

Plasma-Assisted Chemical Vapor Deposition of Titanium Oxide Layer at Room-Temperature

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ABSTRACT

Plasma-assisted chemical vapor deposition (PCVD) at pressure as low as 3 mtorr using titanium-tetra-isopropoxide (TTIP) and oxygen mixed gas plasma generated by 13.56 MHz radio frequency power (RF-power) below 70 W were applied to deposit titanium-oxide layer at temperature under 40°C. Plasma optical emission spectroscopy and FTIR indicated that density of OH group in the amorphous layer was related to the density of OH or H₂O in the plasma and the species was formed on electrode to induce the RF-power. Hydrophilicity on the layer was dependent on the density of chemisorbed OH, but was degraded by the excess OH. The PCVD-TiO_x coating was demonstrated on polyethylene terephthalate and showed good hydrophilic property with the contact angle of water about 5°.

KEYWORDS

PCVD; Amorphous Titanium-Oxide; FTIR; Hydroxyl; Hydrophilicity

1. Introduction

Titanium dioxide (TiO₂) has been extensively investigated in view of photo-induced applications using the photo-catalytic reactions and the hydrophilicity [1,2], in addition to electronic and optoelectronic applications [3,4]. Especially, anatase-TiO₂ is preferred for the photo-induced applications because of higher surface reaction during UV-irradiation than another crystal structures (brookite, rutile) [5]. It has been well recognized that the photocatalytic reaction inducing UV-light irradiation on the TiO₂ surface is related to the Ti³⁺-sites which are reduced from the surface Ti⁴⁺ by photoexcited electrons, accompanying oxygen vacancies generated by the photo-excited holes [6]. The Ti³⁺-sites at the photo-activated TiO₂ surface, which adsorb OH by the redox reaction for H₂O molecules and generate bridging -OH, resulted in the super-hydrophilicity. In the sequence, it is basically important to control the crystallinity of TiO₂ including impurity concentration and surface morphology. For the

synthesis, a low wet- [7,8] or dry-process [9-11] has been applied to enhance the photo-induced property. Plasma-assisted chemical vapor deposition (PCVD) that is expected to have some advantages for the low temperature deposition, control of the grain structure, step coverage and so on has also been a candidate for suitable synthesis process of the TiO₂ films. In the process, titanium tetra-iso-propoxide (TTIP) seems to be more sufficient as preliminary precursor than titanium tetrachloride (TiCl₄) in view of contamination in the layers [12]. Previously, we demonstrated the PCVD of anatase-TiO₂ for highly hydrophilic performance at 380°C using TTIP and O₂ [13], in which the deposition was achieved in low pressure of 3 mtorr by the plasma-cracked precursors and the thermal dissociation of TTIP on the surface. However, the hydrophilic property was degraded with decreasing deposition temperature and not responsible to UV-irradiation on the amorphous layer deposited at low temperatures under 280°C. On the other, Nakamura *et al.* reported an interesting result that amorphous TiO_x layers deposited by PCVD at low temperatures around 150°C

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show good hydrophilicity after UV-irradiation [14]. They suggested that the hydroxyls including in the layer play an important role for the hydrophilicity. The result expects that amorphous TiO_x layer with hydrophilic conversion by UV-irradiation can be deposited at room-temperature, which is required to perform hydrophilic coatings on organic materials such as PET, resin etc., but the deposition condition has to be precisely optimized with investigation of the decomposition sequence because the adsorptions such as water, hydroxyl and/or hydrocarbons frequently occur with high sticking-coefficient.

In this paper, amorphous TiO_x layer at near room-temperature under 50°C using TTIP and oxygen gas was demonstrated by PCVD in the low pressure of 3 mtorr investigating the reactive species to enhance the decomposition of TTIP optimizing the deposition condition for the hydrophilic performance. FTIR measurements were also carried out to evaluate residual impurities such as hydroxyls and hydrocarbons.

