Preparation of Ti-Si binary oxide thin film photocatalysts by the application of an ionized cluster beam method

Masato Takeuchi, Masaya Matsuoka, Hiromi Yamashita, and Masakazu Anpo*

Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Ti-Si binary oxide thin films with various Ti contents were prepared in a dry process by using an Ionized Cluster Beam (ICB) deposition method with multi ion sources. From the results of UV-VIS measurements, the transmittance of these binary oxide thin films is very high compared to pure TiO_2 thin films, indicating that the Ti-oxide exists in a highly dispersed state in the SiO_2 matrices. The EXAFS spectra of these thin films with lower Ti content exhibited only a sharp preedge peak attributed to the highly dispersed Ti-oxide species which differs from the peaks of anatase TiO_2 thin films.

UV light irradiation of these Ti-Si binary oxide thin films in the presence of NO were found to lead to the evolution of N_2 and O_2 with a good linearity against the irradiation time. The lower the Ti content, the higher the reactivity and the selectivity for the formation of N_2 were. These results clearly indicate that the highly dispersed Ti-oxide species plays an important role in the formation of N_2 and O_2 for the photocatalytic decomposition of NO under UV light irradiation.

Keywords: Ti-Si binary oxide thin film, Ionized Cluster Beam method, Photocatalysts

1. Introduction

In recent years, TiO_2 thin films coated on glass, tile and various architectural materials have been actively and widely investigated since TiO_2 thin films exhibit not only photocatalytic reactivity but also super-hydrophilic property under UV light irradiation (Heller *et al.*, 1995; Negishi *et al.*, 1998; Wang et al., 1997). We have also reported that TiO_2 thin films prepared on a quartz substrate by ion engineering techniques such as an ionized cluster beam (ICB) deposition method, work as a photocatalyst under UV light irradiation (Takeuchi *et al.*, 2000) while the Ti-Si binary oxides having lower Ti content prepared by the sol-gel method were found to have Ti-oxide species dispersed in the SiO_2 matrices and to exhibit higher photocatalytic reactivity for the decomposition of NO into N_2, O_2 and N_2O as well as a high selectivity for the formation of N_2 under UV light irradiation (Anpo *et al.*, 1997; Yamashita *et al.*, 1998). In this study, we deal with the preparation of Ti-Si binary oxide thin films having different Ti contents by using an ICB deposition method and the characterization of these thin films by XAFS and UV-VIS absorption measurement.

2. Experimental

Ti-Si binary oxide thin films were prepared by an ICB deposition method with Ti and Si ion-sources and a schematic diagram of this method is shown in Fig. 1. The metals Ti and SiO as the source materials were heated up in each crucible and the vapors were introduced into the high vacuum chamber. At this time, the Ti and SiO clusters reacted with the O_2 molecules (oxygen pressure:2×10^{-4} Torr) in the chamber to produce stoichiometric TiO_2 and SiO_2 clusters. Using electron beam irradiation, ionized TiO_2 and SiO_2 clusters were accelerated by an electric field (acceleration voltage: 500 V) and bombarded onto the quartz substrate. By controlling each deposition rate, the Ti/Si ratio can be strictly controlled. The resulting Ti-Si binary oxide thin films were characterized by various spectroscopic means such as XAFS (BL-7C, KEK, Tsukuba) and UV-VIS absorption measurements. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K with an Si(111) two-crystal monochromator. The photocatalytic properties of these thin films were also investigated by carrying out the photocatalytic decomposition of NO under UV light (λ>270 nm) irradiation.

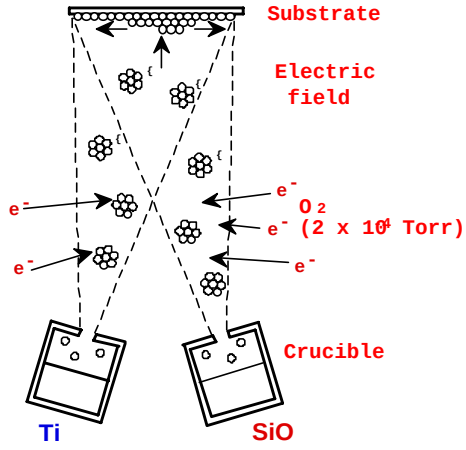

Fig. 1 Schematic diagram of the ICB deposition method with Ti and Si ion-sources.

