Microcolumnar and Granular Structures of TiO_2 Films Prepared by Laser CVD using Nd:YAG Laser

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Abstract. Microcolumar and granular TiO_2 films were prepared by laser chemical vapor deposition using Nd:YAG laser. Effects of deposition temperature on phase and microstructure were investigated. Single-phase rutile TiO_2 films were prepared at 760–936 K, whereas mixtures of rutile and anatase TiO_2 films were obtained at 975–1014 K. Single-phase anatase TiO_2 films were prepared at 1067 K. Rutile TiO_2 films prepared at 899–936 K showed feather-like microcolumnars with a pyramidal cap. Anatase TiO_2 films prepared at 1067 K consisted of granular grains. Deposition rates were ranged from 3 to 50 μm h^{-1}.

Introduction

Titanium dioxide (TiO_2) has been extensively studied as photocatalytic and photoinduced superhydrophilic materials since environmental concern has been widely-recognized as a serious problem [1,2]. TiO_2 has three polymorphs, *i.e.*, rutile, anatase and brookite. Anatase and rutile are commonly known as a low- and high-temperature phases, respectively. Since anatase and brookite transform to rutile at a high temperature, rutile is a thermodynamically stable phase. However, it is not still well-understood whether anatase and brookite are low-temperature or metastable phase. Actually, the phases have been strongly affected by synthesis route. The characteristics such as photocatalytic properties would also depend not only phase but also synthesis route.

Photocatalytic reactions occur at gas/solid interface, and thus the surface area of catalyst should be maximized [3]. Porous, columnar and granular morphologies are preferable having a high-relative surface area. Preparation technique affects the phase and microstructure of the film. Most common method to prepare porous film can be a sol-gel method; however, sol-gel films often have a drawback of cracking and agglomeration during drying process. Porous films can be hardly prepared by physical vapor deposition such as sputtering and pulsed laser ablation.

Chemical vapor deposition (CVD) is a versatile technique to prepare porous, columnar and granular films by controlling deposition conditions [4]. We have developed a new CVD route utilizing high-power lasers (laser CVD) to prepare oxide and non-oxide films with various microstructures at significant high deposition rate (several hundred micrometers per hour). The feather-like structure characterized by high surface area with many branches and microcolumns was grown by laser CVD, and porous SiO_2 and Y-Si-O [5,6] and feather-like Al_2O_3, Y_2O_3-ZrO_2 and CeO_2 films have been prepared [7–10].

In the present study, microcolumar and granular TiO_2 films containing the feather-like structure were prepared by laser CVD using Nd:YAG laser. The effects of deposition temperature on phase and microstructure were investigated.

Experimental procedure

Figure 1 illustrates a schematic of laser CVD apparatus. Ti-diisopropoxy-dipivaloylmethanate ($Ti(O\textit{i}Pr)_2(dpm)_2$) was used as a precursor. It was heated at 453 K and its vapor was carried into a chamber with Ar gas (0.17 Pa m^3 s^{-1}). O_2 gas was separately introduced into the chamber through a

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double-tube nozzle (0.17 Pa m^3 s^{-1}). The total pressure in the chamber was held at 600 Pa. Yttria-stabilized zirconia (YSZ) plate (8 mm × 8 mm × 1 mm) was used as a substrate. The substrate was heated on a hot stage at a preheating temperature 673 K, and a thermocouple was inserted backside of the substrate to measure the deposition temperature. A continuous-wave mode Nd:YAG laser beam (Lee Laser Series 800; wavelength: 1064 nm; diameter: 12 mm) was introduced through a quartz window to irradiate the whole substrate. The laser power changed from 50 to 240 W.

The crystal phase was analyzed by X-ray diffraction (XRD, Rigaku RAD-2C) using Cu Kα X-ray radiation. The surface and cross-sectional morphology was observed by a scanning electron microscope (SEM, Hitachi S-3100H).

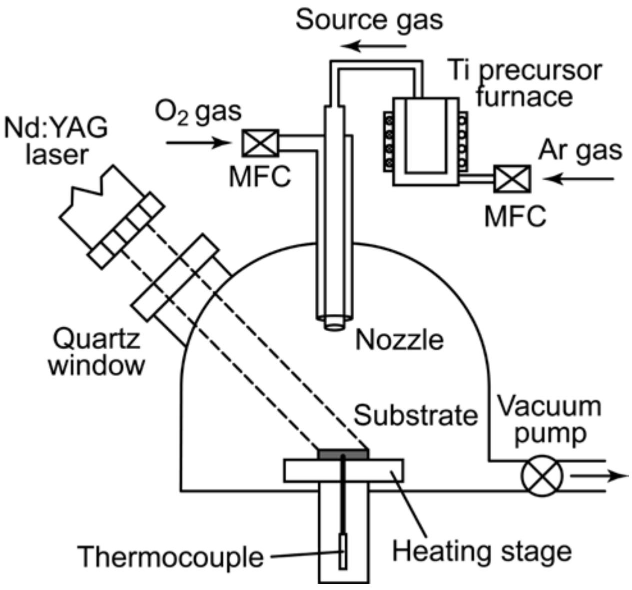

Fig. 1 A schematic of laser CVD apparatus.

