Photocatalytic decomposition of NO on titanium oxide thin film photocatalysts prepared by an ionized cluster beam technique

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Transparent TiO_2 thin film photocatalysts were prepared on transparent porous Vycor glass (PVG) by an ionized cluster beam (ICB) method. The UV-VIS absorption spectra of these films show specific interference fringes, indicating that uniform and transparent TiO_2 thin films are formed. The results of XRD measurements indicate that these TiO_2 thin films consist of both anatase and rutile structures. UV light ($\lambda > 270$ nm) irradiation of these TiO_2 thin films in the presence of NO led to the photocatalytic decomposition of NO into N_2, O_2 and N_2O. The reactivity of these TiO_2 thin films for the photocatalytic decomposition of NO is strongly dependent on the film thickness, i.e., the thinner the TiO_2 thin films, the higher the reactivity.

Keywords: TiO_2 thin film photocatalyst, ionized cluster beam deposition method, ion engineering technique, decomposition reaction of NO

1. Introduction

TiO_2 thin film photocatalysts prepared by the sol–gel method have been utilized in many fields not only due to its photocatalytic reactivity but also because of its useful antibacterial and superhydrophilic properties [1–4]. However, the sol–gel method of preparing TiO_2 thin film photocatalysts is a wet process in itself, necessitating the use of solvents and calcination treatments at high temperature. It is therefore important to develop TiO_2 thin films which show high photocatalytic performance and have high mechanical and physical stability when supported on various substrates in any desired form at a low cost.

In this study, we have studied the possibility of applying an advanced ionized cluster beam (ICB) method as an effective dry process in the design of highly reactive TiO_2 thin film photocatalysts. The general advantages of the ICB method [5] are: (1) contamination with various impurities can be easily prevented since the process is performed in a high vacuum chamber; (2) high crystallinity TiO_2 films can be prepared without calcination at high temperatures; and (3) the various physical and chemical properties of the thin films, such as the thickness, can be controlled and it can be applied on various substrates, even on substrates having little resistance to heat. Along these lines, TiO_2 thin film photocatalysts have been prepared by applying such an ICB method and their physical and chemical properties have been characterized by means of various molecular spectroscopic measurements. Furthermore, the photocatalytic reactivity for the decomposition of NO into N_2, O_2 and N_2O under UV light irradiation at 275 K has been investigated.

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2. Experimental

TiO_2 thin films were prepared by the ICB method [6–11] and a schematic diagram of the method is shown in figure 1. Titanium metal used as the source material was heated up to about 2200 K in the crucible and titanium vapor was introduced into the high vacuum chamber producing titanium clusters. At this time, the titanium clusters reacted with the O_2 molecules in the chamber and stoichiometric TiO_2 clusters were formed (oxygen pressure 2×10^{-4} Torr). Using electron beam irradiation, ionized TiO_2 clusters were accelerated by an electric field (acceleration voltage 500 V) and bombarded onto the substrate. The temperature of the substrate was then heated up to 623 K to prepare a good crystallinity in the TiO_2 thin films. The resulting transparent TiO_2 thin films were then characterized by various spectroscopic means such as XRD and UV-VIS absorption measurements. The photocatalytic properties of these TiO_2 thin films were also investigated by carrying out the photocatalytic decomposition of NO under UV light ($\lambda > 270$ nm) irradiation.

3. Results and discussion

Figure 2 shows the XRD patterns of the TiO_2 thin films as well as powdered TiO_2 (P-25) as reference. For the thin films in which the film thickness was smaller than 100 nm,

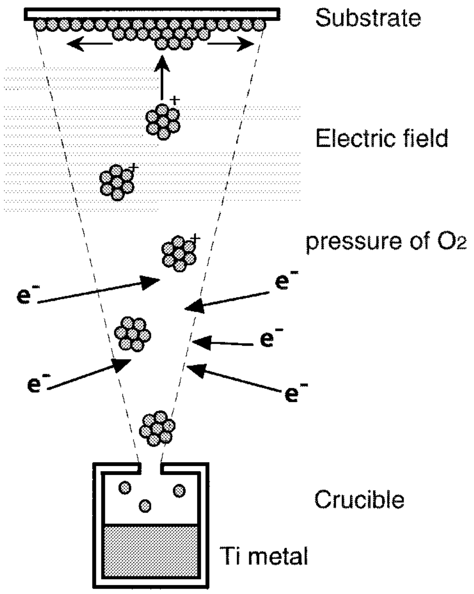

Figure 1. Schematic diagram of the ICB deposition method.

