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Preparation of Highly Oriented TiO_2/ZnO Films by Pulsed Laser Deposition

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Highly oriented TiO_2 films consisting of anatase TiO_2 (001) and rutile TiO_2 (100) were grown using a highly oriented ZnO (0001) buffer layer with nanometer sizes grain on quartz glass substrates. TiO_2 thin films were deposited by pulsed laser deposition (KrF excimer laser) in an oxygen atmosphere. The quality of films and crystallographic relationships were assessed by x-ray diffraction, x-ray pole figures and Rutherford backscattering spectroscopy (RBS)/channeling. The typical TiO_2 films were deposited at 500°C in 13.3 Pa of oxygen pressure. The anatase-rutile ratio in such phase mixed films was controlled by oxygen pressure during the deposition. From scanning electron microscopy observation, the deposited film was found to have a rough surface consisting of coarse grains with about 100 nm sizes. It was possible to improve photocatalytic activity for the decomposition of the organic dyes by the growth of TiO_2 on highly oriented ZnO buffer layer.
Key words: Photocatalysis, TiO_2, ZnO, PLD, XRD

1. INTRODUCTION

The photocatalytic properties of titanium dioxide (TiO_2) have attracted much interest from the viewpoints of basic science and applications. The excellent dielectric features in electronic, optical and photo-electrochemical properties of TiO_2 have been utilized for dielectric layers in thin film capacitors, anti-reflection coating layers, gas sensor and photocatalysts. Especially interesting is the photocatalytic property [1], and it can be utilized to decompose toxic gases into safe gaseous compounds using solar energy [2]. For improving photocatalytic activity of TiO_2 films, the control of crystal quality and the fabrication of effective large surface area were required. TiO_2 is known to crystallize in three different crystallographic structures: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic), and the rutile, which is most stable, has been extensively studied and widely used. Several works were reported about epitaxial rutile and anatase films by metal-organic chemical vapor deposition (MOCVD)[3], ion beam sputtering [4, 5], pulsed laser deposition (PLD) [6-9]. However, the growth of epitaxial TiO_2 films was necessary to use the high quality single-crystal substrates such as $SrTiO_3$, $LaAlO_3$, α-Al_2O_3. In order to utilize the photocatalytic activity of epitaxial TiO_2 films, it is essential that techniques for preparation films on glass or polycrystalline substrate be available. Zinc oxide (ZnO) is one of the most suitable materials to use as a buffer layer. Since ZnO films are highly c-axis oriented, self-textured ZnO thin films have been prepared on any substrate such as quartz glass [10, 11]. Furthermore, high quality epitaxial ZnO films have been synthesized on α-Al_2O_3 substrates [12-14]. The surface morphology of highly oriented ZnO films, hexagonal shaped grains with nanometer sizes have been observed [11]. Thus, ZnO buffer layer on substrate can be realized the fabrication of TiO_2 films consisting of highly oriented grains with nanometer sizes. In the present study, highly oriented TiO_2 films were grown using a highly oriented ZnO (0001) buffer layer on quartz glass substrates by pulsed laser deposition in an oxygen atmosphere. The crystal quality, the crystallographic orientation relationships between film and substrate, and photocatalytic activity of films are reported.

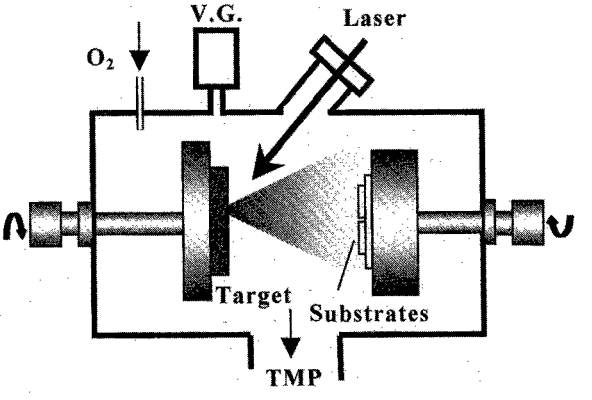

Fig. 1. Schematic figure of the pulsed laser deposition apparatus.

