Deposition of Photocatalytic TiO$_2$ Films by Planar Magnetron Sputtering System with Opposed Ti Targets

Kikuo Tominaga,$^1$ Kenji Okada, Yoshinori Miyamoto, Shinya Ohkura, Kentaro Shiraiishi, Kazuya Kusaka, Takahiro Ueno, and Takao Hanabusa

Institute of Science and Technology, The University of Tokushima, Minami-josanjima 2-1, Tokushima, 770-8506 Japan

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TiO$_2$ films are deposited on glass substrate in O$_2$/Ar gas mixtures by facing target planar magnetron (FT-PM) sputtering, and the effects of the sputtering system on the crystal phases and axis orientation of TiO$_2$ films are investigated for as-deposited films. Deposition is carried out by two systems: In the first system the opposing magnets have opposite polarities of internal permanent magnets in each target holder; this leads to confinement of the electrons therefore weak electron bombardment on the substrate. The result is poor grain growth with low quality anatase films with poor photocatalytic activity. In the second system the opposing magnets have the same polarities each other; the electron bombardment becomes strong and grain growth is enhanced. The results indicate a high quality anatase film with very good photocatalytic activity.

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I. INTRODUCTION

Titanium dioxide (TiO$_2$) has attracted many researchers because of its high refractive index in the rutile phase and excellent photocatalytic properties in the anatase phase [1–5]. The photocatalytic effect appears on the TiO$_2$ surface, so the deposition of TiO$_2$ films were investigated as well as TiO$_2$ powders and many deposition methods have been developed for anatase TiO$_2$. Deposition techniques involving plasma reactions such as reactive ion plating [6], thermal oxidation of sputtered Ti films [7], planar magnetron sputtering [8], magnetron sputtering with facing targets [9, 10], have been proposed. It has been recognized that there is a relationship between the plasma exposure and the TiO$_2$ film properties [11, 12]. However the deposition conditions remained unclear, since the presence of the rutile and anatase phases complicated the deposition conditions and the films were strongly influenced by the plasma owing to their high reactivity to Ti. Recently, anatase TiO$_2$ film deposition gained importance as a transparent conductive material fabrication process [11]. Thus, control of the structural properties of TiO$_2$ films is required for both the fields of photocatalysis and transparent conductive oxides. In the present experiments, we deposited TiO$_2$ films by planar magnetron (PM) sputtering and PM sputtering with opposing Ti targets. We compared the crystallographic orientation, surface morphology and photocatalytic properties of the TiO$_2$ films obtained and investigated the factors influencing the appearance of the anatase or rutile phases in TiO$_2$ films.

II. EXPERIMENTAL

TiO$_2$ films were deposited by reactive sputtering of Ti in gas mixtures of Ar and O$_2$. After the chamber was evacuated to 5×10$^{-4}$ Pa, the gas mixture was introduced through a gas blender (SECB-2, HORIBA). The total gas pressure, $P$, was held at constant during deposition. A 50×50×1.1 mm Corning #1737 was used as substrate. The film thickness was measured by optical interferometry using the refractive index $n = 2.4$ [14].

Figure 1(a) schematizes a planar magnetron sputtering system with a facing two targets of Ti. The permanent magnets in each holder have opposite polarities as indicated in the figure. Thus, energetic electrons are confined between the targets by the magnetic field component parallel to the target axis, so the substrate is isolated from the plasma. Then most energetic electrons are confined

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$^†$Corresponding author: tominaga@ee.tokushima-u.ac.jp
between the two targets. We designate this system as System A.

Another sputtering system, designated as System B, is shown in Fig. 1(b), where the completely the same targets were used in each target. Then the magnetic field expands outwards as shown by dashed lines, so the energetic electrons also diffuse outwards. The substrate are exposed to those energetic electrons.

The target current was maintained at 500 mA and the input powers was about 250 W. The distance between the targets was 10 cm, and the glass substrate was settled at an off-axis position $x$, where $x$ is the distance between the substrate and the target axis as shown in Figs. 1(a) and (b). Ti targets 10 cm in diameter and 3 mm in thickness were held on each target holder.

X-ray diffraction patterns were observed by X-ray diffraction meter (Rigaku) and surface morphology was measured by atomic force microscopy (AFM) measurement. Evaluation of photo-catalytic change of methylene-blue was irradiated with UV light (black light and 1 mW/cm$^2$).

