.1016/j.cattod.2010.10.085

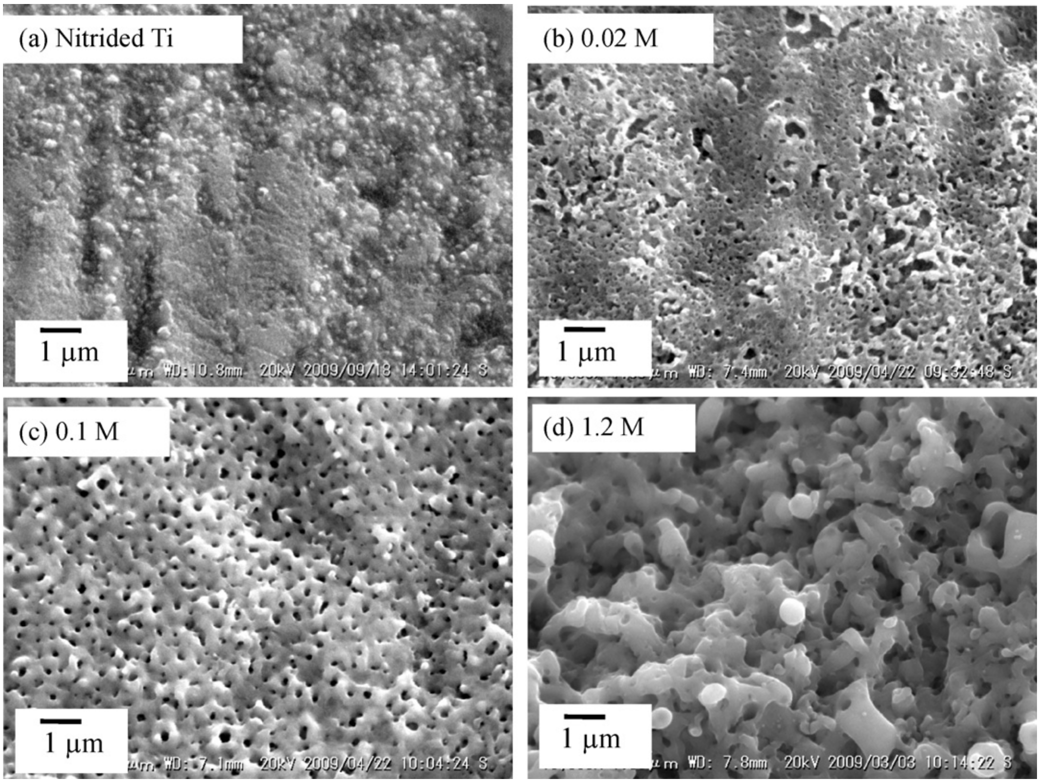

Fig. 1. SEM images of the nitrided Ti (a) and anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 0.02 M (b), 0.1 M (c), and 1.2 M (d).

2. Experimental

2.1. Preparation of photocatalysts

A pure Ti plate (cp-Ti, grade I, 20 mm × 10 mm × 1 mm) was chemically polished using a 40-nm colloidal silica suspension and was thoroughly washed in methanol using an ultrasonic cleaning bath. After cleaning with alcohol, the sample was placed on the titanium stage in the plasma nitriding chamber, and the sample surface was sputtered in a gas mixture of 50% H_2–50% Ar at 973 K under a voltage of 550 V and a pressure of 500 Pa to remove the contamination on the surface. Then, the DC plasma nitriding was performed in a gas mixture of 50% N_2–50% H_2 at a total pressure of 500 Pa at 973 K for 2 h and followed by furnace cooling. The nitrided sample was anodized with a constant current density of 50 mA cm^{-2} for 0.5 h in a sulfuric acid electrolyte (0.02–1.2 M). The anodized sample was rinsed with ultrapure water and then dried at room temperature, followed by annealing at 723 K for 5 h in air atmosphere.

