This is the accepted version of the article submitted to Key Engineering Materials, which has been published in final form at 10.4028/www.scientific.net/KEM.508.279.

# Preparation of Titania Solid Films by Laser CVD using $CO_2$ Laser

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**Keywords:** $TiO_2$, Laser CVD, Solid film, Microstructure

**Abstract.** Titania ($TiO_2$) films having dense and solid microstructure were prepared by laser chemical vapor deposition using $CO_2$ laser. The effects of deposition temperature ($T_{dep}$) and total chamber pressure ($P_{tot}$) on phase and microstructure of $TiO_2$ films were investigated. At $P_{tot}$ = 600 Pa and $T_{dep}$ = 790 K, rutile $TiO_2$ film had a polygonal platelet grains 2 μm in size. At $P_{tot}$ = 600 Pa and $T_{dep}$ = 1010 K, rutile $TiO_2$ film had (110) orientation and consisted of a truncated polyhedron 5–6 μm in size. At $P_{tot}$ = 200 Pa and $T_{dep}$ = 955 K, rutile $TiO_2$ film has a solid columnar having faceted surface. A dense and solid $TiO_2$ film was obtained at $P_{tot}$ = 200 Pa and $T_{dep}$ = 1120 K. The deposition rate of $TiO_2$ solid film was reached 240 μm $h^{-1}$.

## Introduction

Titania ($TiO_2$) has attracted much attention as protective and optical coatings because of their high resistance to chemical and physical impact, low thermal conductivity, high refractive index and photoinduced catalysis and superhydrophilicity [1,2]. Thick $TiO_2$ films having dense and solid microstructure are suitable as protective coatings. Physical vapor deposition technique, such as sputtering, pulsed laser deposition and electron-beam evaporation, can prepare a dense and smooth film; however, its deposition rate is usually too low (several hundred nanometers per hour) for industrial applications. Thermal spraying can be an alternative thick coating technique, but disadvantages of this method are a porous structure and microcracking in the film.

Chemical vapor deposition (CVD), including thermal CVD, metalorganic CVD and plasma-enhanced CVD, has been widely used for preparing protective coatings with excellent step coverage and a relatively high deposition rate; however, the deposition rates less than several micrometers per hour are still insufficient for thick coatings. We have employed laser CVD to prepare $Y_2O_3$-$ZrO_2$ and $Al_2O_3$ films at high deposition rates (up to 500–600 μm $h^{-1}$) [3,4]. Laser CVD can also prepare dense $SiO_2$ thick films at a significant high deposition rate of 1200 μm $h^{-1}$ [5]. Laser irradiation to the deposition zone during the CVD process can enhance the chemical reactions of the precursor gas and accelerate the surface mobility of adsorbed species on the film surface.

In the present study, $TiO_2$ films having dense and solid microstructure were prepared by laser CVD using $CO_2$ laser.

## Experimental procedure

A schematic of laser CVD apparatus has been reported elsewhere [6]. $Ti(OiPr)_2(dpm)_2$ (titanium diisopropoxy-dipivaloylmethanate) precursor was heated at 453 K and its vapor were carried into the chamber with Ar gas (gas flow rate: 0.17 Pa $m^3$ $s^{-1}$). $O_2$ gas was separately introduced into the chamber through a double-tube nozzle (gas flow rate: 0.17 Pa $m^3$ $s^{-1}$). Precursor gas line and double-tube nozzle were heated at 453 and 473 K, respectively, to prevent condensation of the precursor during transportation. The total pressure in the chamber was held at 200 and 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 of 873 K, and a thermocouple was inserted backside of the substrate to measure the deposition temperature ($T_{dep}$). A $CO_2$ laser beam (Synrad

firestar f200; wavelength: 10.6 μm) was introduced through a quartz window to irradiate the whole substrate. Deposition was conducted for 600 s.

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). A schematic of crystal structure was illustrated by VESTA, a three-dimensional visualization system [7].