2. EXPERIMENTAL

TiO_2 and ZnO films were deposited on α-Al_2O_3 and quartz glass substrates by PLD using a KrF excimer laser (wavelength: 248 nm, Lambda Physik). Figure 1 shows the schematic figure of the PLD apparatus. The laser beam was incident on a target with an incident angle of 45°. It was focused to a 2 × 3 mm rectangle on the target face. Typical laser fluence and repetition rate were 150 mJ/cm^2 and 10 Hz. Both the target stage and substrate holder were rotated during the deposition. A metal Zn (purity: 99.9%) and a single crystal TiO_2 (rutile) targets were used for ZnO and TiO_2 film deposition, respectively. The substrates were separated by about 5 cm from the target. The deposition chamber was evacuated up to a base pressure of about 6×10^{-4} Pa using a turbomolecular pump (TMP). Oxygen gas (purity: 99.99 %) was flowed into the chamber through a mass-flow meter controlled by an absolute pressure gauge (Baratron 626, MKS) under the pumping condition. All of the substrates were obtained commercially. They are mirror-polished at both sides, and the typical size is 10 × 10 × 0.5 mm^3. In this study, ~200 nm thick TiO_2 films were deposited at 500°C under oxygen pressure of 1.3 – 26.3 Pa.

The crystallographic relationships between TiO_2 films and ZnO layer were determined by X-ray diffraction measurements using a high-resolution diffractometer (X'Pert-MRD, Philips) The X-ray source was operated at 40 kV and 30 mA for Cu-Kα radiations. Rutherford backscattering spectroscopy (RBS)/channeling analysis using a 3 MV single-stage-accelerator at JAERI/Takasaki was employed to characterize the epitaxial thin films. The analyzing 2.0 MeV $^4He^+$ ions were incident and backscattered particles were detected at 165° scattering angle with a surface barrier detector. The beam size was about 1 mm in diameter and the beam current was about 10 nA typically. Samples were mounted on a 3-axis goniometer to pattern the planar channeling and the axial channeling in the angular coordinate. The film thickness and composition were evaluated from RBS spectra. The surface morphology of the deposited films was examined using a high-resolution field emission scanning electron microscopy (JSM6700F, JEOL). Photocatalytic activity of films was evaluated using the decomposition of methylene blue in aqueous solution monitored by UV-vis spectroscopy.

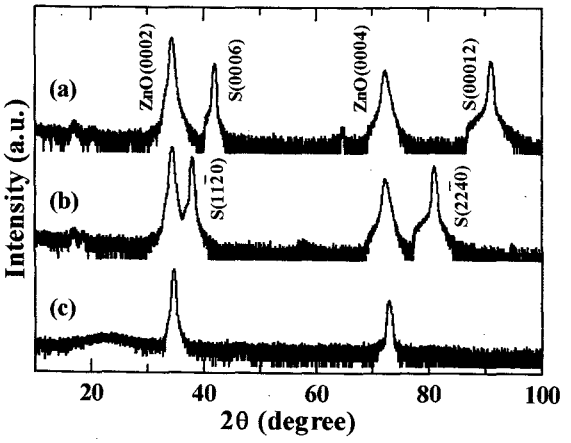

Fig. 2. X-ray diffraction patterns for ZnO films on (a) α-Al_2O_3 (0001), (b) α-Al_2O_3 (11$\bar{2}$0), and (c) quartz glass, respectively. The films were deposited at 500°C under the oxygen pressure of 4.7 Pa.