Results and discussion

Figure 2 shows the XRD patterns of the TiO_2 films prepared on YSZ substrate at various deposition temperatures. TiO_2 has polymorphs of rutile (space group: $P4_2/mnm$; lattice parameters: a = 0.459 nm, c = 0.296 nm) and anatase ($I4_1/amd$; a = 0.378 nm, c = 0.951 nm). At 760–936 K, single-phase rutile TiO_2 films were prepared (Fig. 2(a)). The rutile TiO_2 film prepared 936 K had a (100) orientation. Mixtures of rutile and anatase TiO_2 films were obtained at 975–1014 K (Fig. 2(b)). With increasing deposition temperature, amount of anatase phase increased. Single-phase anatase TiO_2 films were prepared at 1067 K (Fig. 2(c)). The anatase TiO_2 film showed a (001) orientation.

Figure 3 shows the surface and cross-sectional SEM images of the single-phase rutile, mixture of rutile and anatase, and single-phase anatase TiO_2 films prepared at 936, 975 and 1067 K, respectively. Single-phase rutile TiO_2 films prepared at 936 K showed a columnar structure having a feather-like structure with a pyramidal cap (Fig. 3(a), 3(b)). On a mixture of rutile and anatase TiO_2 films prepared at 975 K, nano-sized pyramids formed in a cauliflower-like structure (Fig. 3(c), 3(d)). Single-phase anatase TiO_2 films prepared at 1067 K had granular grains (Fig. 3(e), 3(f)).

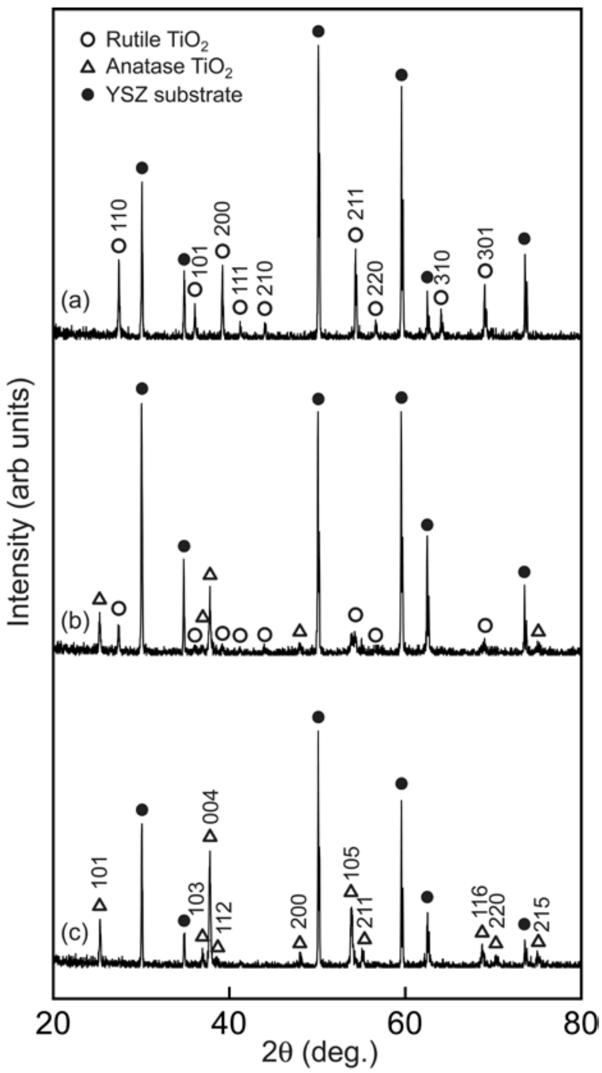

Fig. 2 XRD patterns of the TiO_2 films prepared at 936 (a), 975 (b) and 1067 (c) K.

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The deposition rate increased from 3 to 50 μm h^{-1} with increasing deposition temperature from 760 to 1014 K, and declined to 22 μm h^{-1} at further high temperature to 1067 K.

