

# Application of ion beam techniques for preparation of metal ion-implanted TiO<sub>2</sub> thin film photocatalyst available under visible light irradiation: Metal ion-implantation and ionized cluster beam method

Hiroshi Yamashita,<sup>a\*</sup> Masaru Harada,<sup>a</sup> Junko Misaka,<sup>a</sup> Masato Takeuchi,<sup>a</sup> Yuichi Ichihashi,<sup>a</sup> Fumisato Goto,<sup>b</sup> Masaya Ishida,<sup>b</sup> Toshio Sasaki,<sup>b</sup> and Masakazu Anpo<sup>a\*</sup>

<sup>a</sup>Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 599-8531, Japan, <sup>b</sup>Sumitomo Chemical Co., Ltd., Tsukuba, Ibaragi 300-32, Japan. E-mail: yamashita@chem.osakafu-u.ac.jp

Transparent TiO<sub>2</sub> thin film photocatalysts have been prepared on silica glass plate by an Ionized Cluster Beam (ICB) method. In order to improve the electronic properties of these photocatalysts, transition metal ions (V<sup>+</sup>, Cr<sup>+</sup>, Mn<sup>+</sup>, Fe<sup>+</sup>) were implanted into the TiO<sub>2</sub> thin films at high energy acceleration using an advanced metal ion-implantation technique. The combination of these ion beam techniques can allow us to prepare the TiO<sub>2</sub> thin film photocatalysts which can work effectively under visible light ( $\lambda > 450$  nm) and/or solar light irradiation. The investigation using XAFS and ab initio molecular calculation suggests that the substitution of octahedrally coordinated Ti ions in TiO<sub>2</sub> lattice with implanted metal ions is important to modify TiO<sub>2</sub> to be able to adsorb visible light and operate under visible light irradiation.

**Keywords:** photocatalysis, TiO<sub>2</sub>, metal ion-implantation, ionized cluster beam method, visible light utilization.

## 1. Introduction

The utilization of TiO<sub>2</sub> semiconductor as photocatalyst has recently attracted a great deal of attention especially for environmental applications (Anpo & Yamashita, 1997; Fujishima *et al.*, 1998; Yamashita *et al.*, 1998). Although TiO<sub>2</sub> is known as the most stable and highly reactive photocatalyst, the new concept should be developed for the design of the unique photocatalytic system which can operate efficiently not only under UV light irradiation but also under visible light irradiation (Anpo *et al.*, 1999; Yamashita *et al.*, 1999). Furthermore, it has been desired to develop the TiO<sub>2</sub> thin film having the efficient photocatalytic reactivity and the high mechanical and physical stability in being supported on various substrates in any desired forms (Takeuchi *et al.*, 2000; Yamashita *et al.*, 2000).

In the present study, transparent TiO<sub>2</sub> thin film photocatalysts have been prepared on silica glass plate by an Ionized Cluster Beam (ICB) method and the modification of their electronic properties by an advanced metal ion-implantation has been carried out to achieve the utilization of visible light for the photocatalytic degradation of organic pollutants. Mechanism of these unique performance induced by the metal ion-implantation

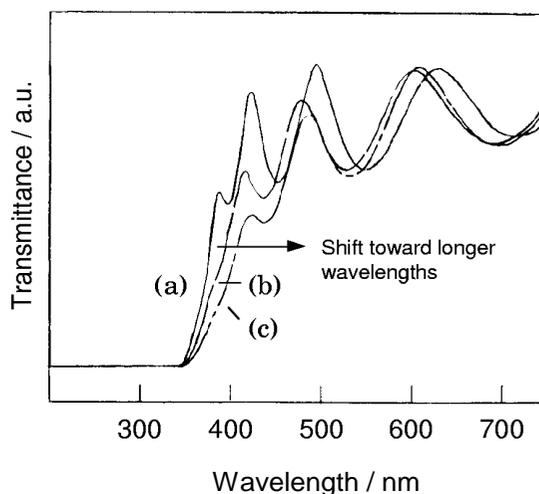
has been investigated by XAFS analysis and theoretical calculations.