2.2. Characterization of photocatalysts

The crystallographic structure of the anodic oxide was determined by X-ray diffraction (PANalytical X'Pert diffractometer, Netherlands) with Cu K_α radiation (0.15406 nm), at a scan rate of 1° min^{-1}, and a rotating detector. The sample was set in a thin-film geometry arrangement at 0.5° glancing angle. Microstructure observation was conducted with a scanning electron microscopy (SEM, KEYENCE VE-8800, Japan) at an operating voltage of 20 kV.

X-ray photoelectron spectroscopy (XPS) measurements were conducted with an electron spectrometer (ESCA1600, Ulvac-Phi, Japan) equipped with monochromated Al–K_α radiation. The diffuse reflectance spectra were measured with a UV–vis spectrophotometer (Jasco V-550, Japan) equipped with an integration sphere. The depth profile of sulfur was investigated with Auger Electron Spectroscopy (AES, JEOL JAMP-7100E, Japan), and Ar ion sputtering was carried out at energy of 3 keV and the sputtering rate of 0.083 nm s^{-1} for SiO_2.

2.3. Photocatalytic activity tests

The photocatalytic activity was evaluated using MB bleaching tests, wherein the photocatalyst was placed in a disposable PMMA cell (1 cm × 1 cm × 4.4 cm) containing 2 ml of 3.19 mg L^{-1} MB aqueous solution. Visible or UV light from a Xe lamp (Asahi Spectra, Max-301, 300 W, Japan) was passed through a 365, 400, 440, 500, or 530 nm band pass filter. The bandwidth of the passed light was about 10 nm. The intensity of the irradiated light was 0.3 mW cm^{-2} at the surface of the cell. The MB bleaching test was carried out by measuring the absorbance of MB at 664 nm using a UV–vis spectrophotometer after illumination for 1, 2 and 3 h. Prior to the bleaching tests, the photocatalysts were immersed in MB solutions for more than 12 h to complete the adsorption of MB molecules on the surface of the photocatalyst.

3. Results and discussion

Fig. 1 shows the microstructures of the nitrided Ti (a) and anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 0.02 M (b), 0.1 M (c), and 1.2 M (d). The nitrided Ti exhibits gold color, suggesting a formation of TiN and/or Ti_2N on the surface of the substrate. With an increase in the concentration of sulfuric acid, the anodic oxide shows nano-sized pores. When the concentration of sulfuric acid becomes 1.2 M (d), the formation of nano-sized pores with various sizes due to coalescence of pores were observed. Consequently, the surface roughness and area of the oxide increased and the oxide layer on the substrate with approximately 7 μm in thickness was observed, which was similar to the corresponding of the anodic oxide on pure Ti [18].

Fig. 2 shows XRD profiles of the nitrided Ti and the anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 0.02,

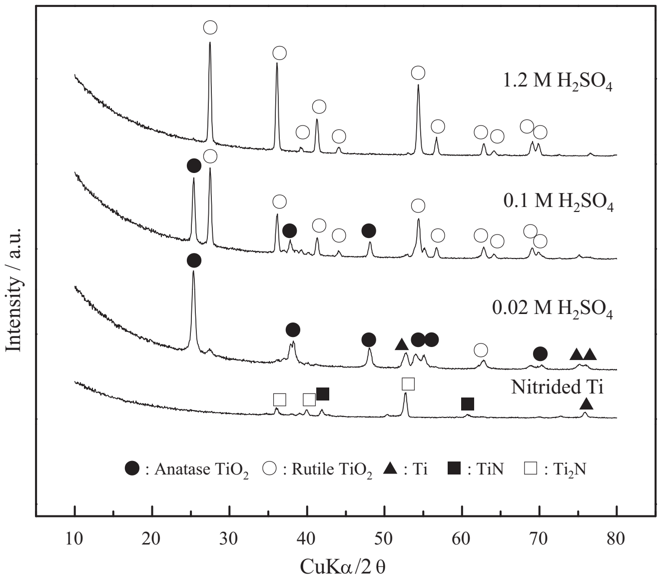

Fig. 2. XRD profiles of the nitrided Ti and the anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 0.02, 0.1, and 1.2 M.