3. Results and Discussion

Figure 2 shows the UV-VIS absorption spectra of Ti-Si binary oxide thin films with different Ti contents by the transmittance method. A remarkable shift in the absorption edge towards shorter wavelength regions can be seen with the decrease in the Ti content. This shift in the absorption edge is attributed to the size quantum effect arising from the presence of an ultrafine Ti-oxide species dispersed within the SiO_2 matrices.

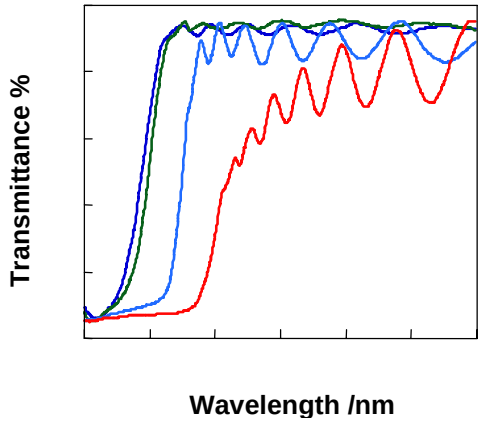

Fig. 2 UV-VIS transmittance spectra of TiO_2/SiO_2 binary oxide thin films prepared on quartz substrates by an ICB deposition method with Ti and Si ion-sources. The amount of TiO_2 (left to right): 6.6, 9.5, 50.1, 100%.

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In order to investigate the local structure of the Ti-oxide species in the thin films, the Ti K-edge XAFS spectra were measured at the BL-7C of KEK in Tsukuba. Figure 3 (left) shows the XANES spectra of the Ti-Si binary oxide thin films with different Ti contents. In the spectra with lower content (< 10 %), only a sharp preedge peak attributed to the highly dispersed Ti-oxide species which differs from that of the anatase TiO_2 thin films can be seen. As the Ti content increases, the intensity of the sharp preedge becomes smaller, indicating that the size of the ultrafine Ti-oxide clusters becomes larger with the increase in Ti content.

Figure 3 (right) also shows the Fourier transforms of the EXAFS spectra of these thin films. In all of the binary oxide thin films, a strong peak at around 1.6 Å which is attributed to the neighboring O atoms (Ti-O) can be seen, but a peak at around 3.0 Å which is attributed to the Ti-O-Ti bond cannot be observed, indicating that no aggregated TiO_2 species exist but ultrafine Ti-oxide clusters. Also, from the investigations of the curve fitting of the EXAFS spectra, we could obtain the information on the coordination numbers of Ti atom in the binary oxide thin films with a TiO_2 content of 6.6 and 9.5 % are 4.3 and 4.4, respectively. These results clearly indicate that Ti-oxide species are highly dispersed in the amorphous SiO_2 matrices. including the 4-fold Ti-oxide species, are highly dispersed within the SiO_2 matrices.

UV light irradiation of these Ti-Si binary oxide thin films in the presence of NO were found to lead to the evolution of N_2 and O_2 with a good linearity against the UV light irradiation time. The lower the Ti content, the higher the photocatalytic reactivity and selectivity for the formation of N_2 were. These results clearly indicate that the highly dispersed Ti-Oxide species play an important role in the formation of N_2 and O_2 for the photocatalytic decomposition of NO under UV light irradiation

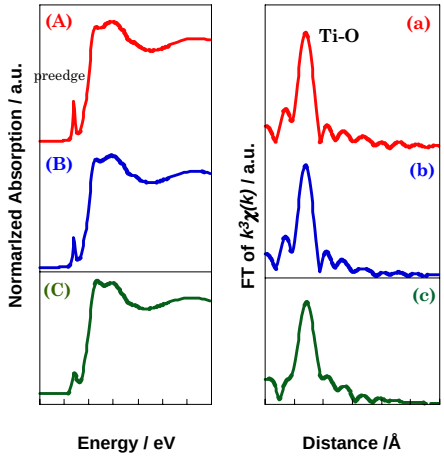

Fig. 3 XANES (A-C) and Fourier transforms of EXAFS (a-c) of the TiO_2/SiO_2 binary oxide thin films prepared by an ICB deposition method with Ti and Si ion-sources. The amount of TiO_2 (top to bottom): 6.6, 9.5, 50.1 %.

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