

Plasma-Assisted Chemical Vapor Deposition of TiO₂ Thin Films for Highly Hydrophilic Performance

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ABSTRACT

Titanium-oxide layer was grown on glass substrate by plasma-assisted chemical vapor deposition (PCVD) using oxygen gas plasma excited by radio-frequency power at 13.56 MHz in the pressure as low as 3mtorr at relatively low temperature below 400°C, and studied on the crystallographic properties with the hydrophilic behavior comparing to the layer deposited by low-pressure chemical vapor deposition (LPCVD). Raman spectra indicated anatase-phase TiO₂ layer without amorphous-phase could be formed above 340°C by simultaneous supply of plasma-cracked and non-cracked titanium-tetra-iso-propoxide (TTIP) used as preliminary precursor. Surface Scanning Electron Microscope images indicated the PCVD-layer consists of distinct nanometer-size plate-like columnar grains, in contrast to rugged micrometer-size grains in the LPCVD-layer. Extremely small water contact angle about 5° in dark and the quick conversion to super-hydrophilicity by UV-irradiation with a light-power density as low as 50 W/cm² were observed on the PCVD-layer grown at 380°C, while the large initial contact angle was above 40° and the response for the UV-irradiation was gradual on the LPCVD-layer.

Keywords: PCVD; Titanium-Oxide Films; Anatase-TiO₂; Hydrophilicity

1. Introduction

Titanium dioxide (TiO₂) has been extensively investigated in view of photo-induced applications using the photo-catalytic reactions and the hydrophilicity on the surface [1,2], in addition to electronic and optoelectronic applications [3,4]. Commonly, anatase-phase TiO₂ is preferred for the photo-induced applications because of the efficient surface reaction by UV-irradiation compared to another crystal phases (brookite, rutile) [5]. In addition, the defects in the crystal should be also taken into account to control the reaction because it is recognized that the Ti³⁺ sites reduced from Ti⁴⁺ at the surface by photo-excited electrons accompanying oxygen vacancies generated by the photoexcited holes play an important role in the photo-induced surface reaction [6]. Therefore, a low of wet or dry process to fabricate anatase-TiO₂ layer has been advanced to control the crystallinity such as stoichiometric composition, impurity concentration, surface morphology, crystal orientation and so on. In such processes, wet process such as dip-coating, spray or sol-gel has been widely used for the photocatalytic and hydrophilic coating [7,8] with advantages of the low-cost and the wide-area coatings. In contrast, dry process such as

reactive sputtering [9], electron beam evaporation [10] and metalorganic chemical vapor deposition [11] has been attractively studied to control the growth behavior. Plasma-assisted chemical vapor deposition (PCVD) has been candidate for the TiO₂ synthesis process for low temperature deposition, control of the grain structure and the surface morphology [12-14]. In the PCVD process, titanium tetra-iso-propoxide (TTIP) has been widely used as the preliminary precursor in order to reduce contamination in the layer [15], where O₂ gas is simultaneously used as the oxidant gas for the efficient reduction. The metal oxide dissociated in the plasma [13] brings about the low temperature deposition below 300°C and the formation of highly dense columnar grains compared to the CVD-layers. However, the temperature to grow anatase-phase TiO₂ is increased above 450°C, whereas the anatase-TiO₂ can be grown at the temperature above 300°C by CVD [13]. The unfavorable increase of the growth temperature is probably come from hindering the crystal-phase formation by ion bombardment of excess energy particles [10] and poor surface migration of the metal-oxides on the growth surface. It is noted that the PCVD had been demonstrated in relatively high pressure above 0.1 torr by relatively high rf-power above 100 W [14] aiming at enough dissociation of the precursor in the

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plasma. On the other, the deposition enhanced chemical dissociation by reactive oxidants such as atomic-oxygen results in reduction of the TTIP-dissociation energy and the high growth rate as demonstrated by remote plasma-enhanced CVD [16]. The useful effects brought about the low-temperature growth including anatase-TiO₂, however, the layer grown at 350°C was formed by relatively low dense grains with poor crystallinity compared to the CVD-layer. It is considered that the results indicated the thermal-dissociation of TTIP without enhancement by the reactive oxygen is more effective to growth anatase-phase TiO₂.

