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Enhanced effect of vacuum-deposited SiO_2 overlayer on photo-induced hydrophilicity of TiO_2 film

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Photo-induced hydrophilicity of SiO_2/TiO_2 multilayer film prepared by using the vacuum deposition method was investigated by means of water contact angle measurement. Using black light irradiation of the films centering at a wavelength of 365 nm, an extreme photo-induced hydrophilicity was achieved when the TiO_2 film was covered by SiO_2 overlayer ranging from 10 to 20 nm in thickness. These multilayer films exhibited much more extreme hydrophilicity than the TiO_2 film without SiO_2 overlayer. The surface analyses revealed that the enhanced photo-induced hydrophilic surface of the multilayer films exhibited an improved photo-catalytic activity towards decomposition of organic substances on their surfaces. It was found that significant growth of the SiOH group occurred in the uppermost surface of the SiO_2 overlayer of the multilayer films through the depth profile measurement of TOF-SIMS. This result suggests that the photo-generated reactive species such as hole created in the TiO_2 film may transmit the SiO_2 layer to reach the surface. The enhanced photo-induced hydrophilicity of the films can be explained by a synergetic effect of the improved photo-catalytic activity of the multilayer film and the stable hydrophilicity of SiO_2 itself. © *2001 Kluwer Academic Publishers*

1. Introduction

TiO_2 is a nontoxic metal oxide semiconductor with many industrial uses. Recently, extremely useful photo-catalytic properties of TiO_2 have been discovered [1–3]. A great deal of attention has been focused on TiO_2 as an efficient photo-catalyst and its use has been applied to environmental problems such as water and air purification and the destruction of microorganisms [4, 5]. The research of TiO_2 as a photo-catalyst started with photo-catalytic resolving of water on TiO_2 electrodes [6], and it was extended to solar energy conversion. The photo-catalytic activity has been explained by oxidation and reduction induced by a pair of hole and electron separated by light irradiation [7–9]. The photo-catalytic activity of TiO_2 is very useful not only in environmental purification by decomposition of organic substances but also in the material industry such as mirrors and glasses owing to its self-cleaning and antifogging effects. The antifogging effect has been attributed to the photo-induced hydrophilic or amphiphilic surfaces [10–12]. On the other hand, the enhanced photo-catalytic effects of composite TiO_2 materials have been reported recently. Some examples are: (1) metal doping to TiO_2 powder [13–16], (2) coupling with other metal

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oxide semiconductors [17, 18], (3) mixing with insulating substances such as SiO_2 or Al_2O_3 [19–21] and (4) mono-layer coverage by SiO_2 [22]. Among them, the investigation of a photo-induced "super hydrophilic" formed by SiO_2 addition to TiO_2 film seems very useful in the mirror and glass industries [23]. It was reported that the specific amount of SiO_2 addition to TiO_2 film prepared by the sol-gel method efficiently lowered the water contact angle on the film surface during UV light irradiation, and that the hydrophilic surface was sustained in dark place longer than on the TiO_2 film without SiO_2. The report concludes that the enhanced photo-induced hydrophilicity of the complex film might be obtained by improved photo-catalytic activity resulting in a high capability of holding absorbed water to the film [23].

In order to investigate the enhanced photo-induced hydrophilicity and photo-catalytic activity of TiO_2 film affected by SiO_2, we have designed SiO_2/TiO_2 multilayer films, which are TiO_2 film overlaid with SiO_2 thin films. An electron beam vacuum deposition method was used rather than liquid phase deposition method such as a sol-gel method to prepare smooth and homogeneous films. The effects of SiO_2 overlayer's thickness on the photo-induced hydrophilicity and self-cleaning effect of the photo-catalytic films are discussed in this study, which will give the hints to develop a new type of the photo-induced "super hydrophilic" films.

2. Experimental

2.1. Preparation and characterization of vacuum deposition films

An electron-beam vacuum deposition apparatus BMC1000 (Shincron Ltd.), was used to deposit the TiO_2 film and the SiO_2/TiO_2 multilayer films on glass plates. The TiO_2 and SiO_2 materials used for the vacuum deposition are a 3N class of purity. The deposition chamber was exhausted to 1×10^{-5} Torr using a rotary pump and a diffusion pump. To prepare the substrate, the SiO_2 film of 120 nm in thickness was deposited on glass plates before the deposition of the films. Using a thickness monitor, which is a double-chromatic photometer, installed in the deposition apparatus, the TiO_2 film was deposited at 240 nm in thickness. The thickness of SiO_2 overlaying the TiO_2 film was set at a range from 5 to 70 nm. During the deposition of the TiO_2 film, oxygen gas was let into the deposition chamber to keep its pressure at 2×10^{-4} Torr. The SiO_2 overlayers were deposited without oxygen gas inlet. During the whole deposition procedure, the temperature of the substrate was kept at 330 °C.

Chemical elements on the surface of the films were measured by an X-ray Photoelectron Spectrometer (XPS), AXIS-HS (Kratos Analytical Ltd.) using X-ray emitted from an Mg anode at a power of 150 W. The pass energy for the XPS measurements was 160 eV to obtain the survey spectra, and 40 eV to obtain the element spectra. The analysis chamber of the instrument was exhausted at approximately 1×10^{-8} Torr and a charge neutralizer was employed to prevent the deviation in XPS spectra due to the surface charging of the films induced by X-ray irradiation.

