



Effect of the local structure of Ti-oxide species on the photocatalytic reactivity and photo-induced super-hydrophilic properties of Ti/Si and Ti/B binary oxide thin films

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Abstract

From the results of various spectroscopic investigations of Ti-oxide-based binary oxides, it was found that tetrahedrally coordinated Ti-oxide species are formed in the thin films of Ti/Si binary oxides with low TiO₂ content, while octahedrally coordinated TiO₂ nano-particles are formed in the Ti/B binary oxide thin films, reflecting the effect of the crystalline structures of the host SiO₂ or B₂O₃ on the local structure of the guest Ti-oxide species, respectively. The photocatalytic reactivity of the TiO₂ thin films was found to be remarkably enhanced by the dispersion of the Ti-oxide moiety into both the SiO₂ and B₂O₃ matrices, whereas the photo-induced super-hydrophilic properties of the TiO₂ thin films were enhanced only by a combination or mixing of the Ti-oxide moiety with B₂O₃.

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1. Introduction

A great deal of attention has been directed towards various useful applications of photocatalysis for the recovery of a clean and safe environment and this field has expanded rapidly with regard to light energy, especially the conversion of solar energy into useful chemical energy using solid photocatalysts such as TiO₂ [1–12]. In particular, TiO₂ thin films have been widely investigated not only for their high photocatalytic

reactivity but also for their unique photo-induced super-hydrophilic properties [13–20]. The preparation methods reported for the TiO₂ thin films so far are the sol–gel method and metal oxide chemical vapor deposition (MOCVD) method. Recently, we have shown that an ionized cluster beam (ICB) deposition method can also be applied as a good technique to produce highly homogeneous and efficient TiO₂ thin film photocatalysts without the need for treatment or calcinations at high temperatures for crystallization after deposition [21]. Moreover, we have reported that binary oxide thin films of different compositions can be easily prepared by the ICB method using multi-ion sources by the control of each deposition rate [22,23].

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In previous literature, we have reported that the photocatalytic reactivity of Ti/Si binary oxides prepared by the coprecipitation method is strongly affected by a change in the composition of the catalyst, i.e., by changing the Ti/Si ratios [24]. Imamura et al. [25] have reported that the Ti/Si binary oxides prepared by the sol–gel method exhibit a high catalytic activity for the selective epoxidation of alkenes. On the other hand, to improve the photo-induced super-hydrophilic properties of the TiO_2 thin films, a combination or mixing of the Ti-oxide moiety with other oxides such as SiO_2 or B_2O_3 have been reported. Especially, the addition of SiO_2 fine particles or the deposition of the SiO_2 thin layer onto the surface of the TiO_2 thin films have been shown to maintain super-hydrophilic properties even under dark conditions for long periods after light irradiation was ceased [26]. However, to date, there have not been any detailed investigations clarifying the effect of the local structure of the Ti-oxide species on the photocatalytic reactivity and photo-induced super-hydrophilic properties of these thin film materials involving the Ti-oxide moiety.

In the present study, Ti/Si and Ti/B binary oxide thin films were prepared by the ICB method using multi-ion sources. Characterization studies were carried out by spectroscopic measurements such as XRD,

XAFS, UV-Vis and IR absorption in order to elucidate the local structure of the Ti-oxide species of these Ti/Si and Ti/B binary oxide thin films. The photocatalytic reactivity of these films was evaluated by the decomposition of NO to produce N_2 and O_2 as the main products as well as N_2O as a minor product under UV irradiation. The photo-induced super-hydrophilic properties were evaluated by measuring the changes in the contact angle of water droplets under UV irradiation and under dark conditions at 298 K.

2. Experimental

2.1. Preparation of the Ti/Si and Ti/B binary oxide thin films

Ti/Si and Ti/B binary oxide thin films with various TiO_2 compositions were prepared by the ICB method on a quartz substrate, as shown in the schematic diagram of Fig. 1. As a pretreatment, the quartz substrates were ultrasonically cleansed for 15 min in acetone, then dried and annealed at 723 K for 5 h in air. The source materials, Ti metal and SiO (or B_2O_3) powder, were heated at high temperatures, then the Ti and SiO (or B_2O_3) vapors were introduced into the high vacuum chamber to produce Ti and SiO