3. RESULTS AND DISCUSSION

The growth condition for highly oriented ZnO films was optimized referring to the crystal quality of ZnO film on the α-Al_2O_3 (0001) substrate. The suitable condition for highly oriented ZnO films was following conditions; laser energy: 150 mJ/cm^2, oxygen gas pressures: 4.7 Pa, substrate temperature: 500°C, target species: Zn metal. Figure 1 shows the X-ray diffraction patterns for ZnO film on the (a) α-Al_2O_3 (0001), (b) α-Al_2O_3 (11$\bar{2}$0), and (c) quartz glass substrates, respectively. It can be seen from Fig. 1, only the (0001) reflections from the ZnO are observed without any reflection from the substrates, which indicates that the ZnO films are grown with c-axis orientation. The in-plane orientations of ZnO films were examined through the pole figure measurement. The epitaxial relationships between ZnO and α-Al_2O_3 substrate were found to be ZnO(0001)/α-Al_2O_3 (0001) with

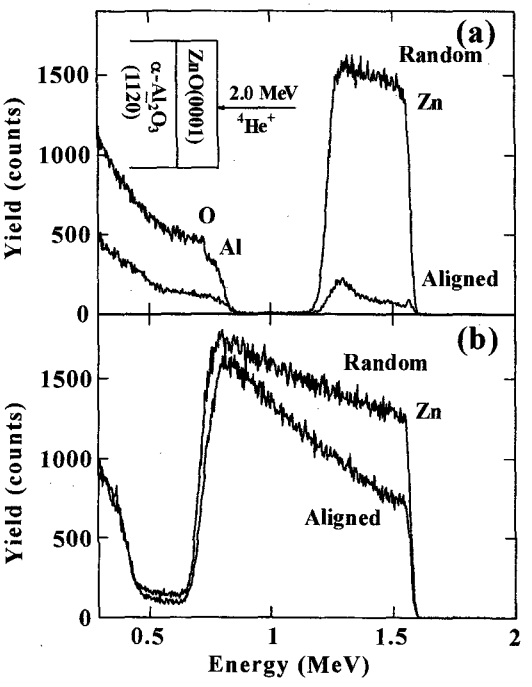

Fig. 3. 2.0 MeV $^4He^+$ RBS/channeling spectra for deposited ZnO films on the (a) α-Al_2O_3 (11$\bar{2}$0), and (b) quartz glass, respectively. The thicknesses of ZnO fims are 233 nm and 571 nm, respectively. The aligned spectrum was taken with the beam directed along the <0001> axis of the ZnO films.

ZnO [10$\bar{1}$0] ||α-Al_2O_3 [11$\bar{2}$0] and ZnO(0001)/α-Al_2O_3 (11$\bar{2}$0) with ZnO [11$\bar{2}$0] ||α-Al_2O_3 [0001] , respectively. The pole figure analysis indicates that the ZnO(0001) on the α-Al_2O_3 (0001) has a twinned structure rotated by 30° with each other around the <0001> direction of the ZnO film. However the ZnO(0001) on the α-Al_2O_3 (11$\bar{2}$0) has no rotational domains. On the other hand, ZnO on quartz glass substrate has a (0001) preferred orientation with randomly oriented in-plane direction. The observation of surface morphology by SEM indicates that the ZnO films consist of coarse grains with about 100 nm sizes (not shown).