2. Experimental

2.1. Deposition of TiO_x Layer

A conventional bell-jar type reactor with the base pressure under 1×10^{-5} torr was used for plasma-assisted chemical vapor deposition (PCVD) of titanium-oxide. Schematic details of the apparatus was shown elsewhere [13]. DC-coil was settled around the bell-jar to induce DC-magnetic field during the deposition. Titanium tetra-iso-propoxide (TTIP, $\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$: 99.7%-purity) used as preliminary precursor was charged into a quartz cell and vaporized at 70°C to introduce into the reactor through a stainless tube without any carrier gas, where the liquid-phase TTIP was preliminary purified at 50°C in vacuum for 3 hrs before the deposition. Pure oxygen gas (99.9999%-purity) was also introduced for the deposition. The supply ratio of O_2/TTIP was controlled by monitoring the reactor pressure using Shultz gage when the TTIP and the O_2 was individually introduced into the reactor. Radio-frequency power (RF-power) at 13.56 MHz was applied through an inductively coupled rf-electrode to discharge the gases in the reactor, where the mixed gas plasma was generated in the pressure as low as 3 mtorr and stabilized by DC-magnetic field of 3000 Gauss. Si-wafers with mirror-surface used as substrates were rinsed in deionized water and dried after removal of contamination on the surface by methanol, and then mounted on a holder with a water cooling system. Prior to the deposition, the reactor was cleaned by oxygen gas plasma excited by 100 W rf-power with closing shutter settled above substrate to remove residual gases such as adsorbed water on the inner wall, then the substrates were exposed in oxygen-gas plasma excited

by 50 W RF-power for 5 min at room-temperature. TiO_x layer with the thickness about 400 nm was deposited at the temperature under 40°C which was monitored by a thermo-couple.

2.2. Evaluation

Thickness of the layer was checked by a surface profiler (DEKTAK150). Hydrophilicity on the layer was evaluated by the contact angle of water when 10 μL deionized water was drop on the layer in air with 50%-humidity at 2°C . A black-light with the peak wavelength at 365 nm and the light power density of $1 \text{ mW}/\text{cm}^2$ was used for UV-irradiation in air on the TiO_x surface. Residual impurities such as hydroxyls and hydrocarbons in the layers were evaluated by a FTIR system (JASCO FT/IR-420). Optical emission spectroscopy of plasma in the reactor was also carried out by UV-Vis spectrometer (OCEAN OPTICS: USB-2000) though a quartz-window on the cell.

3. Results and Discussions

3.1. Dependence on O_2/TTIP Supply Ratio

Figure 1 shows deposition rate of TiO_x layer by induced RF-power of 30 W as a function of TTIP pressure (P_{TTIP}) in the bottom axis and O_2 pressure (P_{O_2}) in the top axis during the deposition. In the process, the layers were deposited in 3 mtorr with a constant exhaust rate, that is, the deposition in the P_{TTIP} of 3 mtorr was performed without O_2 supply. The deposition rate was uniquely increased with the P_{TTIP} , which indicates the deposition was limited by TTIP supply rate, but saturated above 2 mtorr. Plasma optical emission spectra was quite different by O_2 supply as shown in Figure 2, in which the spectrum of O_2 plasma is shown in 1/5-scale and the

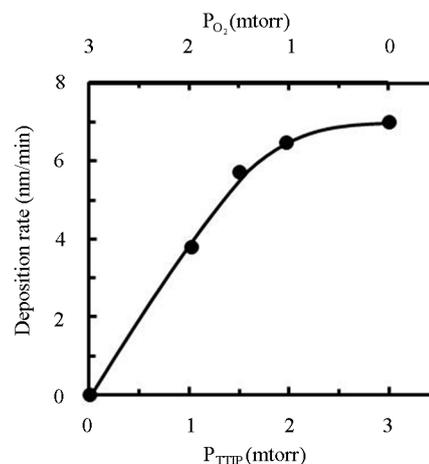


Figure 1. Dependence of TiO_x deposition rate on TTIP-pressure (P_{TTIP} : bottom axis) and O_2 -pressure (P_{O_2} : top axis).

TTIP + O₂ plasma was generated by the P_{TTIP} of 1.5 mtorr (P_{TTIP}/P_{O₂} = 1). Typical emissions due to excited oxygen, hydrogen, carbon-oxides and hydroxyl were observed in the TTIP + O₂ plasma, however, any emission due to excited oxygen could not be detected in the TTIP plasma. The emission spectra suggested TTIP was not only dissociated in TiO-R but also in Ti-OR because the CO₂ and OH emissions could be observed in the TTIP plasma without the emissions due to O and O₂. It is considered that the decomposition sequence was similar to the previous report for PCVD performed in 350 mtorr, in which it was suggested that TTIP can be decomposed by electron impact to Ti and TiO_x in vapor-phase of TTIP + O₂ plasma and then oxidized by O-radical in the vapor phase or on the deposition surface [15]. However, TTIP was scarcely dissociated in the vapor phase at low pressure of 3 mtorr as discussed by the dependence on RF-power in Section 3.2. **Figure 3** shows dependence of the emission intensity due to the excited species on the