0.1, and 1.2 M. In the nitrided Ti, the primary diffraction peaks were observed at 41.8° and 52.3°, which could be attributed to TiN (2 0 0) and Ti_2N (2 1 0), respectively. When the sulfuric acid concentration was low (0.02 M), the main peak was observed at 25.3° and was attributed to anatase (1 0 1). With an increase in the concentration of sulfuric acid, the predominant phase converted from anatase to rutile, wherein the main peak was observed at 27.4° due to rutile (1 1 0).

Fig. 3 shows the apparent rate constants (k_{app}) for MB bleaching on the TiO_2 photocatalysts under UV or visible light illumination, which are calculated using the equation reported in the pervious study [20]. The previous data are also shown as references. Here, the data for N-doped sample (i.e. sulfur-free sample) could not be presented because sulfur was inevitably incorporated in the anodic oxide by the current method due to the composition of the used electrolyte (i.e. sulfuric acid). Anatase TiO_2 prepared in 0.02 M sulfuric acid electrolyte bleached MB under UV light with 365 nm illumination in both cases of pure Ti and nitrided Ti substrates. However, when illuminated with longer wavelengths than UV light, the rate constant of anatase TiO_2 prepared in 0.02 M sulfuric acid electrolyte decreased monotonously, which is similar to that of the commercially available anatase. In contrast, rutile TiO_2 prepared in 1.2 M sulfuric acid electrolyte exhibited an enhanced photocatalytic activity even under visible light illumination. N,S-codoped rutile TiO_2 showed superior activity when the light with the wavelength around 400 nm was illuminated, however it was similar or less than that of S-doped TiO_2 [20] when the light with longer wavelength was illuminated. This could be explained by an employed plasma nitriding condition responsible for modification of band structure through controlling the quantities of the dopants. Therefore, the photocatalytic properties could be improved by selecting the mixture ratio of H_2 and N_2 during plasma nitriding. So far, the effect of N-doping on the photocatalytic activity has been clearly recognized in the photocatalytic decomposition of acetaldehyde under visible light illumination. Systematic study has been in progress.

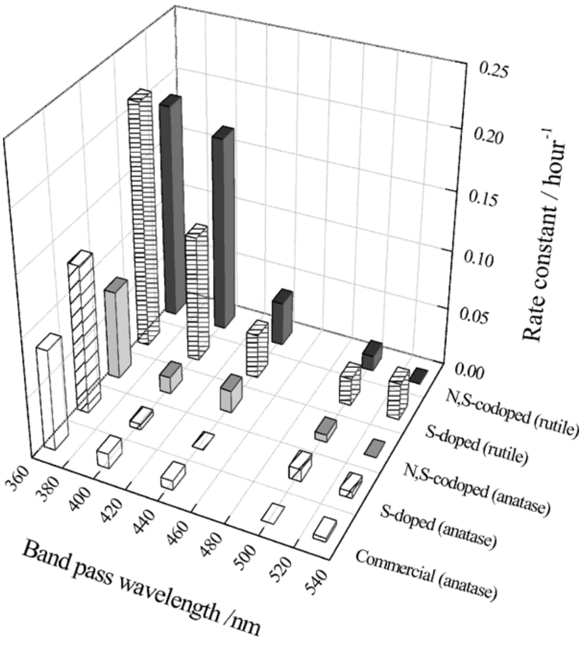

Fig. 3. Apparent rate constants for MB bleaching on the anodic TiO_2 prepared in 0.02 M (anatase), 1.2 M (rutile) sulfuric acid and commercially available TiO_2.: N,S-codoped samples (used nitrided Ti as substrate), S-doped samples (used pure Ti as substrate).