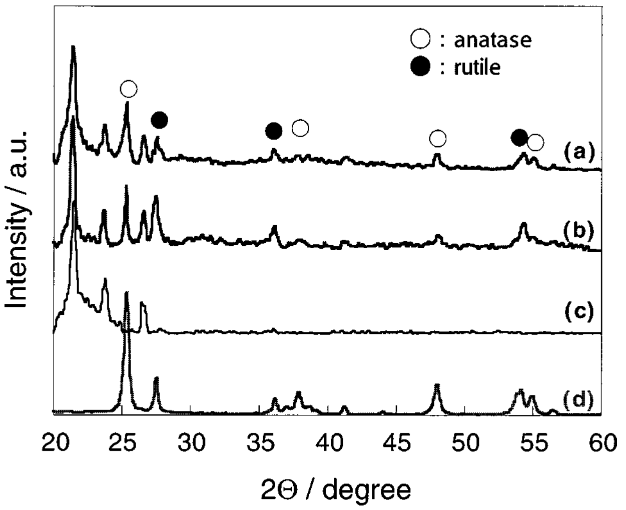

Figure 2. XRD patterns of TiO_2 thin films prepared by an ICB method on porous Vycor glass (PVG). TiO_2 thin films: (a) 500 and (b) 300 nm; (c) PVG (substrate) and (d) TiO_2 (P-25) powder used as reference.

no peaks attributed to the TiO_2 structure could be detected and only peaks due to the SiO_2 substrate were observed. On the other hand, when the film thickness was larger than 300 nm, XRD patterns which could be attributed to the presence of an anatase and rutile structure of TiO_2 could be observed. Since the reference P-25 powdered TiO_2 (Degussa) is a composition of the anatase and rutile structure and exhibits high photocatalytic reactivity, it could be expected that TiO_2 thin film photocatalysts prepared by the ICB method would also exhibit high photocatalytic reactivity.

The UV-VIS absorption spectra of the TiO_2 thin films are shown in figure 3. In these spectra, TiO_2 thin films having a film thickness larger than 100 nm clearly show specific interference fringes, indicating that transparent and uniform TiO_2 thin films were formed in these photocatalysts. As the film thickness decreases, the absorption spectra of the thin

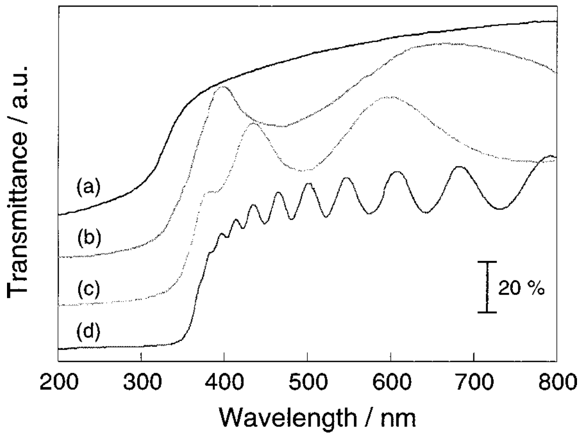

Figure 3. UV-VIS absorption spectra of TiO_2 thin films prepared by an ICB method. Film thickness: (a) 20, (b) 100, (c) 300 and (d) 1000 nm.