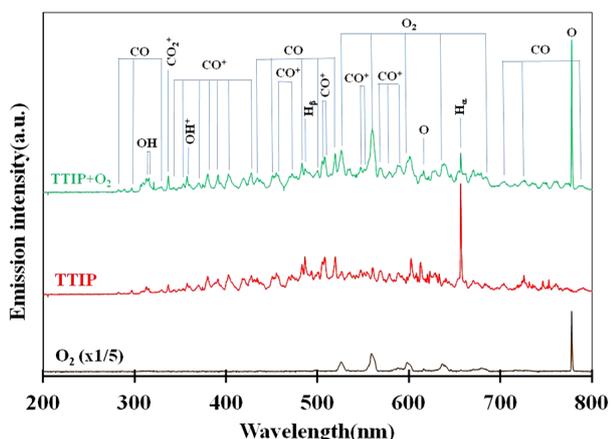


Figure 2. Optical emission spectra of O₂ plasma (black-line), TTIP plasma (red-line) and O₂ + TTIP plasma (green-line).

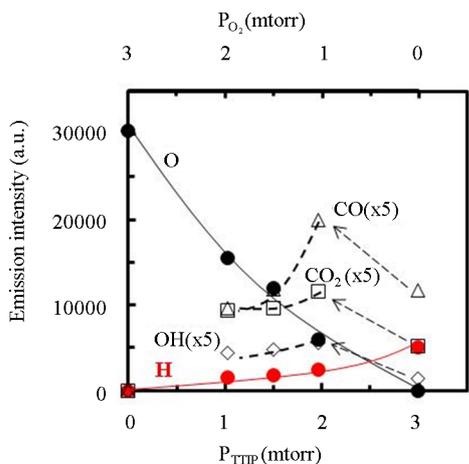


Figure 3. Dependence of optical emission spectra due to excited species in the plasma on the P_{TTIP} and P_{O₂}.

gas supply rate shown by P_{TTIP} and P_{O₂}, where the intensities of CO, CO₂ and OH were extended by 5-times. The intensity of O and H were gradually increased and decreased with P_{O₂} (decreasing P_{TTIP}), respectively. In contrast, the emissions due to CO, CO₂ and OH were significantly increased by O₂ supply comparing to the TTIP plasma as shown by bow-lines and then gradually decreased with decreasing TTIP supply rate. The result could be recognized that CO and H were oxidized by excited oxygen. Commonly, it is expected that OH or H₂O can play a role to enhance TTIP dissociation as demonstrated in Sol-Gel process, which is resulted in the formation of Ti-OH and the oxo-bridging of Ti-O-Ti [16]. It is however seemed in this work that not only OH but also the other species influenced to the dissociation because the deposition rate by using TTIP plasma was comparable in the plasma to that by using TTIP + O₂ plasma with the P_{TTIP} = 2.0 mtorr whereas the emission due to OH was significantly increased in the TTIP + O₂ plasma comparing to that in the TTIP plasma. Previously, it was reported by FTIR studies for TTIP dissociation that atomic oxygen radicals supplied from oxygen remote-plasma enhance the dissociation of TTIP and the dissociation energy is decreased to 27.3 kJ/mol [17]. In contrast, the energy for the dissociation in the PCVD was 4.5 kJ/mol as shown elsewhere [13]. The significantly low dissociation energy in the PCVD comparing to the remote-plasma assisted deposition suggested that charged particles such as electrons and ions were also contributed to the dissociation.