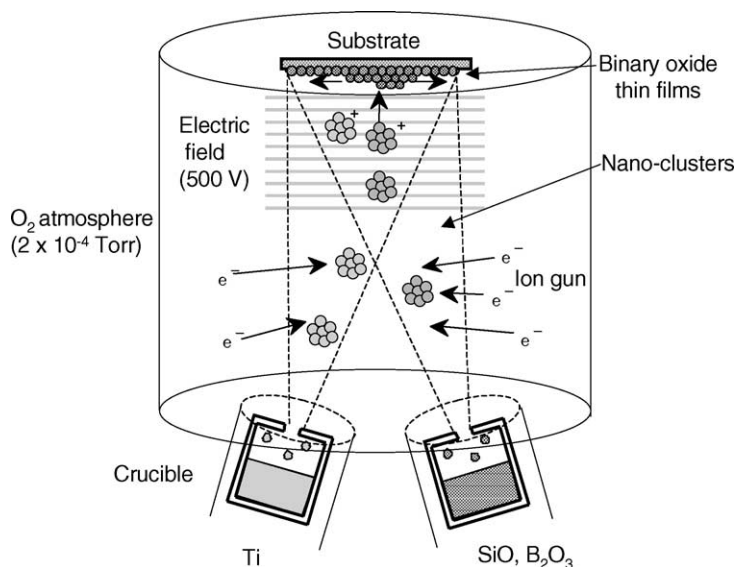


Fig. 1. Schematic diagram of the ICB deposition method using multi-ion sources.

(or B_2O_3) clusters. Stoichiometric TiO_2 and SiO_2 (B_2O_3) nano-clusters were formed on the substrate by the impingement of the ionized and neutral Ti and SiO (B_2O_3) clusters and oxygen gas (2×10^{-4} Torr), respectively. By controlling each deposition rate, the Ti/Si and Ti/B ratios could be accurately determined.

2.2. Characterization

Ti/Si and Ti/B binary oxide thin films were characterized by applying various spectroscopic techniques such as XRD, XAFS (XANES and Fourier transforms of EXAFS), UV-Vis and FT-IR. The XAFS spectra were obtained at the BL-7C facility of the Photon Factory in Tsukuba. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K. UV-Vis absorption spectra were recorded in the transmittance mode at 295 K with a Shimadzu UV-2200A spectrophotometer. The FT-IR spectra were measured with a JASCO FT-IR 660 spectrophotometer at 298 K.

2.3. Evaluation of the photocatalytic reactivity and the photo-induced super-hydrophilic properties of Ti/Si and Ti/B binary oxide thin films

The photocatalytic reactivity of Ti/Si and Ti/B binary oxide thin films were evaluated by the decomposition of NO into N_2 , O_2 and N_2O . Before the reaction, the thin films were pretreated in vacuum for 2 h and in oxygen for 2 h at 723 K. After cooling the thin films at room temperature, they were pretreated at 473 K in vacuum for 2 h again. UV light irradiation was carried out using a 100 W high-pressure Hg lamp (Toshiba, SHL-100 UVQ-2) at 275 K. The reaction products were collected in the gas phase and then analyzed by gas chromatography. The surface wettability (or hydrophilicity) was evaluated by measuring the changes in the contact angle of water droplets at 298 K just after UV irradiation and under dark conditions at 298 K in air. The Sessile drop method was used for the measurement of the contact angle with a commercial contact angle meter (CA-X, Kyowa Interface Science, Saitama, Japan), allowing for an experimental error of $\pm 1^\circ$. UV light irradiation was carried out using a 100 W high-pressure Hg lamp.

3. Results and discussion

3.1. Characterizations of Ti/Si and Ti/B binary oxide thin films

The XAFS spectra (XANES and Fourier transforms of EXAFS) of the Ti/Si and Ti/B binary oxide thin films were measured in order to elucidate the local structure of the Ti-oxide species within these thin films. Fig. 2 shows the XANES spectra of these binary oxide thin films. The XANES spectra of the Ti/Si binary oxide thin films with low TiO_2 compositions (left, Fig. 2) exhibit an intense single pre-edge peak which can be attributed to the tetrahedrally coordinated TiO_2 species. On the other hand, for the Ti/B binary oxide thin films with low TiO_2 compositions (right, Fig. 2), these spectra exhibit three small characteristic pre-edge peaks which can be attributed to TiO_2 with an anatase crystalline structure.