In this paper, PCVD of TiO₂ supporting the crystallization in anatase-phase by thermal-dissociation of TTIP is demonstrated at low-temperature below 400°C and hydrophilic property on the anatase-phase layer is shown with the crystallinity and the surface morphology.

2. Experimental

Figure 1 shows a bell-jar type PCVD apparatus consists of a diffusion-pump (D.P.) and a rotary-pump (R.P.) for TiO₂ deposition. The back-pressure in the chamber was under 1×10^{-5} torr. An inductively coupled electrode to introduce radio-frequency (rf) power at 13.56 MHz was equipped in the chamber between a substrate holder and gas inlets. A Coil to apply DC-magnetic-field of 3000 gauss at the center of the chamber was also settled around the bell-jar to stabilize gas plasma excited by the rf-power, because PCVD in this study was performed in the pressure as low as 3mtorr and the low density plasma excited by 10 W rf-power. In the case of LPCVD, the rf-power was not induced during the growth. The temperatures of substrate holder and gas inlet for preliminary precursor were increased by resistive-heating and controlled by PID-systems.

Titanium tetra-iso-propoxide (Ti(O-i-C₃H₇)₄ : 97%-pu-

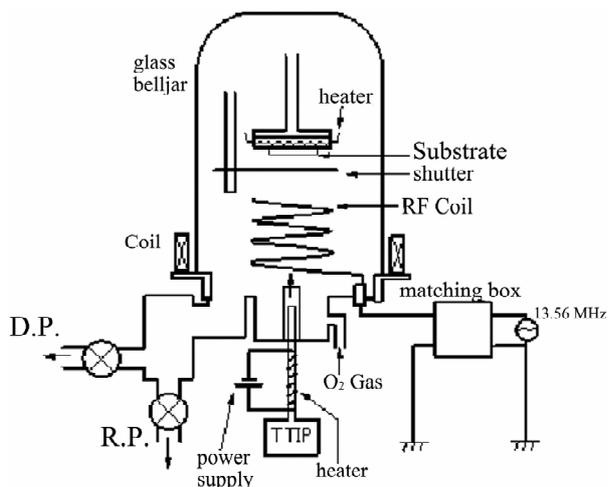


Figure 1. An apparatus of PCVD for TiO₂ deposition.

riety) was used as preliminary precursor. The liquid-phase TTIP was charged in a quartz-cell and then purified in vacuum at 50°C for 3hrs to remove volatile solvent in the liquid. The purified TTIP was vaporized at 70°C and introduced into the chamber without any carrier gas through a stainless tube and a variable-valve at the temperatures about 90°C. Pure oxygen gas (99.9999%-purity) was also introduced through a stainless tube and a variable-valve. The supply ratio of TTIP/O₂ was controlled by monitoring the chamber pressure when the TTIP and the O₂ were introduced into the chamber.

Quartz plates with mirror-surface used as substrates were rinsed in deionized water and dried by a spinner after removal of contaminations from the surface by organic solvents and a hot H₂SO₄ + H₂O₂, and then thermally cleaned at 400°C in the chamber in low pressure below 1×10^{-5} torr for 30 min before the growth. Prior to the growth, inner-wall of the chamber was cleaned by oxygen plasma excited by 100 W rf-power to remove residual gas, and then titanium-oxide layers were grown at low temperatures ranging from 150°C to 400°C.

Thickness of the layer was checked by a contact-type surface profiler (DEKTAK150). The surface morphology was observed by SEM (HITACHI S-800) and the crystallinity was investigated using Raman spectrometer (JASCO NR-1100) using the 514.5 nm line of an Ar⁺ laser (100 mW) as the excitation source. Hydrophilicity on the layer was evaluated by contact angle of water when deionized water (10 μl) was dropped on the layer in air at 20°C with 50%-humidity. The photo-induced hydrophilicity was examined as a function of UV-irradiation time, in which a black-light peak at 365 nm with the low light power density of 50 μW/cm² was used as the light source.