## Results and discussion

Figure 1 shows the XRD patterns of $TiO_2$ films prepared at $P_{tot}$ and $T_{dep}$. At $P_{tot}$ = 600 Pa and $T_{dep}$ = 930 K, XRD patterns can be indexed as rutile $TiO_2$ having (110) orientation (space group: $P4_2/mnm$; lattice parameters: $a$ = 0.459 nm, $c$ = 0.296 nm) with a minor amount of anatase $TiO_2$ ($I4_1/amd$; $a$ = 0.378 nm, $c$ = 0.951 nm) (Fig. 1(a)). At $T_{dep}$ greater than 865 K, single-phase rutile $TiO_2$ films were obtained (Fig. 1(b)), while the (110) orientation degree slightly decreased with increasing $T_{dep}$. At $P_{tot}$ = 200 Pa, XRD patterns of $TiO_2$ films can be indexed as rutile $TiO_2$ irrespective of $T_{dep}$. Rutile $TiO_2$ film prepared at $P_{tot}$ = 200 Pa and $T_{dep}$ = 1120 K showed a significant (110) orientation (Fig. 1(c)).

Ramamoorthy *et al*. calculated surface energies of (110), (100), (001) and (011) surface of rutile $TiO_2$ using first-principles calculations [8]. Figure 2 shows the equilibrium shape of a rutile $TiO_2$ crystal illustrated by Wulff construction with the surface energies. Surface energy of (110), (100), (011) and (001) surface were 15.6, 19.6, 24.4 and 28.9 meV a.u.$^{-2}$, respectively. According to the calculations, (110) surface has the lowest energy, implying a significant (110)-orientation growth of rutile $TiO_2$ films.

Figure 3 shows the surface and cross-sectional SEM images of rutile $TiO_2$ films prepared at various $P_{tot}$ and $T_{dep}$. $TiO_2$ film had polygonal platelet grains 2 μm in size at $P_{tot}$ = 600 Pa and $T_{dep}$ = 790 K (Fig. 3(a)). As shown in Fig. 2, the platelet facet may be (110) surface. At $P_{tot}$ = 600 Pa and $T_{dep}$ = 1010 K, $TiO_2$ film consisted of a truncated polyhedron 5–6 μm in