Fig. 3 shows the Fourier transforms of the EXAFS spectra of these binary oxide thin films. The spectra of the Ti/Si binary oxide thin films exhibit a strong peak at around 1.6 \AA which can be attributed to the Ti–O peak, while for the Ti/B binary oxide thin films, not only the Ti–O peak but also the Ti–O–Ti peak can be seen. The results of the curve fitting analysis of the FT-EXAFS spectra to obtain the coordination number and the bond distance between the Ti and O atoms of

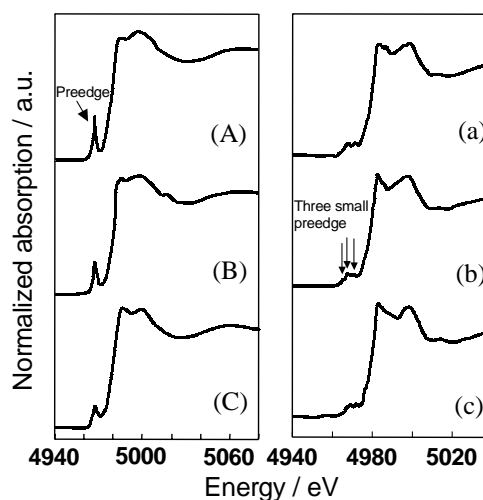


Fig. 2. XANES spectra of Ti/Si (A)–(C) and Ti/B (a)–(c) binary oxide thin films. TiO_2 content (%): (A) 6.6, (B) 9.5, (C) 50.1, (a) 5.0, (b) 10.0 and (c) 50.0.

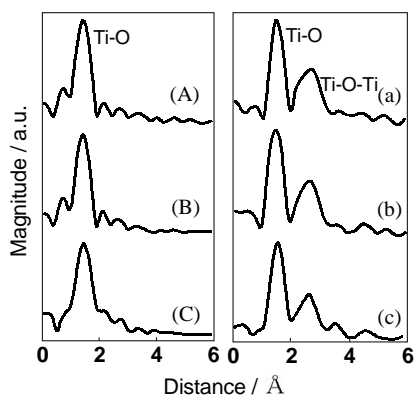


Fig. 3. Fourier transforms of EXAFS of Ti/Si (A)–(C) and Ti/B (a)–(c) binary oxide thin films. TiO₂ content (%): (A) 6.6, (B) 9.5, (C) 50.1, (a) 5.0, (b) 10.0 and (c) 50.0.

the Ti-oxide species in the Ti/Si and Ti/B binary oxides are summarized in Table 1. It is clear that the coordination numbers of the Ti/Si binary oxides with lower TiO₂ compositions are close to 4.0, indicating that the major Ti-oxide species exist in a tetrahedral coordination. However, the coordination numbers of the Ti/B binary oxides are always close to 6.0, even for the Ti/B binary oxide with low TiO₂ content, showing that the major Ti-oxide moiety in the Ti/B binary oxides are present in octahedral coordination [22].

Thus, these results clearly indicate that for Ti/Si binary oxide thin films with low TiO₂ compositions, the tetrahedrally coordinated Ti-oxide species are highly dispersed in the host SiO₂ matrices, whereas for Ti/B binary oxide thin films with low TiO₂ compositions, octahedrally coordinated ultrafine TiO₂ nano-particles are formed in the host B₂O₃ matrices. Furthermore, the bond distance between the Ti

and O atoms of the Ti-oxide species in the Ti/Si binary oxide thin films varies from 1.81 to 1.85 Å with an increase in the TiO₂ compositions from 6.6 to 50.1 wt.%, reflecting the changes in the structures of the Ti-oxides from highly dispersed isolated tetrahedrally coordinated Ti-oxide species to octahedral coordinated TiO₂ anatase nano-particles dispersed in SiO₂ matrices. However, the bond distance between the Ti and O atoms of the Ti-oxide species in Ti/B binary oxide thin films scarcely changes and is almost constant at around 1.90 Å, being in a good agreement with the fact that Ti-oxides in the Ti/B binary oxides are always present as octahedrally coordinated TiO₂ nano-particles dispersed in the B₂O₃ matrices.

