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Comparative Study of TiO_2 Anatase Epitaxial and Polycrystalline Thin Films Grown by Magnetron Sputtering

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Comparative study of Epitaxial and polycrystalline anatase TiO_2 films grown by magnetron sputtering has been performed in order to clarify the photocatalytic behavior of anatase material. Only the polycrystalline anatase film showed a well-defined photocatalytic activity and the epitaxial films (<001> and <204> oriented) hardly showed photocatalytic behavior despite the better crystalline quality compared with that of the polycrystalline film. It was revealed that the anisotropy in the effective mass and the surface roughness could be excluded from the major factor for determining photocatalytic activity in this system. Since the major discrepancy between the epitaxial films and polycrystalline films is the existence of the grain boundaries, further study focusing on the grain boundary effects should be performed for the elucidation of the dominant factor for photocatalytic activity in this system.

Key words: TiO_2, photo-catalytic properties, epitaxy, sputtering

1. INTRODUCTION

Since the discovery of the photosensitizing effect of TiO_2 electrode on the electrochemical decomposition of water [1], TiO_2 has attracted significant attention, and the photocatalytic properties of TiO_2 has become a major area of intensive research. TiO_2 has shown interesting phenomena, such as photo-induced oxidation and reduction, and photo-induced hydrophilic/ hydrophobic switching [2-4] and has been widely considered as the most promising photocatalytic material. Thin film fabrication process for coating photocatalytic TiO_2 on various substances is the key technology for the practical use of this material. Recent progress in sputtering apparatus enabled the large-area high-speed low-temperature growth of TiO_2, upgrading sputtering to be one of the most promising film growth processes of TiO_2 [5].

Recently, Yamagishi et al. reported photocatalytic activity of epitaxial and polycrystalline TiO_2 films grown by sputtering [6]. The photocatalytic activities of the <001> oriented epitaxial TiO_2 films grown on single crystalline substrates were much lower than that of the polycrystalline TiO_2 films grown on glass substrates. They have attributed this inferiority of epitaxial films in photocatalytic activity to the anisotropy of the effective mass of the free electrons in anatase-TiO_2. According to their calculation, the effective mass of the free electrons in anatase-TiO_2 along the <001> direction is three-times as large as those of the other directions. As a result, this large effective mass prevents the electrons from diffusion towards the surface of the sample and reduces the photocatalytic activity in <001>-oriented epitaxial TiO_2 films.

We have recently succeeded in growing epitaxial anatase TiO_2 films with <204> orientation, which could

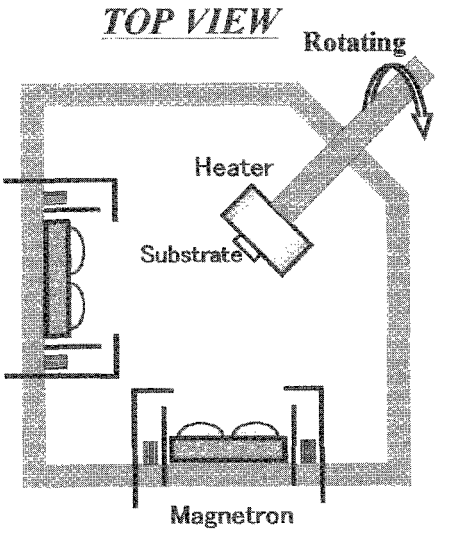

Fig.1. Schematic drawing of the sputtering apparatus used in this study.

Table I Detailed deposition contitions for TiO_2 film growth.

Pressure during growth (Pa)	0.5
Target dimension (mm^3)	200x130x10
Pulse frequency (kHz)	50
Duty cycle (%)	50
Substrate temperature (K)	973(epi.), 473(poly.)
Input Power (W)	500+500
Oxygen flow rate (sccm)	4
Growth rate (nm/min)	~8
Film thickness (nm)	220(epi.), 240nm(poly.)

provide further information on the above-mentioned effective mass model in photocatalytic activity.