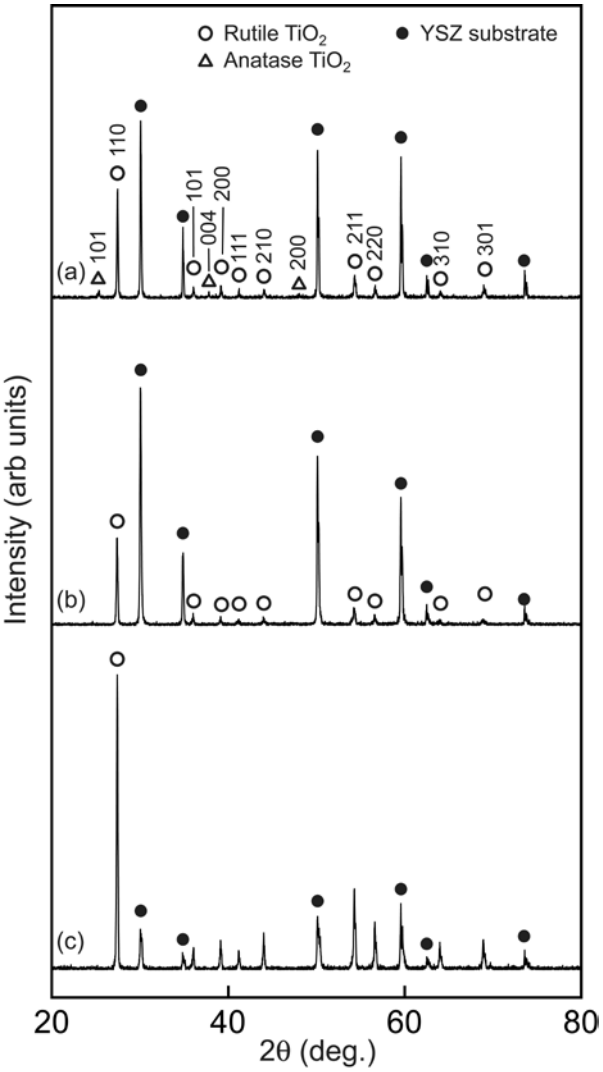


**Fig. 1** XRD patterns of the $TiO_2$ films prepared variosu $P_{tot}$ and $T_{dep}$: 600 Pa and 790 K (a), 600 Pa and 1010 K (b), and 200 Pa and 1120 K (c).

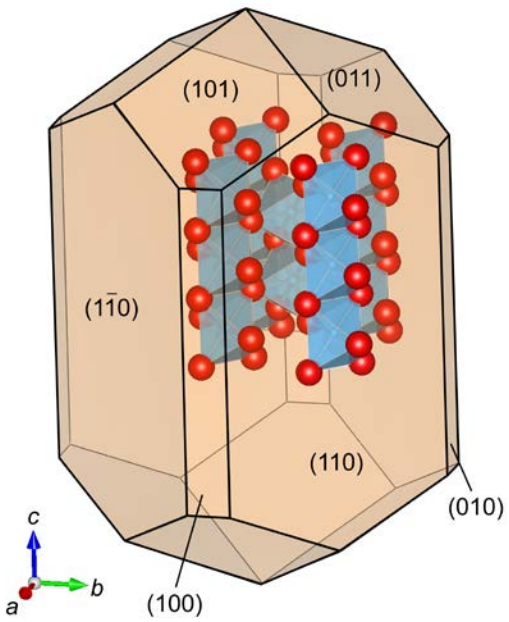


**Fig. 2** The equilibrium shape of a rutile $TiO_2$ crystal based on surface energies.

size (Fig. 3(b)). This truncated polyhedral shape might also be explained by the equilibrium shape of rutile $TiO_2$. $TiO_2$ film has a solid columnar having faceted surface at $P_{tot}$ = 200 Pa and $T_{dep}$ = 955 K (Fig. 3(c), 3(c')). At $P_{tot}$ = 200 Pa and $T_{dep}$ = 1120 K, a dense and solid $TiO_2$ film was obtained (Fig. 3(d), 3(d')). Deposition rates of the $TiO_2$ films were ranged from 120 to 240 μm $h^{-1}$.