The quality of epitaxial ZnO films was characterized through the RBS/channeling analysis. Figure 3 illustrates 2.0 MeV $^4He^+$ RBS spectra for the ZnO film on (a) α-Al_2O_3 (11$\bar{2}$0) and (b) quartz glass substrates taken under the random and the axial channeling condition. The aligned spectrum was taken with the beam directed along the <0001> axis of the ZnO film. In Fig. 3(a) RBS spectra, one can recognize clearly the separated peaks from the ZnO film and α-Al_2O_3 substrate. The peaks at 1.56 MeV and 0.8 MeV correspond to the Zn component in the ZnO film and Al component in the α-Al_2O_3 substrate. Judging from the peak intensity, the high quality ZnO film is grown up from the interface and the interface is not mixed with each other within the depth resolution (~ 10 nm) of this technique. The minimum yield, χ_{min} value, the ratio between the random and the axially aligned yield at the fixed depth near the surface region, gives a measure to evaluate the degree of disorder in crystalline solids. The χ_{min} value in the <0001> aligned spectrum is 0.05 at the just area behind the surface peak of the Zn component in the ZnO film, which suggests that the crystal quality of the ZnO film is high enough as in a bulk single-crystal. The planar channeling analysis around the major axes of the ZnO film and the α-Al_2O_3 gives the evidence that the ZnO <0001> crystallographic axis is parallel to the α-Al_2O_3 <11$\bar{2}$0> axis. As can be seen from Fig.3 (b), axial channeling RBS spectra are obtained from ZnO film on quartz glass substrate even if it has amorphous structure. The yield at 1.56 MeV regions is from the Zn component of the ZnO film at the surface, and the huge reduction of this yield under the axial channeling condition suggests that the deposited film has high crystal quality compare to the interface region. It is found that ZnO films on the quartz glass substrate are highly (0001) oriented with increasing thickness. The results suggest that thicker ZnO films on glass substrate can be useful as a buffer layer for highly oriented oxide films.

The TiO_2 films were prepared under the following conditions; laser energy: 150 mJ/cm^2, oxygen pressures: 1.3 – 26.3 Pa, substrate temperature: 500°C, target species: single-crystal TiO_2 (rutile). Figure 4 shows the X-ray diffraction patterns for TiO_2/ZnO films on quartz glass substrates deposited at various oxygen pressures. It can be seen from Fig. 4 (a)-(c), the structure of deposited TiO_2 film on the highly oriented ZnO (0001) layer is composed of oriented anatase TiO_2 (001) and rutile TiO_2 (100). As the oxygen pressure was increased during the deposition, the component of anatase phase was increased. It is found that the anatase-rutile ratio in such phase mixed films is controlled by oxygen pressure during the deposition. The quality of oriented TiO_2/ZnO films was characterized through the RBS/channeling. But any ion channeling phenomena were not observed from deposited TiO_2 films on (0001) oriented ZnO layers, which suggests that the TiO_2 films have low crystal quality compare to the ZnO layers.

Figure 5 shows the surface morphology of the TiO_2 film on ZnO buffer layer observed by SEM. The TiO_2 film was grown at 500°C under the oxygen pressure of 13.3 Pa. The surface of the film shows coarse grains with about 100 nm sizes. The grain size of the TiO_2 films is comparable to that of ZnO films on quartz glass substrate. The

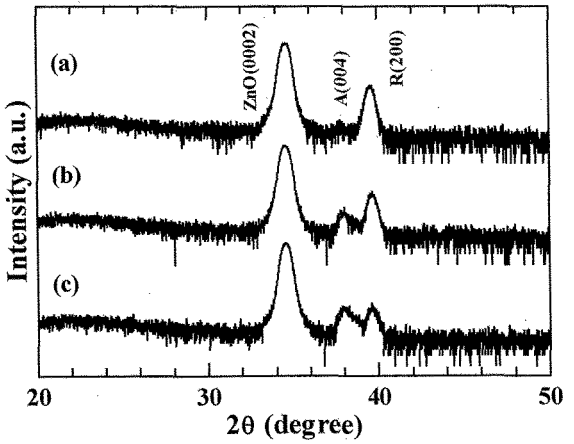

Fig. 4. X-ray diffraction patterns for TiO_2/ZnO films on quartz glass substrate. TiO_2 films were deposited at various oxygen pressures: (a) 1.3 Pa; (b) 13.3 Pa; (c) 26.6 Pa.