## 2. Experimental

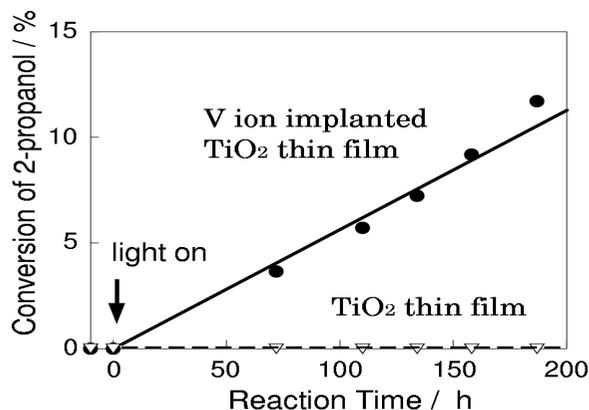
TiO<sub>2</sub> thin film photocatalysts loaded on the plate of PVG porous silica glass (Corning Co., Code-7930, 250 m<sup>2</sup>/g) were prepared by the ICB method (acceleration voltage: 0.2–2.0 kV) using a Ti metal as the source material under a dilute O<sub>2</sub> atmosphere (2.0 × 10<sup>-4</sup> Torr) (Yamashita *et al.*, 2000). The implantation of metal ions (V<sup>+</sup>, Cr<sup>+</sup>, Mn<sup>+</sup>, Fe<sup>+</sup>, etc.) to TiO<sub>2</sub> thin film photocatalysts was carried out using an ion-implanter consisting of a metal ion source, mass analyzer, high voltage ion accelerator (150 keV), and a high vacuum pump (Anpo *et al.*, 1999; Yamashita *et al.*, 1999). Photocatalytic reaction for the liquid-phase degradation of 2-propanol diluted in water was carried out 100 W high-pressure Hg lamp ( $\lambda > 450$  nm) at 295 K. The reaction products were analyzed by gas chromatography. The UV-VIS spectra of the catalysts were measured using a Shimadzu UV-2200A spectrophotometer at 295 K. The XAFS spectra were obtained in the fluorescence mode at 295 K at the BL-9A facility (Nomura & Koyama, 1999) of the Photon Factory at the National Laboratory for High Energy Physics (KEF-PF) in Tsukuba with a ring energy of 2.5 GeV. The normalized spectra were obtained by a procedure described in the previous publication (Yamashita *et al.*, 1996), and Fourier transformations were performed on  $k^3$ -weighted EXAFS oscillations in the range of 3–14 Å<sup>-1</sup>. Ab initio molecular orbital calculation were performed by the density functional theory method using Gaussian-94.

## 3. Results and Discussion

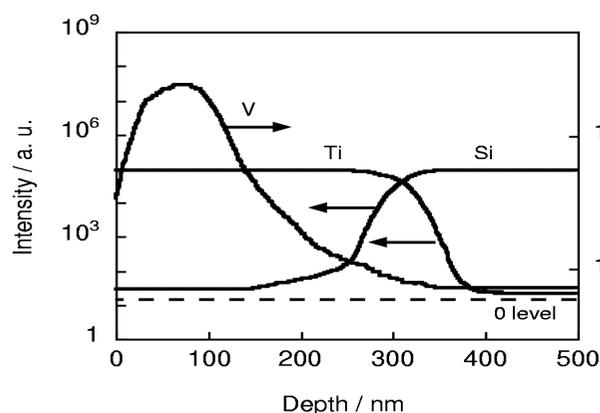
The ICB method is one of the most effective and applicable techniques in preparing active TiO<sub>2</sub> thin film on support materials under mild and dry conditions (Takeuchi *et al.*, 2000; Yamashita *et al.*, 2000). Previously we have found that a TiO<sub>2</sub> thin film prepared by the ICB method exhibit an effective photocatalytic reactivity for the liquid-phase degradation 2-propanol diluted in water at 295 K under UV light ( $\lambda > 280$  nm) irradiation to form CO<sub>2</sub> and H<sub>2</sub>O, while the thin film can not exhibit the reactivity under visible light ( $\lambda > 450$  nm) irradiation.



**Figure 1**  
The UV-VIS spectra of the V ion implanted TiO<sub>2</sub> thin films. The amount of implanted V ions (ions/cm<sup>2</sup>): (a) 0, (b) 3 × 10<sup>16</sup>, (c) 6 × 10<sup>16</sup>.