The UV-Vis absorption spectra measured by a transmittance method for the Ti/Si and Ti/B binary oxide thin films with low TiO₂ content are shown in Fig. 4. For both the Ti/Si and Ti/B binary oxide thin films, when the TiO₂ composition is low, the absorption band of TiO₂ shifts towards shorter wavelength regions. This can be attributed to the presence of a tetrahedrally coordinated Ti-oxide species in the SiO₂ matrices and the quantum size effect due to the formation of the extremely small octahedrally coordinated TiO₂ nano-particles in the B₂O₃ matrices, respectively [22,23].

It is also found that these binary oxide thin films are highly transparent and colorless, having a high transmittance in the visible light region due to their highly homogeneous crystallinity and surface morphology.

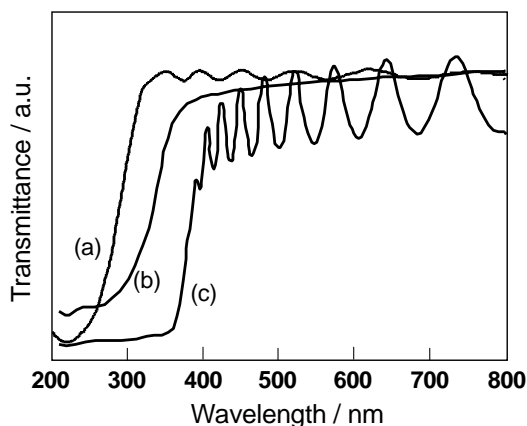


Fig. 4. UV-Vis absorption spectra by transmittance method of Ti/Si and Ti/B binary oxide thin films: (a) Ti/Si (6.6/93.4), (b) Ti/B (5/95) and (c) TiO₂.

Table 1

The results of the curve fitting of Fourier transforms of EXAFS data for Ti/Si and Ti/B binary oxide thin films

Catalyst	Shell	Bond distance (Å)	Coordination number
Ti/Si (6.6/93.4)	Ti–O	1.81	4.3
Ti/Si (9.5/90.5)	Ti–O	1.82	4.4
Ti/Si (50.1/49.9)	Ti–O	1.85	4.9
Ti/B (5/95)	Ti–O	1.91	5.98
Ti/B (10/90)	Ti–O	1.90	5.97
Ti/B (50/50)	Ti–O	1.90	5.97

Furthermore, it should be emphasized that the interference fringes which could be clearly observed for the pure TiO_2 thin film almost disappeared for the Ti/Si and Ti/B binary oxide thin films, especially for the Ti/B binary oxide thin films, as compared with the TiO_2 thin films of the same film thickness, by combination or mixing with SiO_2 and B_2O_3 . This would be of great advantage for applications of these thin films on various substrates since they would not lose their original transparency and colorless properties.

3.2. Photocatalytic reactivity of the Ti/Si and Ti/B binary oxide thin films

UV light irradiation of Ti/Si and Ti/B binary oxide thin films in the presence of NO led to the photocatalytic decomposition of NO into N_2 and O_2 as well as N_2O at 298 K. Fig. 5 shows the reaction time profiles of the photocatalytic decomposition of NO on the Ti/Si (Ti/Si ratio = 6.6/93.4) binary oxide thin films. As shown in this figure, the reaction proceeds with a good linearity against the irradiation time, clearly demonstrating that the decomposition reaction proceeds photocatalytically. Fig. 6 shows the effect of the TiO_2 compositions on the selectivity for the formation of N_2 and the yields of N_2 and N_2O in the photocatalytic decomposition of NO on the Ti/Si binary oxide thin films. As mentioned above, when the TiO_2 composition is low, the tetrahedrally coordinated Ti-oxide

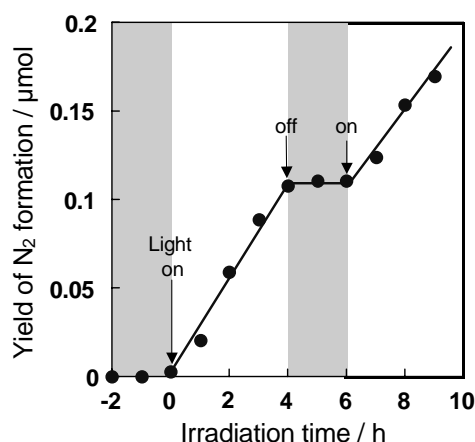


Fig. 5. The reaction time profiles of the photocatalytic decomposition of NO on Ti/Si binary oxide thin film (TiO_2 content: 6.6%) under UV light irradiation at 275 K.