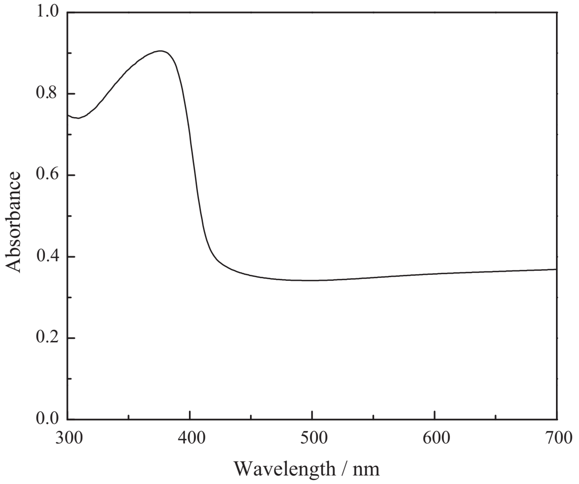

Fig. 4. Diffuse reflectance spectrum of the anodic oxide prepared in an electrolyte of sulfuric acid at a concentration of 1.2 M.

Fig. 4 shows the diffuse reflectance spectrum of the anodic oxide prepared in an electrolyte of sulfuric acid at a concentration of 1.2 M, showing broad absorbance across the UV–vis regions which is in accordance with the wavelength dependence of MB bleaching. However, in the case of the anodic oxide prepared in a low concentration (0.02, 0.1 M) of sulfuric acid aqueous solution, the characteristic spectra could not be obtained probably because the oxide layer is too thin to obtain the suitable diffuse reflectance spectra.

In order to determine the content and chemical state of nitrogen in the oxide, XPS analysis was carried out. Fig. 5 shows XPS spectra of the nitrided Ti and the anodic oxide prepared in an electrolyte of sulfuric acid at a concentration of 1.2 M. In the nitrided Ti substrate, N 1s peak was observed at 396 eV, as shown in (a). This peak is attributed to Ti–N binding in the substrate [6,10,23]. After anodization, a new peak at 400 eV was detected, while the peak at 396 eV disappeared alternatively. This new peak is ascribed to titanium–oxy–nitride (Ti–O–N) [13,24]. In addition, the S 2p XPS spectrum of the anodic oxide (not shown here) showed that the main peak was observed at approximately 169 eV in the same as the previous paper [20]. Related to the chemical states of these dopant concerning the dopant oxidation by generated hole, it is not easy to verify these chemical states by using XPS. For the nitro-