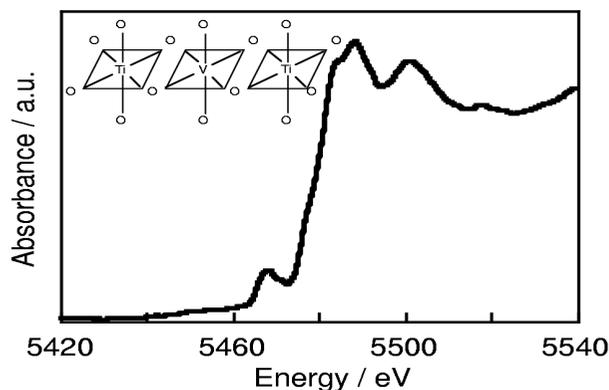
**Figure 2**  
Reaction time profiles of photocatalytic degradation of 2-propanol on the V ion implanted TiO<sub>2</sub> thin film under visible light irradiation ( $\lambda > 450$  nm).



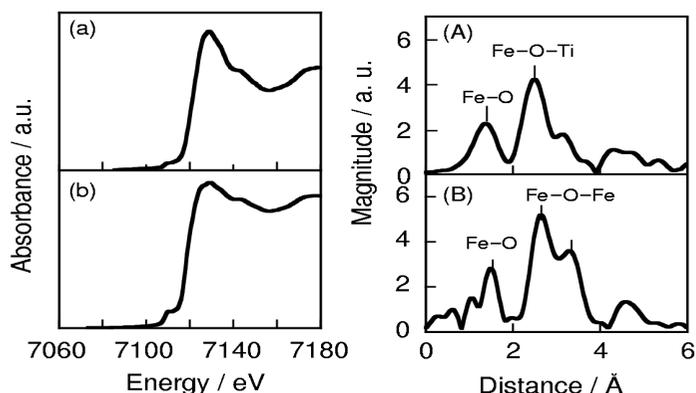
**Figure 3**  
The depth concentration profile of V ions obtained from SIMS measurements with the V ion-implanted TiO<sub>2</sub> film.

In order to improve the electronic properties of these photocatalysts to adsorb the visible light, metal ions (V<sup>+</sup>, Cr<sup>+</sup>, Mn<sup>+</sup>, Fe<sup>+</sup>, etc.) were implanted into TiO<sub>2</sub> thin films at high energy acceleration (150 keV) using a metal ion-implantation technique. As shown in Fig. 1, the UV-VIS absorption spectra of these V ion-implanted TiO<sub>2</sub> thin film photocatalysts are found to shift toward visible light regions depending on the amount of V ions implanted. The ion-implantation with other transition metal ions such as Cr, Mn, Fe, etc. are also effective to modify the properties of TiO<sub>2</sub> thin film to make a large shift in the absorption band to the visible light region.

As shown in Fig. 2, these metal ion-implanted TiO<sub>2</sub> thin film catalysts exhibit an effective photocatalytic reactivity for the liquid-phase degradation of 2-propanol diluted in water at 295 K under visible light ( $\lambda > 450$  nm) irradiation, while the unimplanted original TiO<sub>2</sub> thin film cannot exhibit the reactivity. These results clearly demonstrate that the application of such ion engineering techniques as the ICB method and the metal ion-implantation method can allow us to prepare the TiO<sub>2</sub> thin film photocatalysts which can work effectively not only under UV light irradiation but also under visible light irradiation.