Figure 4 shows FTIR absorption spectra of the TiO_x layers deposited by P_{TTIP} of (a) 2.0, (b) 1.5, and (c) 1.0 mtorr, where the P_{O₂}/P_{TTIP} was 0.5, 1.0 and 2.0 respectively. Broad-absorptions around 500 cm⁻¹, which are recognized due to short-range O-Ti-O network in amorphous TiO_x [15], were observed in the all samples and the intensity was scarcely dependent on the P_{O₂}

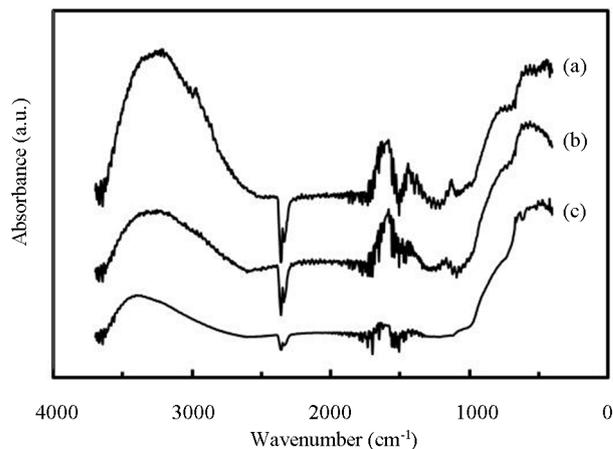


Figure 4. FTIR spectra of TiO_x layers deposited by P_{TTIP} of (a) 2.0, (b) 1.5 and (c) 1.0 mtorr.

P_{TTIP} ratio. In addition, absorptions at 1410, 2850 and 2950 cm^{-1} , which is attributed to $-\text{CH}_2$ (bending), $-\text{CH}_3$ (stretching) and $-\text{CH}_2$ (stretching) respectively [18], were observed in the spectrum (a), but the intensity were notably decreased with increasing the $P_{\text{O}_2}/P_{\text{TTIP}}$ ratio and could not be observed in the spectrum (b) and (c). The broad-spectrum below 2600 cm^{-1} can be assigned to absorptions due to H_2O or OH [18]. In addition, broad-spectrum below 2600 cm^{-1} was clearly observed and the feature was significantly decreased with increasing $P_{\text{O}_2}/P_{\text{TTIP}}$ ratio. It is noted that the broad-spectrum was shifted toward higher wavenumber with increasing the ratio, which indicated the spectrum consists of some spectra. **Figure 5** shows the absorption spectra above 2600 cm^{-1} in the layers deposited by P_{TTIP} of (a) 2.0, (b) 1.5 and (c) 1.0 mtorr with the deconvoluted spectra (blue-line) and the fitted curve (red-line), where Gaussian function was used for the deconvolution. The spectrum could be well reconstructed by four spectra peak at 3015, 3251, 3418 and 3530 cm^{-1} which could be attributed to the absorptions due to physisorbed H_2O (around 3008 cm^{-1}) [19], chemisorbed OH to Ti (around 3200 cm^{-1} , 3400 cm^{-1}) [20] and H_2O_2 (around 3537 cm^{-1}) [21].

Figure 6(a) shows dependence of the integrated intensity related to the hydroxyls on P_{TTIP} . The absorptions were significantly increased with TTIP supply rate (decreasing O_2/TTIP ratio). The feature could be simply described by OH emission intensity in the plasma as shown in **Figure 6(b)**, where the absorption intensity (ABS) was divided by the deposition period (Depo. period). The result linearly dependent on the OH emission intensity clearly indicated the absorption species due to hydroxyls were formed by OH or H_2O in the plasma. In addition, the (ABS)/(Depo. period) for the species was asymptotic to

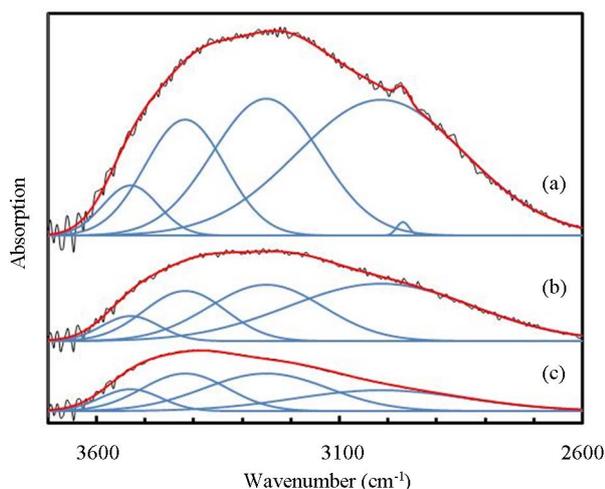


Figure 5. Broad absorption spectra above 2600 cm^{-1} in TiO_x layer deposited by P_{TTIP} of (a) 2.0, (b) 1.5 and (c) 1.0 mtorr (black-line) with the deconvoluted spectra (blue-line) and the fitted curve (red-line).

the OH emission intensity about 850, which indicated that OH or H_2O was also contributed to the deposition without the absorption species.