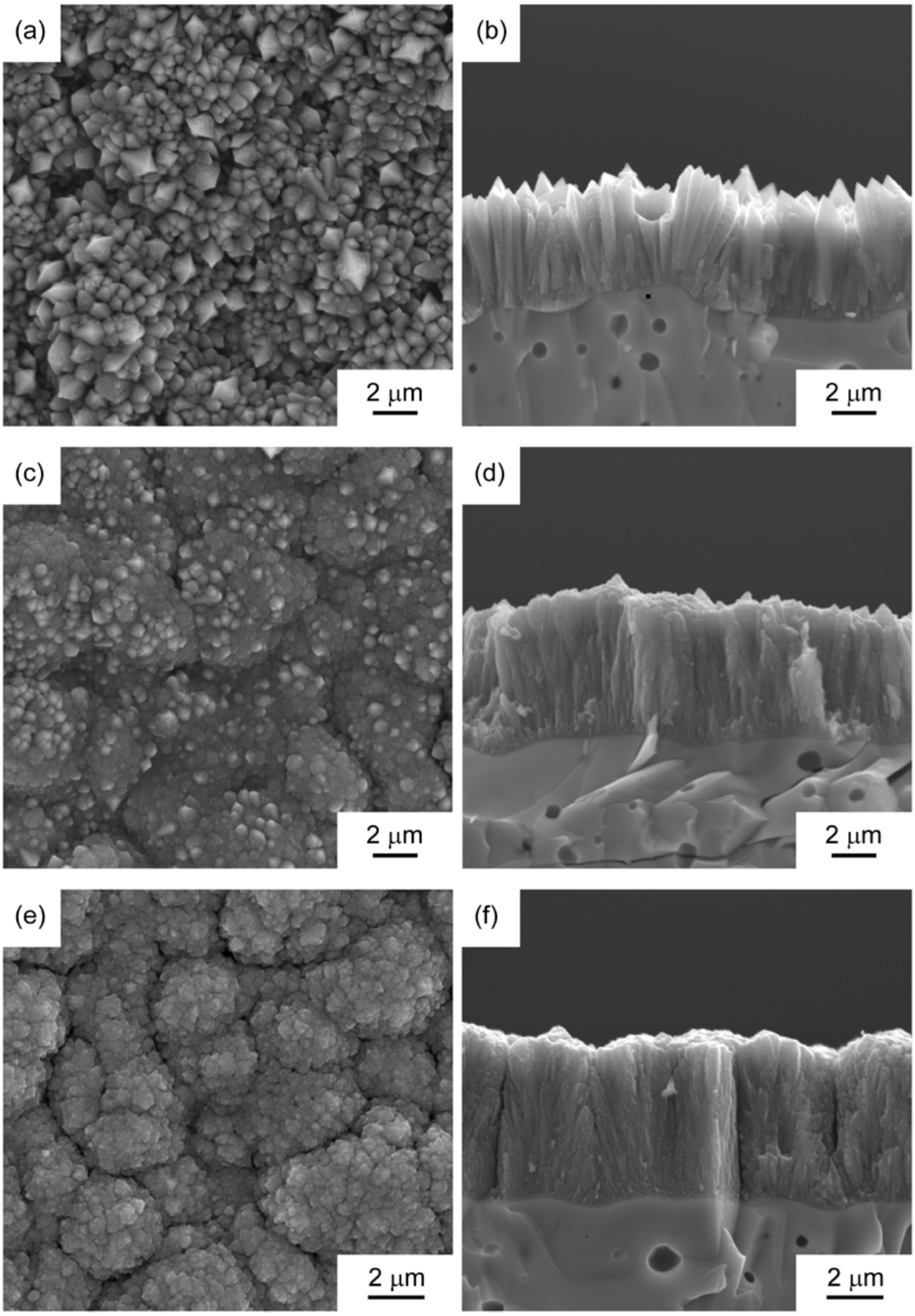

Fig. 3 Surface (a, c, d) and cross-sectional (b, d, e) SEM images of single-phase rutile TiO_2 (a, b), mixture of rutile and anatase TiO_2 (c, d), and single-phase anatase TiO_2 (e, f) films prepared at 936, 975 and 1067 K, respectively.

Summary

Microcolumar and granular TiO_2 films were prepared by laser chemical vapor deposition using Nd:YAG laser. Single-phase rutile TiO_2 film with (100) orientation was prepared at 936 K. Mixtures of rutile and anatase TiO_2 films were obtained at 975–1014 K. Single-phase anatase TiO_2 film with (001) orientation was prepared at 1067 K. Single-phase rutile TiO_2 films prepared at 899–936 K showed a microcolumnar having a feather-like structure with a pyramidal cap. A mixture of rutile and anatase TiO_2 films consisted of nano-sized pyramid and granular grains. Single-phase anatase TiO_2 films prepared at 1067 K had granular grains. Deposition rates were ranged from 3 to 50 μm h^{-1}.

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