3. Results and Discussions

3.1. Growth Rate

Figure 2 shows growth rates of titanium-oxide layers by

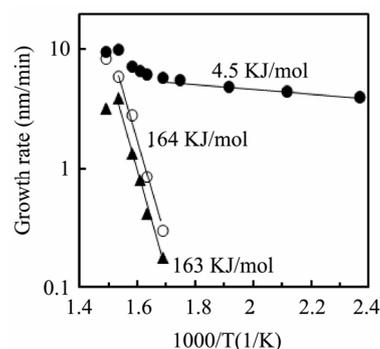
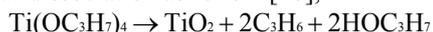


Figure 2. Growth rates of Titanium-oxide layer by PCVD (closed circles), LPCVD (open circles) and thermal-dissociation in PCVD (closed triangles).

PCVD (closed circles) and LPCVD (open circles) at various temperatures, where the O_2 /TTIP supply ratio was controlled to 1. The rate by LPCVD was increased with the growth temperature above 320°C according to Arrhenius relationship and the activation energy was obtained as 164 kJ/mol . The energy value was seemed to be larger than the other reports [13,16] using TTIP and O_2 but similar to the value of 150 kJ/mol by CVD using TTIP in N_2 -gas with the high flow rate [17]. It has been recognized that oxygen reduces the dissociation energy of TTIP, but the large activation energy indicates the dissociation of TTIP by LPCVD in such low pressure of 3mtorr with the small supply ratio of O_2 /TTIP was owing to thermal-dissociation as follow [18],



On the other hand, two activation energies were observed by PCVD. The activation energy in the low temperature below 300°C was 4.5 kJ/mol which was in good agreement with the previous report by PCVD [13] but much lower than that by thermal-dissociation enhanced by reactive-oxygen [16]. The significant low energy indicated that the preliminarily precursor was dissociated to titanium-oxides in the plasma as described elsewhere [13]. In contrast, the activation energy between 300°C and 380°C was determined as 163 kJ/mol (closed-triangles in **Figure 2**) after removal the growth rate extrapolated from the rate in the low temperature region performed by the plasma-cracked precursors. The activation energy above 300°C was coincident to that by LPCVD. It was reported that activation energy of TTIP-dissociation was reduced by plasma-excited oxygen [16], however, the enhanced dissociation was not observed in this work because the collision probability between TTIP and oxygen was relatively small in such low pressure with the small O_2 /TTIP supply ratio. The decreased growth rate above 400°C was believed to be caused by the depletion of the precursor at the growth surface due to the high desorption coefficient or the volumetric dissociation in the gas-phase. It should be concluded from these results that the PCVD above 300°C was performed by supply of the metal-oxides dissociated in the plasma, which was expected to form highly dense grain growth by the high-sticking coefficient, and thermal dissociation of TTIP, which was expected to enhance the crystallization into the anatase phase.

3.2. Raman Spectra

Figure 3 shows Raman spectra of 600 nm-thick titanium-oxide layers grown by PCVD at various temperatures. Typical peaks corresponding to anatase- TiO_2 were appeared at 144 , 399 , 514 and 639 cm^{-1} in the layers grown above 340°C , where the peaks were attributed to E_g , B_{1g} , B_{2g} and E_g vibration modes respectively [19]. However, any peaks except a weak broadband around

450 cm^{-1} , which was recognized due to amorphous phase of TiO_x [20], could not be observed for the layer grown at 250°C .

The broadband was decreased with the deposition temperature and disappeared in the layer grown above 340°C . The broadband was appeared for the layer grown at the temperature ranging from 300°C to 330°C but the weak E_g -band could be also observed. It is noted here that the low-temperature about 300°C to form anatase- TiO_2 was much lower than 450°C by PCVD reported previously [13], but consistent with the temperature for anatase- TiO_2 growth by LPCVD using TTIP as single precursor [21]. The significantly low temperature to form anatase- TiO_2 suggested that the crystallization could be supported by the non-cracked TTIP which was simultaneously supplied with the plasma-cracked precursors and thermally dissociated on the growth surface. **Figures 4(a)** and **(b)** show growth rate ratio by the CVD-mode ($\text{GR}_{\text{thermal}}$) and the PCVD-mode ($\text{GR}_{\text{plasma}}$) thermal-dissociation as a function of the growth temperature and integrated intensity of E_g -mode peak at 144 cm^{-1} as a function of the $\text{GR}_{\text{thermal}}/\text{GR}_{\text{plasma}}$ ratio, respectively. The ratio of $\text{GR}_{\text{thermal}}/\text{GR}_{\text{plasma}}$ except the open circle (grown at 400°C) was rapidly increased with the growth tempera