3.2. Dependence on Induced RF-Power

Figure 7 shows dependence of (a) deposition rate and (b) optical emission intensity on the induced RF-power, where the $P_{\text{TTIP}}/P_{\text{O}_2}$ ratio was kept to 1.0 ($P_{\text{TTIP}} = P_{\text{O}_2} = 1.5$ mtorr). Although any deposit could not be observed when the RF-power was not induced, the deposition rate was increased with the RF-power and then decreased by the power above 70 W. In general, TTIP can be dissociated to the metal-oxides in the gas-phase and on the deposition surface. It was previously reported for amorphous TiO_x deposition by PCVD using TTIP and O_2 that the deposition rate is dependent on the density of atomic oxygen radical and decreased with increasing the induced RF-power from 5 W to 20 W in 350 mtorr because of increasing the gas-phase dissociation in the plasma [22]. In contrast, the deposition rate was increased with the RF-power below 50 W in this work, which is considered to be derived from the increased mean-free path in the low pressure of 3 mtorr. On the other, intensity of optical emission from the plasma was linearly increased with the RF-power. If TTIP was dissociated in the gas phase of the plasma, density of hydrogen and hydroxyls should be increased with the RF-

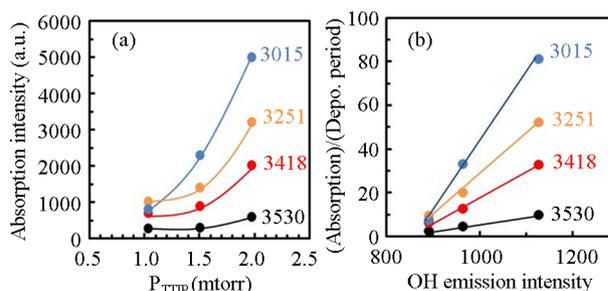


Figure 6. (a) Integrated intensity of absorptions concerned to hydroxyls in TiO_x layers for P_{TTIP} and (b) the absorption intensity divided by the deposition period for OH emission intensity in the plasma.

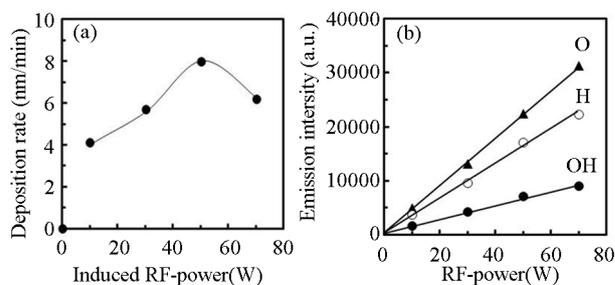


Figure 7. Dependence of (a) deposition rate and (b) optical emission intensity on the induced RF power, where the supply rate of $P_{\text{TTIP}}/P_{\text{O}_2}$ was 1.0 ($P_{\text{TTIP}} = P_{\text{O}_2} = 1.5$ mtorr).

power, and the emission intensity should be super-linearly increased with the RF-power because the emission intensity was expected to be in proportion to the density of particle and the electron density in the gas phase. Therefore, it is concluded from the result that not only oxygen density but also hydrogen and hydroxyls density were not dependent on the RF-power. In the process introducing RF-power through the electrode settled in reactor, the gases can be efficiently dissociated on the electrode, in which the density of the dissociated species are fundamentally dependent on the density of precursor in the reactor.

Figure 8 show FTIR spectra of PCVD-TiO_x layers deposited by RF-power of (a) 10, (b) 30, (c) 50 and (d) 70 W, where the P_{TTIP} was 0.15 mtorr. The feature of the broad-absorption below 2600 cm⁻¹ was dependent on the RF-power. Figure 9 show variations of (a) integrated intensity of deconvoluted FTIR spectra for the OH-related absorptions and (b) (ABS)/(Depo. Period) for the RF-power, where the thickness of layers were about 400 nm in the samples. Absorptions due to CH_x were not observed in the samples. The absorption due to physisorbed H₂O around 3530 cm⁻¹ was gradually decreased