III. RESULTS

Figure 2(a) shows X-ray diffraction patterns of films deposited at $x = 40$-70 mm by the System A with opposing Ti targets. The total pressure, $P$, was maintained at 0.2 Pa, and the gas flow ratio of O$_2$ to Ar, $f$(O$_2$/Ar), was 2/8. The substrate was maintained at room temperature. The substrate was not heated intentionally, but the energetic electrons incident on the substrate holder heated the substrate to a maximum of 100°C. The A in the figure denote the anatase phase. The deposition rate at $x = 40, 50, 70$ mm were 910, 990, and 660 nm/h, respectively. The deposition rate reached its maximum value (990 nm/h) at $x = 50$ mm; it decreased with further increase in $x$. For all films, only the anatase phase was observed, and the preferential axis-orientation did not change with $x$. At $x = 40$ mm, where the substrate was near the plasma region between the targets, no peaks of A(101) and A(211) were observed. Upon increasing $x$ to 70 mm, the position where the plasma exposure decreased and the deposition rate decreased to 2/3 of that at $x = 50$ mm, only the A(101) peak was identified.

Figures 2(b) and (c) are X-ray diffraction patterns of the films deposited by the System A at $P = 0.5$ Pa and 1.0 Pa under $f$(O$_2$/Ar)=2/8, respectively, for the substrate
FIG. 4: AFM images of the films deposited at (a) \( x = 40 \) mm and (b) \( 60 \) mm by System A, and at (c) \( x = 40 \) mm and (d) \( 60 \) mm by System B.

FIG. 5: Change in the concentration of methylene blue as a function of UV irradiation time

positions \( x = 40, 50, 60 \) and \( 70 \) mm. Only anatase phase appeared for at all pressures. All figures show the same pattern, which indicates that the diffraction pattern did not depend on the total pressure.

For the films deposited by the System B at \( P = 0.2 \) Pa under \( f(O_2/Ar) = 2/8 \), the X-ray diffraction patterns are shown in Fig. 3 as a parameter of \( x \). Although the substrate was not heated intentionally, but the energetic electrons incident on the substrate holder heated the substrate to a maximum of 300\(^\circ\)C. Mixed orientation of A(101), R(110) and A(112) were observed at larger \( x \) values. However, we could observe no peak at \( x = 40 \) mm, when the substrate was near the plasma region.

Figures 4(a) and (b) shows AFM images for the above System A. At \( x = 40 \) mm in Fig. 4(a), the grain size was small and the surface roughness is also small. Increasing \( x \) to 60 mm showed smaller grain size and smooth surface. On the contrary, the films deposited by the System B showed much larger grain size apparently. A larger grain size was observed at \( x = 40 \) and \( 60 \) mm. These results indicate that a appropriate electron bombardment on the substrate enhances the grain growth.

Figure 5 shows the concentration change of the methylene blue under UV irradiation for the films indicated in Fig. 4. The concentration of methylene blue decreased monotonically with the irradiation time in those films. The decomposition performance index was also estimated. The results are shown in Fig. 5. The values of decomposition performance index of 14.0 and 9.2 were obtained for the electron confined system. The value of 9.2 was the same as that reported for the films by conventional DC reactive sputtering by Noguchi et al. [15]. The performance index increased to 14.0 at \( x = 40 \) mm. The same trend was for the films deposited by the System B. In this case, the excellent values of 23.2 and 18.0 were attained at \( x = 40 \) mm and \( 60 \) mm, much higher than those of the electron confined system. These results indicate that the
photocatalytic properties was improved by an appropriate electron irradiation on the substrate.

IV. CONCLUSIONS

We have investigated the influence of the sputtering condition on the film structure, film morphology and photocatalytic performance by using planar magnetron (PM) sputtering systems, Systems A and B. When the electron bombardment is relatively weak in the System A in Fig. 1(a), the grain growth is not enough, and the decomposition performance index is nearly the same as that of conventional reactive DC sputtering. When the electron bombardment becomes strong in the System B in Fig. 1(b), the grain growth was enhanced and the decomposition performance index showed much higher values than that of conventional reactive DC sputtering. This indicates that the electron bombardment is effective in depositing excellent photocatalytic TiO$_2$ films. At the present stage, the role of the electron bombardment is not simply the increase of the substrate heating, since the X-ray diffraction patterns becomes amorphouslike at the increased electron bombardment. The irradiation of energetic ions will be induced with the electron radiation.

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