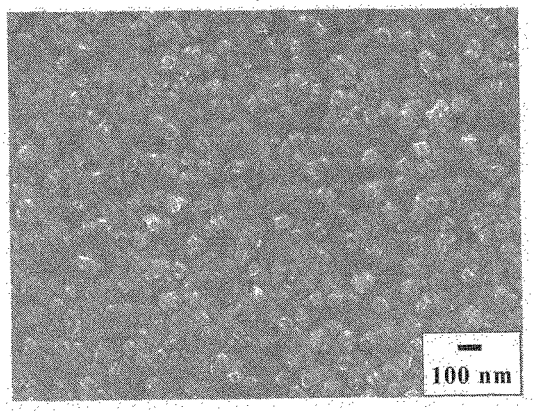

Fig. 5. SEM image of TiO_2 surface grown at 500°C under the oxygen pressure of 13.3 Pa.

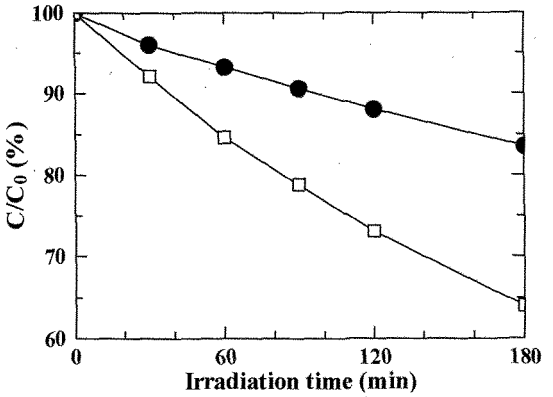

Fig. 6. Decomposition of methylene blue in an aqueous solution (1×10^{-5} mol dm^{-3}) by the (□) TiO_2/glass and (•) TiO_2/ZnO/glass as a function of the UV light irradiation time.

surface morphology implies that each grain corresponds to single crystal of rutile and anatase TiO_2 structures. These grains have grown epitaxailly on the highly oriented ZnO (0001) buffer layer.

Photocatalytic activity of films was evaluated using the decomposition of methylene blue in aqueous solution. The progress of the degradation reaction was followed by monitoring the decrease in the absorbance of aqueous dye solutions as a function of the UV-light irradiation time counted from the beginning. The UV-light (1.0 mW/cm^2) with a black light lamp was used. The result of TiO_2/ZnO films deposited with different oxygen pressure showed that the TiO_2 film deposited on the ZnO buffer layer at 500°C under the oxygen pressure of 13.3 Pa, consisting of oriented anatase TiO_2 (001) and rutile TiO_2 (100) (referred to Fig. 4), had a high efficiency for the decomposition reaction. Figure 6 shows the photocatalytic behavior of the (□) TiO_2/ZnO and (•) TiO_2 films on quartz glass substrates during the degradation of methylene blue. Each TiO_2 films were deposited at 500°C under the oxygen pressure of 13.3 Pa. The TiO_2/ZnO film shows a high efficiency for the decomposition reaction. The above results reveal that the ZnO buffer layer on glass substrate is very useful for improving photocatalytic properties of the present TiO_2 film. This film had a large specific surface area due to its coarse grains with about 100 nm sizes (SEM image of Fig. 5), which leads to a strong adsorption ability. The TiO_2 films are composed of oriented anatase TiO_2 (001) and rutile TiO_2 (100), which provide photo-activated electrons and holes in the surface without any influences from imperfections. Furthermore, the oxidization site of anatase TiO_2 is mainly on the (001) face [15], which also improves photocatalytic activities.

4. CONCLUSIONS

We prepared oriented TiO_2 films using a highly oriented ZnO (0001) buffer layer on quartz glass substrate by PLD. Films were analyzed by X-ray diffraction and ion beam channeling techniques. The TiO_2 films were composed of ~100 nm sizes grains with anatase TiO_2 (001) and rutile TiO_2 (100) oriented growth. It is found that the anatase-rutile ratio in such phase mixed films is controlled by oxygen pressure during the deposition. These TiO_2 films have a photocatalytic activity for decomposition of organic dyes higher than that of TiO_2 films on glass substrate. The improvement in the photocatalytic activity of TiO_2 film using a ZnO buffer layer is due to increase in surface area and highly oriented crystal growth.

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