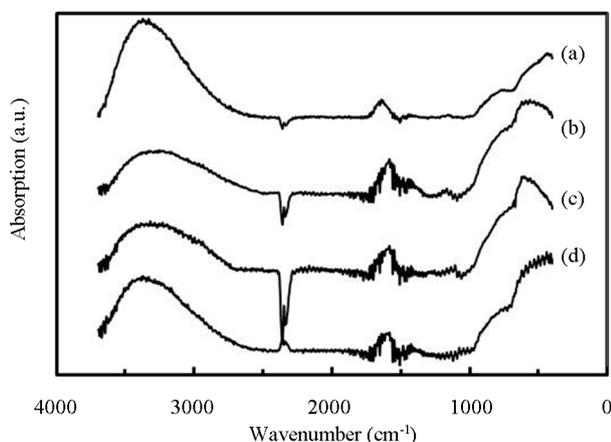


Figure 8. FTIR spectra of TiO_x layers deposited by RF-power of (a) 10, (b) 30, (c) 50 and (c) 70 W, where P_{TTIP} was 1.5 mtorr.

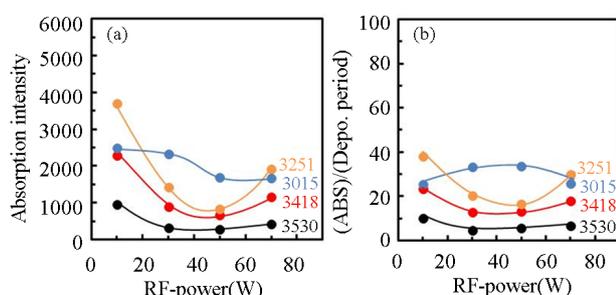


Figure 9. Variation of (a) integrated intensity of deconvoluted OH-related absorptions in TiO_x layers and the intensity divided by the deposition rate for induced RF-power.

with increasing RF-power whereas density of OH or H₂O was not dependent on the RF-power. In contrast, the other absorptions were decreased with increasing RF-power but increased by the RF-power of 70 W. For the (ABS)/(Depo. Period), the physisorbed H₂O was slightly increased with the RF-power but decreased by the RF-power of 70 W. On the other, the (ABS)/(Depo. Period) due to chemisorbed OH were minimized by the RF-power of 30 - 50 W. It has been well recognized that TTIP is easily dissociated to Ti-(OH)_x at room-temperature by water contribution [16]. The hydrolysis was also included in the PCVD process, especially, in the case of low RF-power such as 10 W, in which the supplied H₂O was partially consumed to dissociate TTIP. On the other, it is considered that the contribution of electron and/or excited species such as radicals and ions should be taken into account to the deposition sequence, for example, in Ti-O-Ti network formation from Ti-OH and in dissociation of supplied H₂O on the deposition surface. Therefore, the density of Ti-OH was decreased with the RF-power and that of H₂O was decreased by the RF-power of 70 W. It is noted here that when electrons are supplied to the deposition surface, however, Ti-O-Ti is dissociated to Ti-O, Ti be-cause the Ti⁴⁺ is reduced to Ti³⁺, and then Ti-OH is formed by supplied H and OH. As a result, density of Ti-OH was increased with the RF-power above 50 W.

3.3. Hydrophilicity

Figures 10 show contact angle of water (θ_{water}) on TiO_x layer deposited by (a) various TTIP supply rate (P_{TTIP}) and (b) various RF-power, where the θ_{water} was evaluated after UV-irradiation for 1 hour (black-circles) and then after exposure in air for 2-weeks (red-circles). θ_{water} was decreased with decreasing P_{TTIP} (increasing P_{O₂}/P_{TTIP}). In contrast, θ_{water} was decreased with the RF-power but increased on the layers deposited by the RF-power above 50 W. Although amorphous TiO_x deposited at relatively high temperature above 250°C is not in response to UV-irradiation [16] for the hydrophilicity,

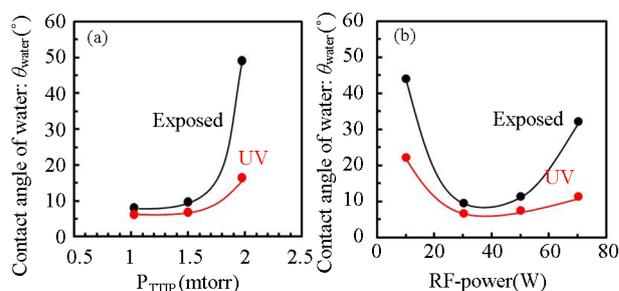


Figure 10. Contact angle of water on TiO_x layer deposited by various (a) P_{TTIP} and (b) RF power after UV-irradiation (red-circles) and after exposure for 2-weeks in air (black-circles).