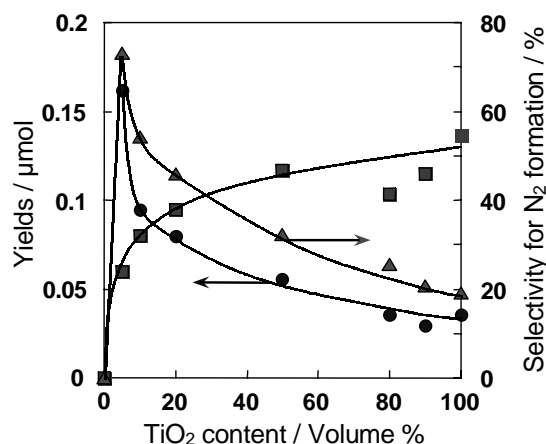


Fig. 6. The effect of TiO_2 contents on the yields of N_2 (plotted circles) and N_2O (plotted squares) and the selectivity for the formation of N_2 (plotted triangles) in the photocatalytic decomposition of NO on Ti/Si binary oxide thin films under UV light irradiation at 275 K.

species are formed as the major Ti-oxide species. Upon excitation of these Ti-oxide species by UV light, the charge transfer excited state of these species, $(\text{Ti}^{3+}-\text{O}^-)^*$, are formed. These excited $(\text{Ti}^{3+}-\text{O}^-)^*$ species have a high and unique photocatalytic activity for various reactions [27–31], reacting with NO molecules to decompose into N_2 and O_2 with high efficiency and selectivity at 298 K. However, when the TiO_2 content is increased, nano-clusters and even nano-particles of TiO_2 with octahedral coordination are formed, their photocatalytic behavior being the same as with TiO_2 semiconducting photocatalysts, where UV irradiation forms electrons in the conduction band and holes in the valence band, respectively, leading to the formation of N_2O and NO_2 . Thus, when the TiO_2 content was increased, the yields and selectivity for the formation of N_2 decreased. These results are in good agreement with our previous study where it was found that only highly dispersed tetrahedrally coordinated Ti-oxide species decomposes NO into N_2 and O_2 , while octahedrally aggregated Ti-oxides or nano-particles decompose NO into N_2O and NO_2 [27,29].

On the other hand, it was found that for the Ti/B binary oxide thin films, even when the TiO_2 composition is low, ultrafine TiO_2 nano-particles with octahedral coordination are formed in the host B_2O_3 . As can be

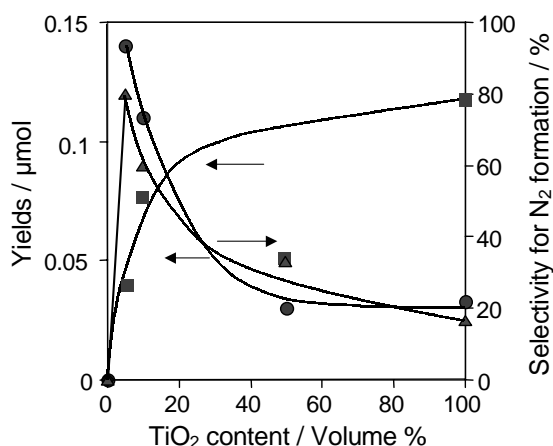


Fig. 7. The effect of TiO₂ contents on the yields of N₂ (plotted circles) and N₂O (plotted squares) and the selectivity for the formation of N₂ (plotted triangles) in the photocatalytic decomposition of NO on Ti/B binary oxide thin films under UV light irradiation at 275 K.

seen in Fig. 7, being in contradiction to the argument for Ti/Si binary oxide systems, it was found that UV irradiation of the Ti/B binary oxide thin films with low TiO₂ content in the presence of NO leads to the formation of N₂ and O₂ with a high selectivity [22,23]. Thus, in the host B₂O₃, highly dispersed octahedrally co-