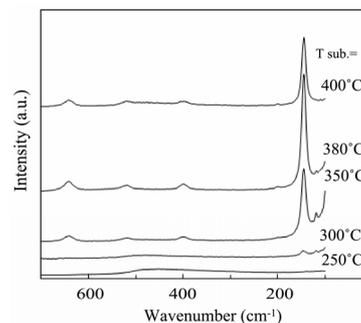


Figure 3. Raman spectra of PCVD-layers with 600 nm-thickness grown at various temperatures.

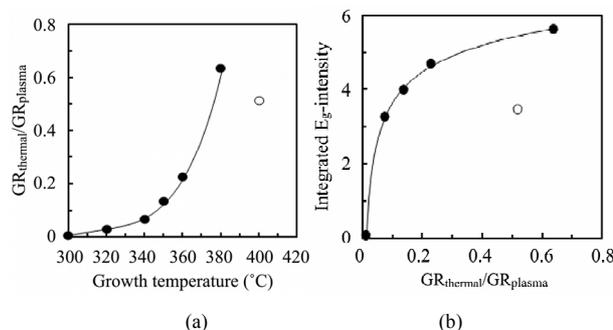


Figure 4. (a) Relative growth rate by thermal dissociation ($\text{GR}_{\text{thermal}}$) compared to growth by plasma cracked precursors ($\text{GR}_{\text{plasma}}$) as a function of the growth temperature; and (b) E_g -intensity as a function of $\text{GR}_{\text{thermal}}/\text{GR}_{\text{plasma}}$, where the open circles shows for the layer grown at 400°C .

ture above 300°C according to rapid increase of the thermal dissociation of TTIP. In contrast, the intensity of E_g -mode was rapidly increased and gradually saturated with the ratio of $GR_{\text{thermal}}/GR_{\text{plasma}}$, which indicated crystallization in anatase-phase was enhanced by relatively small amount of the thermally dissociated TTIP compared to the supply of the plasma-cracked precursors. In the case of the growth at 400°C, decrease of the E_g -band intensity (open circle in **Figure 4(b)**) and the weak broadband due to amorphous-phase (**Figure 3**) suggested the dissociated precursor in the gas-phase was simultaneously supplied on the growth surface.

Figure 5 shows the E_g -band spectra of PCVD- and LPCVD-TiO₂ layers grown at 380°C with 600 nm-thickness, where the background was numerically removed in the spectra. The spectrum with the FWHM of 10.7 cm⁻¹ of the PCVD-layer was slightly sharper than that of the LPCVD-sample with the FWHM of 12.0 cm⁻¹. Additionally, Raman-spectrum shift of the PCVD-TiO₂ was small below 1 cm⁻¹, while the shift of the LPCVD-layer was about 2 cm⁻¹. It is recognized that the Raman-spectrum shift is originated from residual stress in the layer [22] on the substrate with different thermal-expansion coefficient. Previously, Alhomoudi *et al.* reported E_g -band of anatase-TiO₂ layer was shifted toward higher wavenumber above 3 cm⁻¹ broadening about 23 cm⁻¹ in the thick layer about 600 nm, where the layer was grown by reactive-sputtering around 300°C, and concluded the spectrum shift and broadening were caused by residual compressive stress and large distribution of the orientation of grains in the layer, respectively [23]. In contrast, both of the shift and the broadening were much smaller in the PCVD-TiO₂ layer as shown above, which clearly indicated the residual stress in the PCVD-layer was relaxed and speculated the layer consisted of uniform grains.