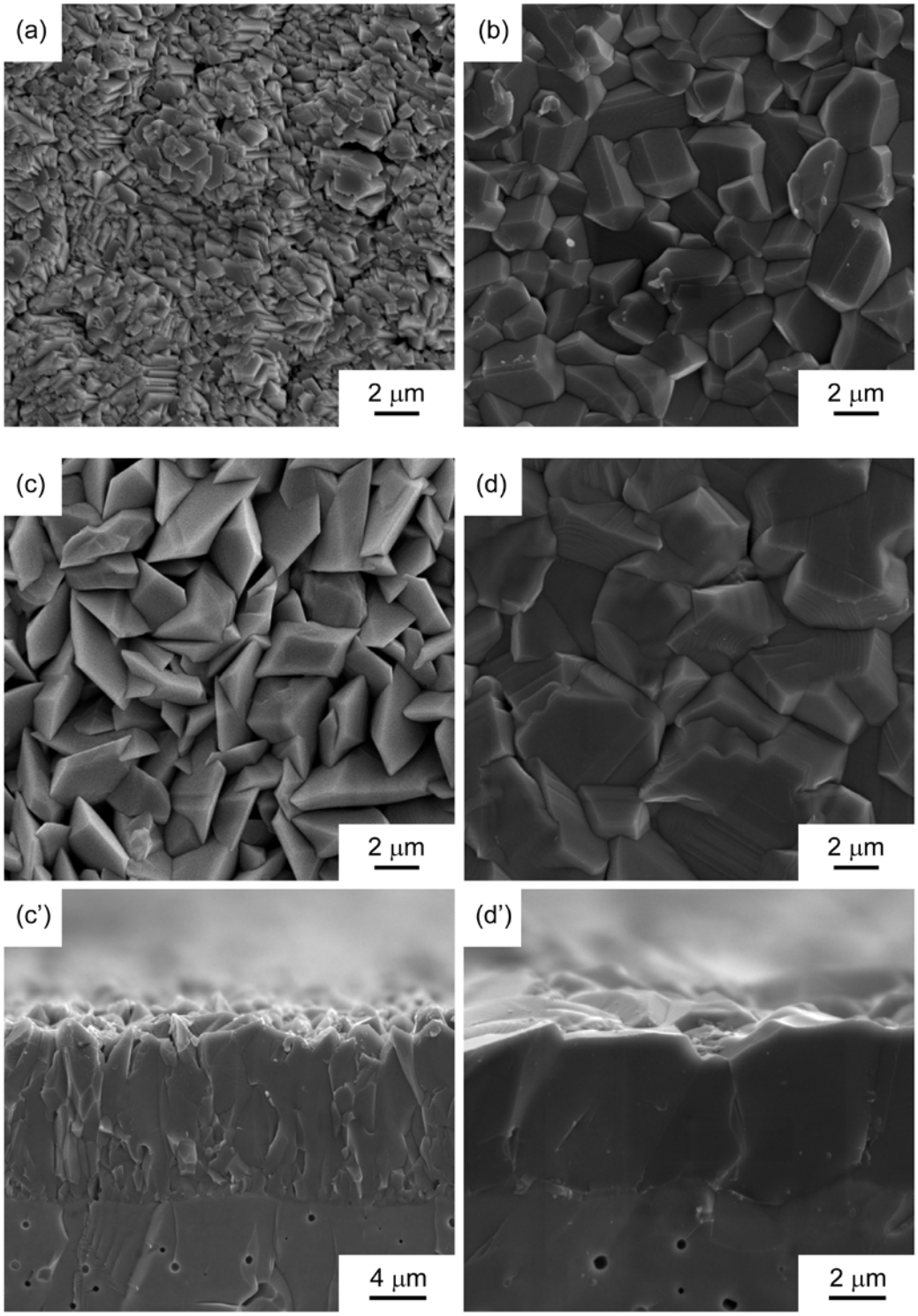


**Fig. 2** Surface (a-d) and cross-sectional (c', d') SEM images of $TiO_2$ films prepared at various $P_{tot}$ and $T_{dep}$: 600 Pa and 790 K (a), 600 Pa and 1010 K (b), 200 Pa and 955 K (c), and 200 Pa and 1120 K (d).

**Summary**

Rutile $TiO_2$ films having dense and solid microstructure were prepared by laser CVD using $CO_2$ laser. At $P_{tot}$ = 600 Pa and $T_{dep}$ = 790 K, rutile $TiO_2$ film had polygonal platelet grains 2 μm in size. At $P_{tot}$ = 600 Pa and $T_{dep}$ = 1010 K, rutile $TiO_2$ film had (110) orientation and consisted of a truncated polyhedron 5–6 μm in size. At $P_{tot}$ = 200 Pa and $T_{dep}$ = 955 K, rutile $TiO_2$ film has a solid columnar having faceted surface. A dense and solid $TiO_2$ film was obtained at $P_{tot}$ = 200 Pa and $T_{dep}$ = 1120 K. Faceted microstructure of the rutile $TiO_2$ films can be associated with the equilibrium shape of a rutile $TiO_2$. The deposition rate of $TiO_2$ solid film was reached 240 μm $h^{-1}$.

**Acknowledgements**

This work was supported in part by Global COE Program of the Materials Integration and the Rare Metal Substitute Materials Development Project, New Energy and Industrial Technology Development Organization (NEDO). This work was also supported in part by the Japan Society for the Promotion of Science, Grant-in-Aid for Young Scientists (B), No. 22760550, and by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research (A), No. 22246082.

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