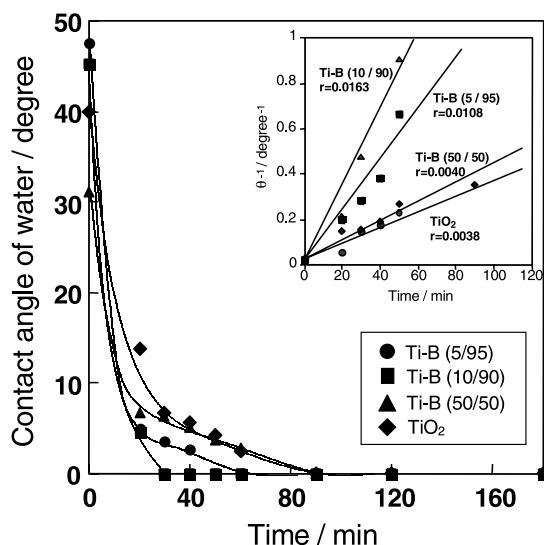


Fig. 8. The changes in the contact angle of water droplets under UV light irradiation on the Ti/B binary oxide thin films.

ordinated Ti-oxide nano-clusters can decompose NO molecules into N₂ and O₂ with high efficiency and selectivity at 298 K. A study on the true nature of the photocatalytic activity of highly dispersed octahedrally coordinated Ti-oxide nano-clusters formed in the host B₂O₃ is now in progress.

3.3. Photo-induced super-hydrophilic properties of the Ti/Si and Ti/B binary oxide thin films

The contact angle of water droplets for the TiO₂ thin films was found to dramatically decrease under UV light irradiation and finally achieve 0°, i.e.,

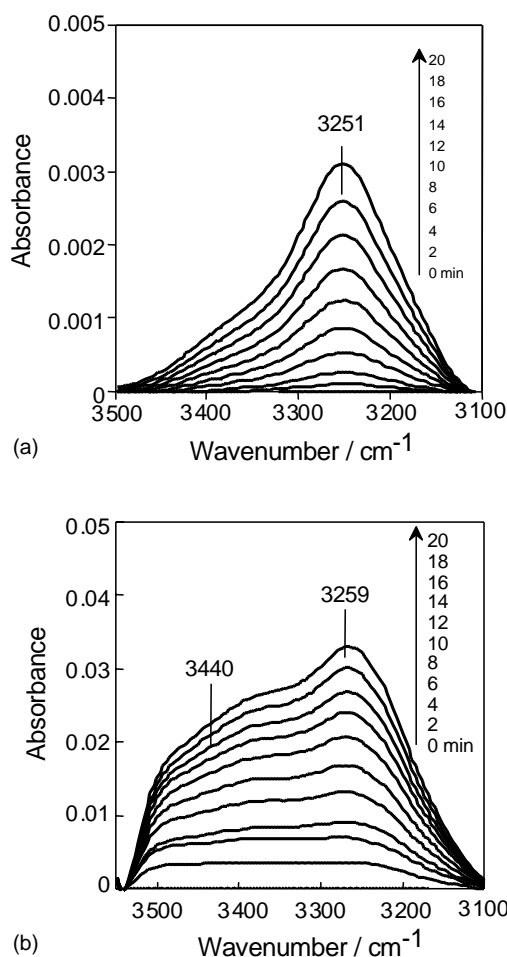


Fig. 9. The changes in the FT-IR spectra (differential spectra) of TiO₂ (a) and Ti/B binary oxide thin film (b) under UV light irradiation in air.

super-hydrophilicity. However, for the Ti/Si binary oxide thin films, the contact angle of the water droplets did not change dramatically. On the other hand, as shown in Fig. 8, for the Ti/B binary oxide thin films, all of the samples except the pure B_2O_3 achieved super-hydrophilicity, reaching a water contact angle of 0° under UV light irradiation. The insert figure shows the initial decrease rate of the photo-induced hydrophilicity of these binary oxide thin films. The decrease rate in the contact angle for the Ti/B binary oxide thin films was found to be much greater than that for the pure TiO_2 thin films. Especially, for binary oxide thin films containing more than 90% B_2O_3 , the rate was several times higher than the pure TiO_2 thin films.