3.3. Surface Morphology

Figures 6(a) and **(b)** show surface SEM images of 600 nm-thick PCVD-layer and LPCVD-layer grown at 380°C,

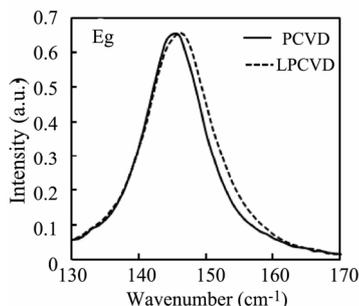


Figure 5. E_g -band spectra of PCVD (solid-line) and LPCVD-layer (dotted-line), where the both layers were grown at 380°C.

respectively. Relatively large and rugged grains with sub-micrometer size were found in the LPCVD-layer, which indicated the growth was performed by the low density nucleation at the initial stage and/or the secondary nucleation in the deep grain boundaries. In contrast, the PCVD-layer was formed by highly dense plate-like nano-grains with the width around 45 nm. It can be easily recognized that the significant difference of the grain feature compared to the LPCVD-layer was caused by highly dense nucleation at the initial stage and preferential growth along the thickness. The nucleation with high density could be performed by the plasma cracked metal-oxides with the high sticking coefficients, then the grains were grown by simultaneous supply of the plasma-cracked precursors and non-cracked TTIP, where the grain growth was governed by supply of the plasma-cracked precursors in PCVD-mode as shown in **Figure 4(b)**. In addition, it is considered that the distinct nano-grains in the PCVD-layer resulted in relaxation of the bi-axial stress observed in the Raman spectrum.

3.4. Hydrophilicity

Figure 7 shows contact angle of water on the PCVD-layers grown at various temperatures ranging from 250°C to 380°C as a function of irradiation time of UV-light

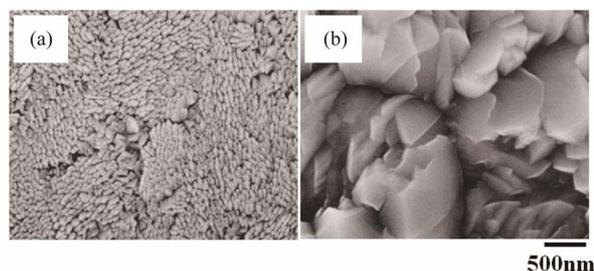


Figure 6. Surface SEM images of 600 nm-thick TiO₂ layers grown by (a) PCVD and (b) LPCVD at 380°C.

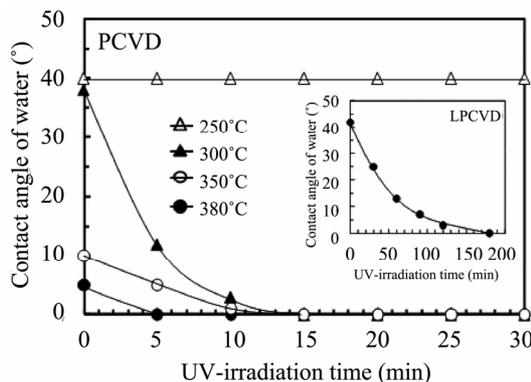


Figure 7. Contact angle of water on TiO₂ layers grown at various temperatures by PCVD as a function of UV-irradiation time. The inset shows variation of the angle on CVD-TiO₂ layer grown at 380°C for UV-irradiation time.

peak at 365 nm-wavelength with the low power density of $50 \mu\text{W}/\text{cm}^2$. The inset shows the dependence of LPCVD-TiO₂ layer grown at 380°C. Here, the grown layer was initially treated in atmosphere by the UV-irradiation for a few hours required to achieve super-hydrophilicity and exposed in air in dark for 1 month, and then the contact angle on the layers irradiated by the UV-light for each time was evaluated after the initial contact angle was checked before the UV-irradiation.