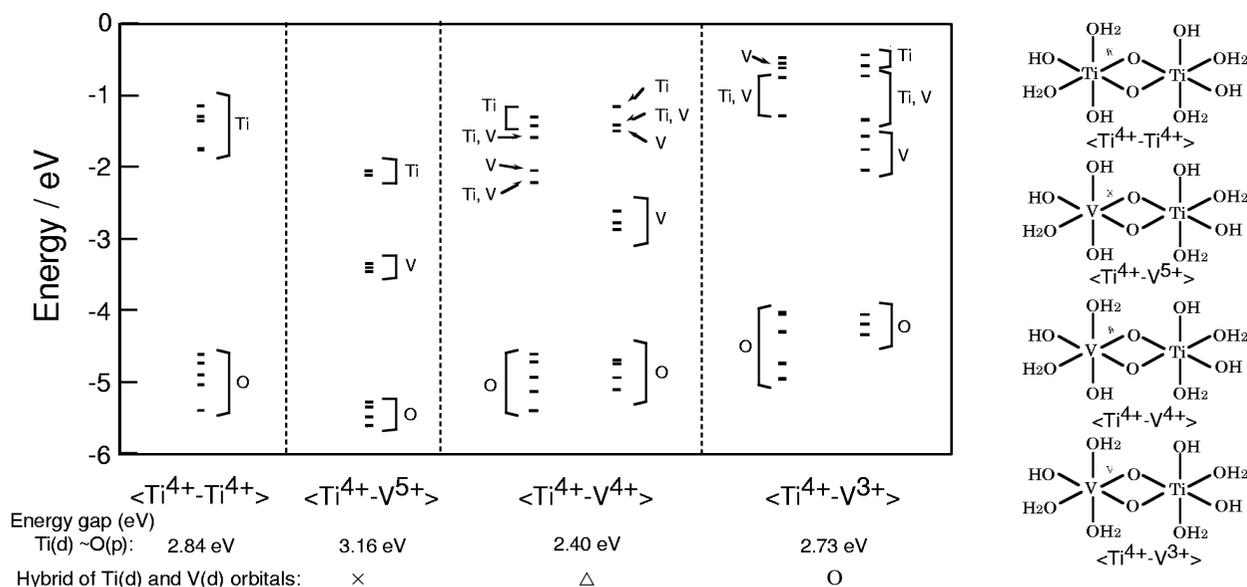
**Figure 4**  
The V K-edge XANES spectrum of V ion-implanted TiO<sub>2</sub> thin film and the structural model of implanted metal ion.



**Figure 5**  
The XANES (a, b) and FT-EXAFS (A, B) spectra of the Fe ion-implanted TiO<sub>2</sub> thin film (a, A) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (b, B).

Figure 3 shows the depth concentration profile of V ions obtained from SIMS measurements with the V ion-implanted TiO<sub>2</sub> thin film photocatalysts where ion-implantation was performed at 150 keV. The most V ions are implanted within the bulk of TiO<sub>2</sub> thin film photocatalyst but not on the top surface of TiO<sub>2</sub> thin film. The deeper the ions were implanted in the bulk of TiO<sub>2</sub> thin film with the increase in the acceleration energy. These results indicate that the modification of the electronic properties of TiO<sub>2</sub> thin film to adsorb the visible light can be carried out using the metal-ion implantation without the serious destruction of surface structure of TiO<sub>2</sub> thin film.

Figure 4 shows the V K-edge XANES spectrum of V ion-implanted TiO<sub>2</sub> thin film. V ion-implanted TiO<sub>2</sub> shows a very weak preedge peak in its XANES spectrum. Considering the observation of this weak preedge peak and its peak position (Wong *et al.*, 1984), it is found that V ions exist as V<sup>3+</sup> or V<sup>4+</sup> ions in octahedral coordination in the lattice position of TiO<sub>2</sub>. Figure 5 shows the XANES and Fourier transforms of EXAFS (FT-EXAFS) spectra of the Fe ion-implanted TiO<sub>2</sub> thin film. The Fe ion-implanted TiO<sub>2</sub> thin film exhibits a XANES spectrum without any intense preedge peaks. And in the FT-EXAFS, a peak due to the neighboring titanium atoms in TiO<sub>2</sub>



**Figure 6**

The energy level of higher-lying MOs of the cluster model of V ion-implanted  $\text{TiO}_2$ .

lattice (Fe-O-Ti) can be observed as well as a peak due to the neighboring oxygen atoms (Fe-O). These peak positions are different from those of  $\alpha\text{-Fe}_2\text{O}_3$  (Fe-O-Fe, Fe-O), respectively. Although the total quality of spectra is not so good for analysis, the results obtained by the curve-fitting analysis of the EXAFS spectra indicate that the Fe ion-implanted  $\text{TiO}_2$  thin film consists of 6-coordinated Fe ions (CN=5.8) with an atomic distance of 1.97 Å. These results indicate that Fe ions exist as isolated octahedrally coordinated  $\text{Fe}^{3+}$  species substituting lattice  $\text{Ti}^{4+}$  ions in the lattice of  $\text{TiO}_2$ . These results obtained using XAFS technique suggest that the substitution of octahedrally coordinated  $\text{Ti}^{4+}$  ions in  $\text{TiO}_2$  lattice with implanted metal ions is important to modify  $\text{TiO}_2$  so as to adsorb visible light and operate as an efficient photocatalyst under visible light irradiation.