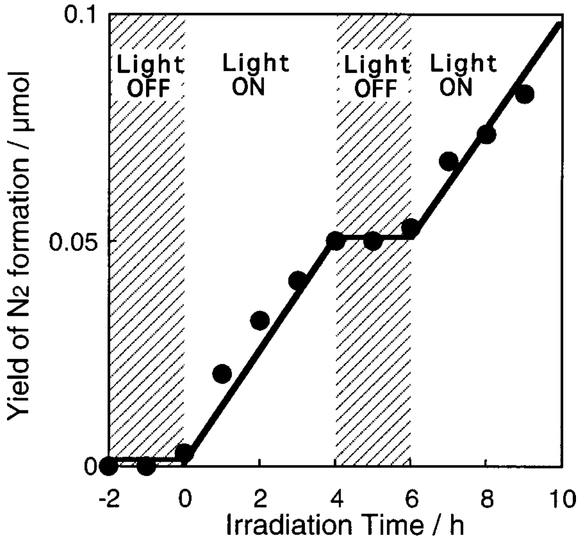

Figure 4. The reaction time profiles of the photocatalytic decomposition of NO on TiO_2 thin film (film thickness 100 nm) under UV light ($\lambda >$ 270 nm) irradiation at 275 K.

films were found to shift toward shorter wavelength regions. This can be attributed to the quantum size effect of the thin films caused by the presence of TiO_2 particles of small size as a composition of the transparent TiO_2 thin films.

In the presence of NO, UV light ($\lambda > 270$ nm) irradiation of TiO_2 thin film photocatalysts prepared by the ICB method led to the photocatalytic decomposition of NO into N_2, O_2 and N_2O at 275 K. Figure 4 shows the reaction time profiles of the photocatalytic decomposition of NO. The yield of the formation of N_2 (and O_2) increases linearly with the UV irradiation time. The formation of these reaction products did not occur under dark conditions. Moreover, as shown in figure 4, as soon as UV irradiation was discontinued, the photocatalytic reaction immediately ceased. Thus, it was clearly shown that TiO_2 thin film photocatalysts prepared by the ICB method exhibit high photocatalytic reactivity for the direct decomposition of NO. The photocatalytic reactivity of these TiO_2 thin films was found to be comparable or even higher as compared with

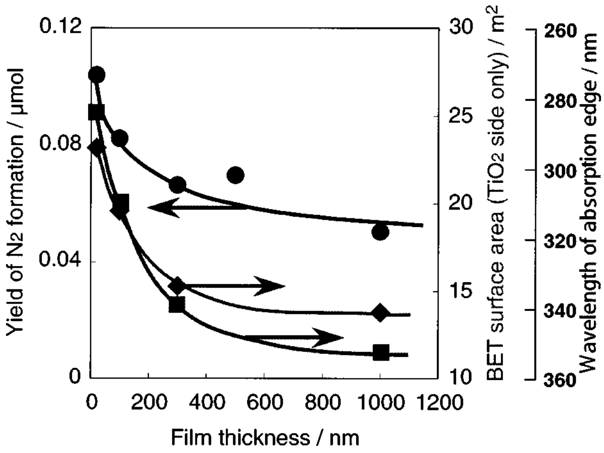

Figure 5. The effects of the film thickness on the photocatalytic reactivity of TiO_2 photocatalysts for the decomposition of NO (●) under UV light irradiation, the BET surface areas (♦), and the wavelength of absorption edge (■).

TiO_2 thin films prepared by the sol–gel method. It was also found that the photocatalytic reactivity strongly depends on the thickness of the films. Figure 5 shows the effect of the TiO_2 film thickness on the photocatalytic reactivity and the BET surface areas, as well as the wavelength of absorption edge of the thin film photocatalysts. TiO_2 thin films having small film thickness show much higher photocatalytic reactivity. As the film thickness increases, the photocatalytic reactivity becomes lower. The BET surface areas and the wavelength of the absorption edge show the same tendency towards the photocatalytic reactivity. These results clearly show that the photocatalytic properties of the TiO_2 thin films are dependent on the film thickness.

In summary, transparent TiO_2 thin films were successfully prepared using an ICB method. Our TiO_2 thin films worked efficiently and effectively as photocatalysts for the decomposition of NO into N_2, O_2 and N_2O under UV light irradiation at 275 K. The crystalline structure and electronic state of the TiO_2 thin films varied along with their photocatalytic reactivity which strongly depended on the film thickness, i.e., as the film thickness decreases, the photocatalytic reactivity increases.

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