The hydrophilicity on the PCVD-layer including the initial angle and the hydrophilization feature by the UV-irradiation was significantly dependent on the growth temperature. The contact angle was around 40° before the UV-irradiation and not responsible to the irradiation on the layer grown at low temperature below 250°C. Nakamura *et al.* previously showed the amorphous titanium-oxide deposited at low temperature below 200°C by PCVD included hydroxyl which plays an important role of the hydrophilicity and the contact angle on the layer was responsible for UV-irradiation [24]. However, absorption due to -OH bond could not be observed in FTIR spectrum of the amorphous-phase PCVD-layer grown at 250°C, and the contact angle was not responsible for the UV-irradiation. On the other, the contact angle on the layer consists of anatase- and amorphous-phase mixture grown at 300°C was reduced by the UV-irradiation but the initial contact angle was similar to the amorphous-sample. In contrast, the initial contact angle on the layer grown above 340°C, which consists of anatase-phase grains without amorphous-phase, was obviously decreased with the growth temperature and the prompt hydrophilization was observed by the UV-irradiation. Especially, the contact angle on the PCVD-layer grown at 380°C was extremely small about 5° before the UV-irradiation and quickly converted to super-hydrophilicity within 5 min by the UV-irradiation. It is recognized that Ti³⁺ sites reduced from Ti⁴⁺ in TiO₂ crystal cause the hydrophilic conversion. The influence of surface morphology should be also considered in the hydrophilicity, however, the grain structure as shown in **Figure 3** was scarcely dependent on the growth temperature. Therefore, it can be concluded that the hydrophilic property dependent on the growth temperature was originated from the density of Ti³⁺ sites at the surface. On the other, the large initial contact angle about 40° and the gradual response for the UV-irradiation were observed on LPCVD-layer grown at 380°C (inset of **Figure 7**), while the layer consists of anatase-TiO₂ without the amorphous-phase. Capillary effect in addition to chemical property on the surface should be taken into account to recognize the significantly different feature of hydrophilic properties. Previously, Katsumata *et al.* showed the hydrophilic conversion during UV-irradiation was enhanced on the sol-gel derived TiO₂ layer consists of nano-grains with

the size around 50 nm by comparison of the property on the layer consists of relatively large 150 - 200 nm grains [25]. They found out that the difference of hydrophilizing rate by UV-irradiation was originated from homogeneity of the surface and suggested the hydrophilizing was enhanced by two-dimensional capillary effect on the homogeneous microstructure. Although the grain-structure in the PCVD layer as shown in **Figure 6(a)** was different from the sol-gel derived layer, the surface consists of nano-grains was homogeneous compared to remarkably heterogeneous surface of the LPCVD as shown in **Figure 6(b)**. It has been also recognized that the hydrophilicity after UV-irradiation is gradually degraded in dark since the life-time of -OH bond at the surface is not so long, however, long-time storage behavior for the super-hydrophilicity above 5 hrs was observed on the PCVD-TiO₂ layer. This useful behavior was speculated by percolation of water into the nano-scale slits between the grains as shown in **Figure 6(a)**, where the percolated water was probably kept in the pores for long-time avoiding the evaporation compared on the surface. Of course, the storage behavior could not be observed on the LPCVD-layer, in which the contact angle was gradually increased to 40° within 1 hr after exposure in dark.

4. Conclusion

Titanium-oxide layers were grown on quartz substrates by PCVD using TTIP and oxygen mixed gas plasma with O₂/TTIP supply ratio of 1 in the pressure as low as 3 mtorr at low temperatures below 400°C, and then characterized by the growth behavior and the hydrophilicity comparing to the layer by LPCVD. The PCVD was performed by plasma-cracked precursors and thermally dissociated TTIP, while the LPCVD was owing to thermal dissociation of TTIP. Raman spectra investigated anatase-TiO₂ could be grown above 300°C by the PCVD. Further, it was revealed that the crystallinity of anatase-TiO₂ was significantly dependent on the ratio of the PCVD-mode and the CVD-mode during the growth, where non-cracked TTIP played a role to enhance the crystallization of the plasma-cracked precursors on the growth surface. SEM observations showed that the PCVD anatase-phase TiO₂ layer was formed by homogeneous nano-size columnar grains, whereas the LPCVD layer consists of heterogeneous micro-size grains. Initial contact angle of water before UV-light irradiation was dependent on the growth temperature and drastically decreased on the layer grown above 340°C. The initial contact angle about 5° on the PCVD layer grown at 380°C showed the excellent hydrophilicity without UV-irradiation was performed by the PCVD. The contact angle on the PCVD-layer was quickly reduced and showed super-hydrophilicity within 5 min by UV-light irradiation

with the low light power density of $50 \mu\text{W}/\text{cm}^2$, while the long time about 3 hrs was required for the LPCVD layer. The PCVD-layer also showed interesting storage behavior of the super-hydrophilicity as long as 5 hrs in dark after the UV-irradiation, whereas the contact angle on the LPCVD-layer was increased up to 40° within 1 hr in dark.

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