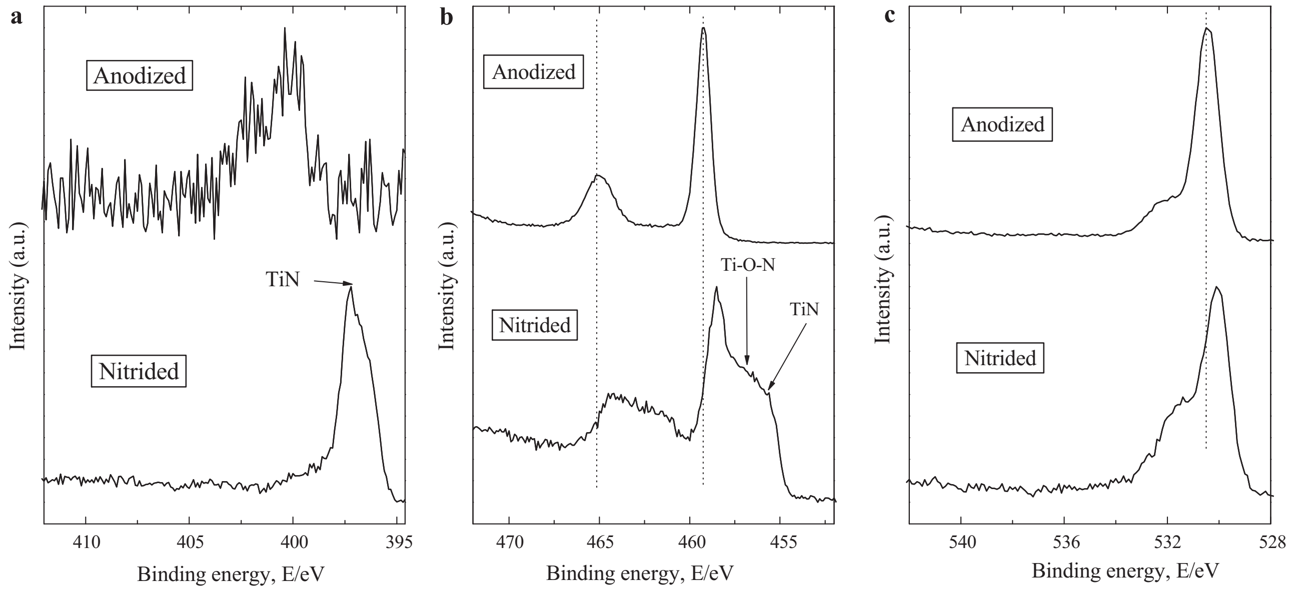

Fig. 5. (a) N 1s, (b) Ti 2p, (c) O 1s XPS spectra of the nitrided Ti (lower line) and the anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 1.2 M (upper line).

gen oxidation, close binding energy between the concerned species of NH_4^+ and N–O makes it difficult. However, we have considered that a slight improvement of photocatalytic activity in N,S-codoped TiO_2 as compared with S-doped TiO_2 suggests low possibility of nitrogen oxidation. In contrast, the unique chemical state of sulfur ascribed to SO_4^{2-} or SO_2 was recognized, while no distinct difference was found after illumination. The XPS spectra of the Ti 2p and O 1s are shown in Fig. 5(b) and (c), respectively. The Ti 2p XPS spectrum of the nitrided Ti substrate exhibits an asymmetrical profile with shoulder peak around 455 eV, indicating the presence of intermediate between TiN and TiO_2 [23]. After anodization, the peak shifted 0.6 eV higher energy than that of the nitrided Ti due to the charge shift. The spectrum exhibits a symmetrical profile, which indicates that reduced Ti^{3+} ions are not present in the anodic oxide [20]. The shoulder peak in the O 1s XPS spectra is observed at approximately 533 eV due to the adsorption of hydroxyl groups [25]. These hydroxyl groups on the TiO_2 surface are responsible for the superhydrophilicity [17].

Table 1 shows the N and S contents in the anodic oxides are estimated from the relative area intensities of the N 1s, S 2p, Ti 2p, O 1s and C 1s spectra. These results indicate that the anodic oxide prepared in 1.2 M sulfuric acid electrolyte includes higher concentrations of N and S than those prepared in 0.1 M. We have reported that the amount of S in the anodic oxide increased with an increase of the concentration of sulfuric acid in the electrolyte [20]. However, it is noteworthy that not only a content of S but also that of N in the anodic oxides increased with an increase of the concentration of sulfuric acid in the electrolyte. This is probably because the application of a high conversion voltage generates high electric field, which promotes inward diffusion to the anodic oxide from both the electrolyte and the substrate due to its high-applied energy density (current density of 10^4 A cm^{-2}, reaching temperatures near to 8000K) [26]. In addition, the existence of sulfuric acid in an electrolyte can give a high reactivity against Ti due to low resistance to sulfuric acid with high concentration, which might facilitate the diffusion of nitrogen contained in nitrided Ti substrate into the oxide layer formed on the surface in anodization process.

AES analysis was conducted for the anodic oxide prepared in 1.2 M sulfuric acid electrolyte to investigate the depth distribution of sulfur. The inset in Fig. 6 shows the AES differential spectra before and after Ar ion sputtering for 60, 120 and 240 s. Here, the spectrum due to the nitrogen KLL transition is not shown because its energy overlaps that of the titanium LMM transition located at 380 eV. The ratios of the height of the sulfur (LVV) to titanium (LMM) peaks during Ar ion sputtering are plotted against the sputtering time in Fig. 6. The high peak height ratios observed at the beginning of sputtering was partially attributable to the contaminations originating from the sulfuric acid in the electrolyte. With the progress of the sputtering, the ratios of the peak height monotonously decreased, but detected throughout the analysis. These results suggest that sulfur

Table 1
N and S contents in nitrided Ti anodized in sulfuric acid electrolyte.