Moreover, from the results of the FT-IR measurements, as shown in Fig. 9, the peak intensity at around 3250 cm^{-1} , which can be attributed to the hydrogen bond between the physisorbed water and surface OH groups, increases with the UV light irradiation time. As can be seen in Fig. 9, the extent of the changes in the intensity of these peaks for the Ti/B binary oxide thin films is 10 times greater than for the pure TiO_2 thin films under the same UV light irradiation conditions. As soon as UV light irradiation was discontinued, the contact angle of the water droplets for the TiO_2 thin films immediately increased and returned to its initial value. However, for the Ti/B binary oxide thin films,

only half the value could be recovered. Such behavior was found to show a good agreement with the FT-IR data, in which the decrease in the hydrogen bonding formed by the UV irradiation was fast for the Ti/Si binary thin films, and slow for the Ti/B binary oxide thin films. We have, therefore, concluded that the photo-formed hydrogen bonding between the surface OH groups and physisorbed H_2O is closely associated with the photo-induced super-hydrophilic properties. It was also concluded that the Ti/B binary oxide thin films exhibit more efficient formation of hydrogen bonding and their stability is higher than for the pure TiO_2 and Ti/Si binary oxides, leading to the more enhanced photo-induced super-hydrophilic properties of these Ti/B binary oxide thin films. This can be attributed to the high wettability of the B-oxides, which is the host moiety of the Ti/B binary oxides.

To clarify the origin of photo-induced super-hydrophilicity, it can be said to be [32]: (1) due to the formation of surface oxygen vacant sites which promote the dissociative adsorption of H_2O which wets the surface; or (2) the photocatalytic oxidative degradation of the adsorbed organics. However, as can be seen in Fig. 10, the parallel relationship between the photocatalytic activity and the photo-induced super-hydrophilicity observed with the Ti/B binary oxides as a function of Ti-oxide content (as TiO_2)

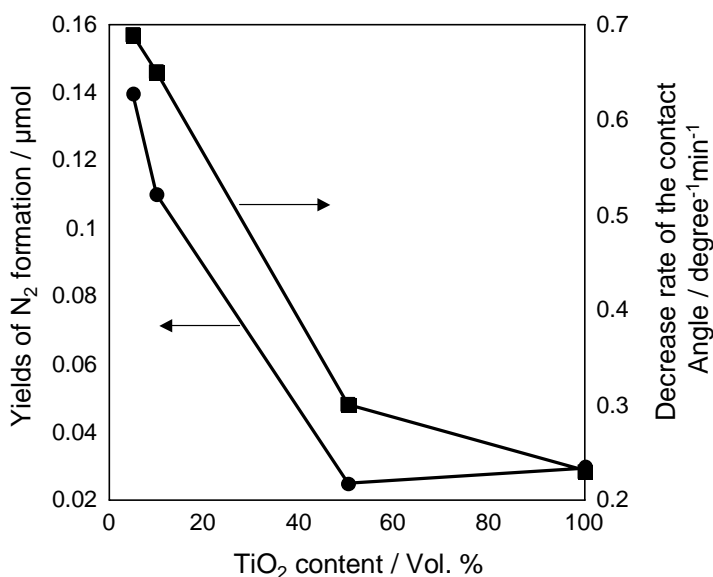


Fig. 10. Correlation between the yields of the formation and decrease in rate of the contact angle of water on Ti/B binary oxide thin films.

suggest that the photocatalytic oxidative degradation of the adsorbed compounds would seem to be the more reasonable mechanism to explain the photo-induced super-hydrophilic properties. Detailed experiments to provide more background are now underway.

These results clearly suggest that by the combination or mixing of the Ti-oxide moiety with appropriate oxide partners or host oxides, the photocatalytic activity and/or photo-induced super-hydrophilicity of the Ti-oxides could be remarkably improved, leading the way to various potential applications of titanium oxide materials.

4. Conclusions

Highly transparent Ti/Si and Ti/B binary oxide thin films were successfully prepared by the ICB method using multi-ion sources. Ti/Si binary oxide thin films including highly dispersed Ti-oxide species in tetrahedral coordination were found to exhibit higher photocatalytic reactivity as compared to the pure TiO₂ thin films, but lower photo-induced hydrophilic properties than the pure TiO₂ thin films.

On the other hand, Ti/B binary oxide thin films including ultrafine TiO₂ nano-particles having octahedral coordination dispersed in the host B₂O₃ were found to exhibit both higher photocatalytic reactivity and higher photo-induced hydrophilic properties as compared to the pure TiO₂ thin films.

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