2. EXPERIMENTAL

TiO_2 films were deposited by a pulse-powered magnetron sputtering apparatus (MiniLabCoater 200: Fraunhofer–Institut für Elektronenstrahl- und Plasmatechnik) equipped with two rectangular targets [5] making a right angle with each other (fig.1). High purity Ti (99.9%) metal plates (200x130x10mm) were mounted on the magnetrons and used as starting materials. The substrate was rotated during growth for the uniformity in film thickness. The details of the deposition conditions for the growth of TiO_2 films are listed in table I. Three kinds of substrates: $LaAlO_3$(100), $LaAlO_3$(110), quartz glass were used as substrates. The lattice constant of the a,b-axis $LaAlO_3$ (0.3788nm) shows almost perfect matching between that of the anatase-TiO_2 (0.3785nm) and an excellent epitaxial growth is expected. The substrates were ultrasonically cleaned with alkaline lotion (SEMICO.CLEAN) and then with deionized- water for 10 minutes and finally annealed at 1000 °C in an oxygen atmosphere for two hours in order to get atomically flat surface. The crystalline structures of the films were analyzed by an X-ray diffraction apparatus specially designed for evaluating single crystalline samples (X'Pert MRD, PANalytical). The surface morphologies of the films were observed by Atomic Force Microscopy (AFM) (Digital Instruments, NanoScope II). Photocatalytic activities of the TiO_2 films were evaluated by the photoreduction of Ag ions at the film surface. The TiO_2 films were dipped in the aqueous $AgNO_3$ solution (0.01 mol/l) and were irradiated by a Hg-Xe lamp (100 mW/cm^2) for 30 seconds. Ag is deposited on TiO_2 film surface due to the following reactions [7]:

$$TiO_2 + h\upsilon \rightarrow h^+ + e^- \quad (1)$$

$$e^- + Ag^+ \rightarrow Ag \quad (2)$$

$$1/2H_2O + h^+ \rightarrow H^+ + 1/4O_2 \quad (3)$$

where h^+, e^-, h, and υ denote a hole, an electron, the Planck's constant and the frequency of lights, respectively. The deposition rates of Ag onto the surface of TiO_2 film were calculated from the thickness of Ag determined by a profilometer (Sloan, Dektak3030) and the UV irradiated period

3. RESULTS AND DISCUSSION

3.1 Crystalline structures of the films

Figure 2 shows the standard θ / 2θ X-ray diffraction patterns of the TiO_2 films grown on $LaAlO_3$(100):(a), $LaAlO_3$(110):(b), and glass:(c) substrates, respectively. Only the peaks originating from the (00l) diffractions of anatase-TiO_2 appear in fig.1(a). It was also confirmed that this film possessed a fourfold rotation symmetry around the anatase <001> axis. Thus the epitaxial orientation relationship between the $LaAlO_3$(100) substrate and the anatase film was confirmed to be: anatase(001) // $LaAlO_3$(100), anatase<100> // $LaAlO_3$<010>. Only the anatase(204) diffraction was observed in fig.1(b) and a twofold rotation symmetry was observed around the anatase<204> axis.

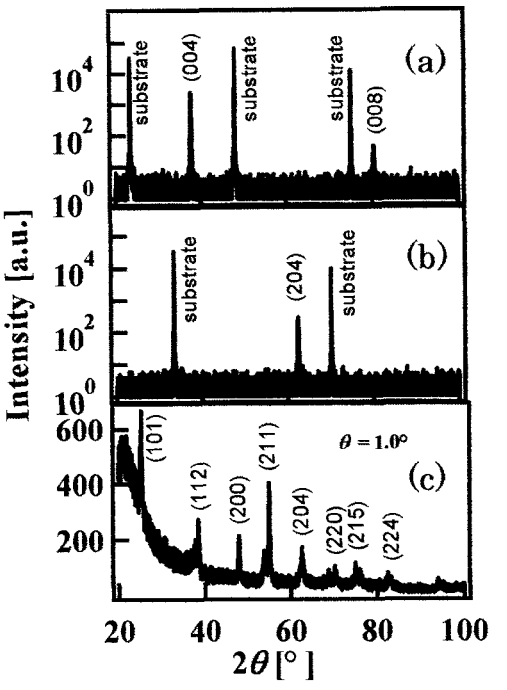

Fig.2. X-ray diffraction patterns of (a): anatase-(001), (b): Anatase-(204), and (c): polycrystalline anatase, respectively.

It was also confirmed that this film possessed a fourfold rotation symmetry around the anatase <001> axis. Thus the epitaxial orientation relationship between the $LaAlO_3$(100) substrate and the anatase film was confirmed to be: anatase(001) // $LaAlO_3$(100), anatase<100> // $LaAlO_3$<010>. Only the anatase(204) diffraction was observed in fig.1(b) and a twofold rotation symmetry was observed around the anatase<204> axis. According to these X-ray diffraction analysis, the epitaxial orientation relationship on $LaAlO_3$(110) substrate was revealed to be: anatase(204) // $LaAlO_3$(110), anatase<010> // $LaAlO_3$<001>. The film grown on the glass substrate showed a polycrystalline structure of anatase-TiO_2 as shown in fig.1(c). Thus three anatase films with different c-axis orientation were obtained.

3.2 Surface morphology of the films

Figure 3 shows the AFM micrographs of (a): anatase-(001), (b):anatase-(204) and (c) polycrystalline-anatase, respectively. The anatase-(001) film showed a very flat surface with the mean roughness value (Ra) of 0.3nm. While the anatase-(204) film and the polycrystalline-anatase film showed larger Ra value of 8.0nm and 8.6nm, respectively.