To prove this mechanism induced by the metal ion-implantation, the theoretical approach using an ab initio molecular orbital calculation on the basis of the density functional theory has been carried out. Because of the capacity of the ab initio calculation, the binuclear cluster models having the octahedral coordination similar to the coordination of anatase  $\text{TiO}_2$  have been applied. In these cluster models, the metal ions having various electric charges ( $\text{V}^{5+}$ ,  $\text{V}^{4+}$ ,  $\text{V}^{3+}$ ) are substituted with  $\text{Ti}^{4+}$  ion octahedrally coordinated in the lattice position of  $\text{TiO}_2$ . As shown in Fig. 6, the models having  $\text{V}^{4+}$  ion  $\langle \text{Ti}^{4+}-\text{V}^{4+} \rangle$  and  $\text{V}^{3+}$  ion  $\langle \text{Ti}^{4+}-\text{V}^{3+} \rangle$  can have the energy gap of Ti(d) - O(d) smaller than that of un-implanted pure Ti-oxide  $\langle \text{Ti}^{4+}-\text{Ti}^{4+} \rangle$ . With these models the overlap of Ti(d) and V(d) orbitals are observed. These results indicate that the mixing of the Ti(d) orbital of Ti-oxide and the metal(d) orbital of the implanted metal ions in the low electric charge is essential to decrease the energy gap between Ti(d) and O(p) orbitals of Ti-oxide. Considering this mechanism, it can be proposed that in the metal ion implanted  $\text{TiO}_2$  photocatalyst the overlap of the conduction band due to Ti(d) of  $\text{TiO}_2$  and the metal(d) orbital of

the implanted metal ions can decrease the band gap of  $\text{TiO}_2$  photocatalyst to enable to adsorb the visible light.

In conclusions, the present results have demonstrated that the combination of the ICB method and metal-ion implantation can allow us to prepare the  $\text{TiO}_2$  thin film photocatalysts which can adsorb the visible light and operate effectively under visible light ( $\lambda > 450$  nm) and/or solar light irradiation. The XAFS analysis and theoretical calculations indicate that the substitution of Ti ions with the isolated metal ions implanted into the lattice position of the bulk of  $\text{TiO}_2$  photocatalyst is the determining factor for the utilization of visible light and solar light and the metal-ion implantation method is the most efficient and smart technique to design these advanced material.

## References

- Anpo, M. & Yamashita, H. (1997). *Heterogeneous Photocatalysis* edited by M. Schiavello, pp. 133-169. London: Wiley Inc.
- Anpo, M., Ichihashi, Y., Takeuchi, M. & Yamashita, H. (1999). *Stud. Surf. Sci. Catal.* **121**, 305-309.
- Fujishima, A., Hashimoto, K. & Watanabe, T. (1998). *TiO<sub>2</sub> Photocatalysis*, Tokyo, Bkc Inc.
- Heller, M. A. (1995). *Acc. Chem. Res.* **28**, 503-507.
- Nomura, M. & Koyama, A. (1999). *J. Synchrotron Rad.* **6**, 182-184.
- Takeuchi, M., Yamashita, H., Matsuoka, M. & Anpo, M. (2000). *Catal. Lett.* **12**, 876-879.
- Wong, J., Lytle, F. W., Messmer, R. P. & Maylotte, D. H. (1984). *Phys. Rev. B* **30**, 5596-5608.
- Yamashita, H., Matsuoka, M., Tsuji, K., Shioya, Y. & Anpo, M. (1996). *J. Phys. Chem.* **100**, 397-402.
- Yamashita, H., Honda, M., Harada, M., Ichihashi, Y. & Anpo, M. (1998). *J. Phys. Chem. B* **102**, 10707-10711.
- Yamashita, H., Ichihashi, Y., Takeuchi, M. & Anpo, M. (1999). *J. Synchrotron Rad.* **6**, 451-453.
- Yamashita, H., Harada, M., Tani, A., Takeuchi, M., Ichihashi, Y. & Anpo, M. (2000). *Stud. Surf. Sci. Catal.* **130**, 1931-1936.