Concentration of sulfuric acid (M)	N 1s (at.%)	S 2p (at.%)
0.1	0.4	1.2
1.2	0.9	1.5

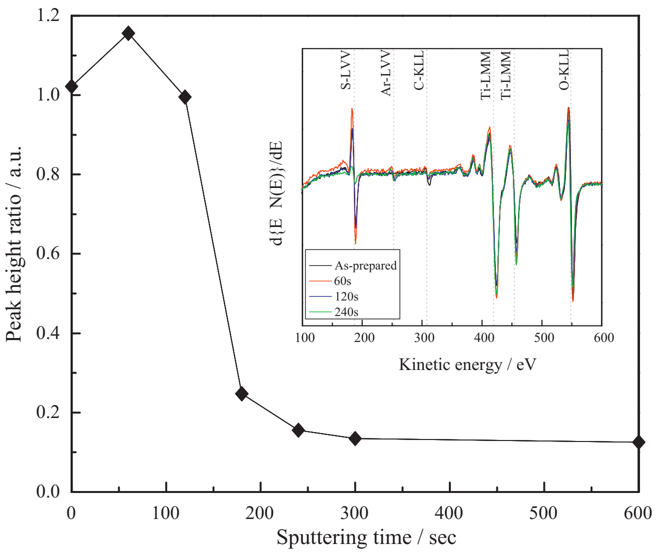

Fig. 6. A plot of the peak height ratio of sulfur (LVV) to titanium (LMM) during Ar ion sputtering. Inset shows AES differential spectra of the anodic oxide prepared in 1.2 M sulfuric acid electrolyte before and after Ar ion sputtering for 60, 120 and 240 s.

was distributed over the anodic oxide. This is in good agreement with the results of the previous study [20].

N,S-codoped rutile TiO_2 prepared here exhibited photocatalytic activity under illumination with light of a wavelength longer than 413 nm corresponding to the band gap of pristine rutile TiO_2 (3.0 eV), indicating that the band gap is narrowed by N,S-codoping. When the light with longer wavelength than 440 nm was illuminated, N,S-codoped TiO_2 showed similar or less photocatalytic activity than S-doped TiO_2. This might be possibly because the amount of N dopant in the anodic oxide is insufficient to incorporate N 2p localized states above the top of O 2p valence band, thereby causing low activity due to a little mixing of N with O 2p states responsible for band gap narrowing of TiO_2 [6]. Thus, in order to elucidate the electronic structure of the N,S-codoped TiO_2, first-principles calculation is in progress. In addition, Onoda and Yoshikawa [27] reported that a pre-nitridation treatment on pure Ti had an accelerating effect on the photocatalytic activities of the anodized TiO_2 films for a photodegradation of acetaldehyde. Thus, further studies to explore the effects of N,S-codoping on visible light response of the anodicTiO_2 are in progress.

4. Conclusions

In this study, we successfully prepared N,S-codoped TiO_2 by anodic oxidation of plasma-nitrided Ti substrate in a sulfuric acid electrolyte and the photocatalytic activity was investigated. The codoped photocatalysts effectively bleached MB aqueous solution under visible light illumination, especially illuminated with the light with around 400 nm wavelength. XPS and AES analyses revealed the presence of nitrogen and sulfur in the anodic oxide. These results suggested that the enhanced photocatalytic activity under visible light illumination was due to the band gap narrowing of pristine TiO_2 by nitrogen and sulfur codoping.

Acknowledgements

The authors wish to thank Ms. Y. Matsuda from Tohoku University for her assistance in evaluation of photocatalytic activities, to Mr. S. Sugiyama from Tohoku University for his sample preparation and Mr. Y. Murakami from Tohoku University for his measurements of auger electron spectroscopy and to Prof. Y. Saito, Mr. R. Asaka and Mr. K. Imamura from Waseda University for the quantum calculation of band structures.

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