3.3 Photocatalytic activity

Figure 4 shows the photocatalytic activities of the films measured by photoreduction of Ag ions on the film surface. The higher Ag deposition rates correspond to the higher photocatalytic activities. The two kinds of epitaxial anatase-TiO_2 films (anatase-(001) and anatase-(204)) hardly showed photocatalytic activities compared with that of the polycrystalline-anatase film.

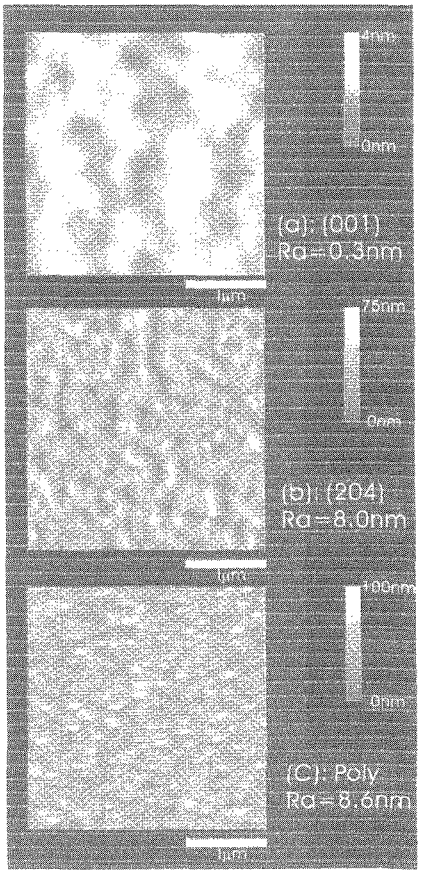

Fig.3. AFM micrographs of (a): anatase-(001), (b): anatase-(204), and (c): polycrystalline anatase, respectively.

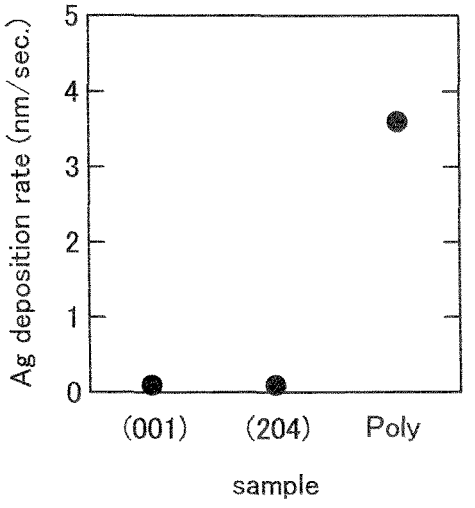

Fig.4. The photocatalitic activities of the films measured by photoreduction of Ag ions on the film surface (a): anatase-(001), (b): anatase-(204), and (c): polycrystalline anatase, respectively.

Yamagishi *et al.* [6] also compared the photocatalytic activities of the anatase-(001) and polycrystalline-anatase films and concluded that the faintness of the photocatalytic activity in the anatase-(001) film was due to the effective mass of the electrons in anatase-TiO_2. According to their calculation, the effective mass of electrons along the anatase-<001> is three times as large as those of any other directions of anatase. This heavy effective mass prevent the electrons from moving towards the surface of anatase-(001) films and reduce the photocatalytic activities.

However, the anatase-(204) film also hardly showed photocatalytic activity while the polycrystalline-anatase film possessed a well defined photocatalytic activity (Fig.4). The absence of photocatalytic activity in the anatase-(204) film cannot be explained by the above mentioned anisotropy in the effective mass since the <001> axis is inclined in the anatase-(204) film and the effective mass towards the sample surface is much smaller (~1/3) than that of the anatase-(001) film.

The two films with equivalent surface roughness (the anatase-(204) and the polycrystalline-anatase films) showed striking difference in photocatalytic activity. Hence the surface roughness also can be excluded from the major factor for determining photocatalytic activity in this system.

The thickness of the epitaxial films (anatase-(001) and anatase-(204) films, 220nm) was 10% smaller than that of the polycrystalline-anatase film (240nm). However this slight inferiority in thickness also cannot provide explanation for the drastic discrepancy in photocatalytic activity.

4. CONCLUSION

Comparative study of the anatase-(001), anatase-(204) and polycrystalline-anatase films revealed that the anisotropy in the effective mass and the surface roughness could be excluded from the major factor for determining photocatalytic activity in this system. Since the major discrepancy between the epitaxial films and polycrystalline films is the existence of the grain boundaries, further study focusing on the grain boundary effects should be performed for the elucidation of the dominant factor for photocatalytic activity in this system.

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