the contact angle of water OH-included amorphous TiO_x layer is significantly decreased by UV-irradiation [17]. Therefore, it is considered that OH species play a role for hydrophilicity on the layers deposited in this work. **Figure 11** shows dependence of $\text{Cos}(\theta_{\text{water}})$ on the integrated absorption intensity in TiO_x layers grown by various P_{TTIP} and RF-power, in which the absorption intensity is divided by the layer thickness to estimate the density of the species on the surface. In this work, the $\text{Cos}(\theta_{\text{water}})$ was linearly increased with decreasing chemisorbed OH density but seemed to be not dependent on the physisorbed H_2O . In addition, the intensity due to H_2O_2 (3530) was asymptotic to zero at the $\text{Cos}(\theta_{\text{water}}) = 1.0$ but the intensity due to chemisorbed OH (3418, 3251) was not asymptotic to zero at the $\text{Cos}(\theta_{\text{water}}) = 1.0$. The result indicated that chemisorbed OH is necessary for the super-hydrophilicity but the excess species are not suitable for the purpose because of decreasing the Ti-O-Ti network. Especially, H_2O_2 which is expected to be included as Ti-OH-HO-Ti should be removed from the layers.

The PCVD- TiO_x coating at room-temperature was demonstrated on polyethylene terephthalate (PET). **Figure 12** shows features of water droplets on (a) PET and (b) PCVD- TiO_x layer deposited on PET by optimized condition ($P_{\text{TTIP}} = 1.5$ mtorr, RF power = 30 W), where the water was dropped on the TiO_x layer after UV-irradiation for 1 hour. It is noted that any deformation of the

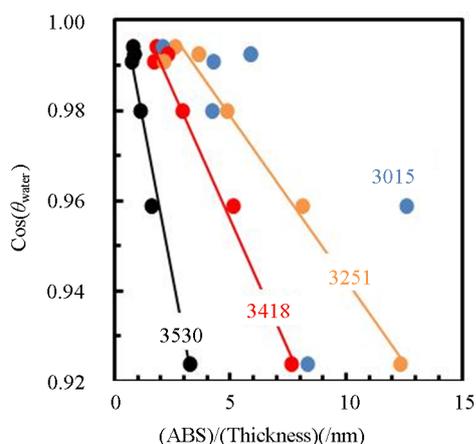


Figure 11. Dependence of $\text{Cos}(\theta_{\text{water}})$ on OH-related absorption intensity, where the absorption intensity in the layer (ABS) is divided by the layer thickness (thickness).

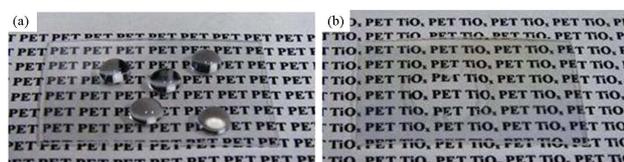


Figure 12. Feature of water droplets on (a) PET and (b) PCVD- TiO_x /PET, in which water of 10 μL was dropped on the PCVD- TiO_x /PET after UV-irradiation.

PET was not observed after the TiO_x deposition. Whereas the θ_{water} was 75° on the PET, the angle was decreased to 5° on the TiO_x layer. The θ_{water} on the TiO_x layer is slightly small comparing to that on TiO_x layer deposited on Si substrate, which was probably derived from the difference of surface roughness. As demonstrated here, the PCVD process at room-temperature can be concluded to be useful for hydrophilic coating on the materials with poor thermal resistance.

4. Conclusion

Plasma-assisted deposition of TiO_x layer at room temperature using TTIP and O_2 gas plasma was studied by FTIR and plasma optical emission spectroscopy. OH content in the layer was significantly related to OH density in the plasma. Optical emission spectroscopy indicated that OH density in the plasma was increased by O_2 supply but not dependent on the induced RF-power, which suggested that TTIP was scarcely dissociated in the plasma at pressure as low as 3 mtorr but efficiently dissociated on RF-electrode. Chemisorbed OH, especially H_2O_2 in the layer was significantly influenced on the hydrophilicity. The PCVD- TiO_x coating was demonstrated on PET and the contact angle of water was decreased to 5° compared with 75° on PET.

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