To estimate the actual thickness of the SiO_2 overlayers, XPS depth profile measurements were carried out using Ar ion etching technique. A surface step meter, New Form Talysurf S5 (Taylor-Hobson Ltd.) was used to measure the etched crater in the SiO_2 overlayer with set thickness of 70 nm, which calibrated the etching time into actual thickness of the film. Crystal structure of the TiO_2 film was analyzed by an X-ray diffractmeter designed for thin film measurement, RINT2400 (RIGAKU Electric Ltd.) using a Cu anode powered at 7 kW. Surface morphology of the films was measured by an Atomic Force Microscope, JSPM4200 (JEOL Ltd,) using a tip of Si at the contact mode probing under an ambient condition (25°C, RH 60%, in air atmosphere).

2.2. Evaluation of the photo-induced hydrophilicity and sustained efficiency

Hydrophilicity of the film surface was estimated by measuring the contact angle of a water droplet of $\phi 1$ mm using a contact angle meter FACE Model CA-X (Kyowa Interface Science Co., Ltd.). The films were put in a dark room for three months before the water contact angle measurements so as to be slightly contaminated and turned hydrophobic on the surface. UV light irradiation was carried out at an ambient condition (25 °C, RH 60%, in air atmosphere) for 4 hours, using a commercial black light lamp (Toyostar Co., Ltd., FL20S BL-B, 23 W) of which emission was centered at 365 nm. The light power was measured to be maintained at 1 mW/cm^2 by a UV meter (Topcon UVR-1).

To evaluate the sustained efficiency of the hydrophilicity, water contact angle measurements of films stored in a dark room, were carried out every day for one week at the ambient condition as is remarked above. The films used in this experiment were the TiO_2 film, the SiO_2 (5 nm in thickness)/TiO_2 and the SiO_2 (20 nm in thickness)/TiO_2 multilayer films, which were prepared to be hydrophilic (about 5 degree of water contact angle) by UV light irradiation, respectively.

2.3. Surface characterizations of photo-induced hydrophilic films

Surface characterizations were performed using surface analysis techniques such as XPS, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurements. XPS measurements were performed to obtain C 1s/(Si 2p + Ti 2p) of the films to evaluate the self-cleaning effect of the surface caused by the UV light irradiation as is remarked above. A PHI TRIFT II (Physical Electronics, Inc.) was used to obtain the TOF-SIMS data with keeping the analytical chamber pressure at 3×10^{-9} Torr. To perform the depth profiling for the films by TOF-SIMS, a Ga ion gun was used both in the analysis and in the etching process at a current of 3.9×10^{-3} nA and 2 nA at 15 keV, respectively. The respective areas were kept at 80 μm^2 and 120 μm^2. The instrument for ATR-FTIR measurement was a Magna750 equipped with Infrared Microscope Nic-Plan (Nicolet Instrument Corporation).

A Micro-ATR objective with a Ge crystal was used as an internal reflection element. The spectra were obtained with 8 cm^{-1} wavenumber resolution using a MCT detector.

3. Results

3.1. Characterization of the vacuum deposition films

The TiO_2 film prepared by an electron beam vacuum deposition method had a smooth surface and was transparent and slightly colored. The stoichiometric ratio of the film determined by O 1s/Ti 2p of the XPS measurement indicated that chemical formula of the film was approximately TiO_2. The X-ray diffractmetry result shown in Fig. 1 proves that the crystalline form of the TiO_2 film has a polycrystalline structure of anatase. Using the Sherrer's equation, the surface crystalline size of the film was estimated as approximately 20 nm in diameter. An AFM image shown in Fig. 2a also suggests that the diameter of the TiO_2 crystalline size on the surface is about 10 to 30 nm.

No change in the transparency and color of the films occurred from the deposition of the SiO_2 overlayer on the TiO_2 film. It is also clear that the SiO_2 overlayer with 20 nm in thickness scarcely influences the morphology of TiO_2 polycrystalline form besides a little increase of the grain size, as shown in Fig. 2b.

It is important to know if the surface shown in Fig. 2b is thoroughly covered by the SiO_2 overlayer. The XPS survey spectra of some SiO_2-overlaid films, which were acquired using 90 degree of take-off angle of photoelectron, are shown in Fig. 3. When the thickness of the SiO_2 overlayer was set to be 20 nm, no Ti 2p peak is observed in a survey spectrum as shown in Fig. 3a. This means that the TiO_2 film is thoroughly covered by the SiO_2 overlayer. In the case where the SiO_2 overlayer was set at 10 nm in thickness, a weak Ti 2p peak is observed (Fig. 3b). However, the Ti 2p peak disappeared when the measurement was performed with 20 degrees of the take-off angle. As shown in Fig. 3c, the spectrum of the film with the 5 nm-set SiO_2 overlayer shows the Ti 2p peak remarkably, which was evaluated at an atomic ratio of Ti/Si as approximately 0.5. The Ti 2p peak shown in the Fig. 3c did not disappear in any take-off angle measurements. These results indicate that the TiO_2 film is thoroughly covered by the SiO_2 overlayer when it is set more than 10 nm in thickness.

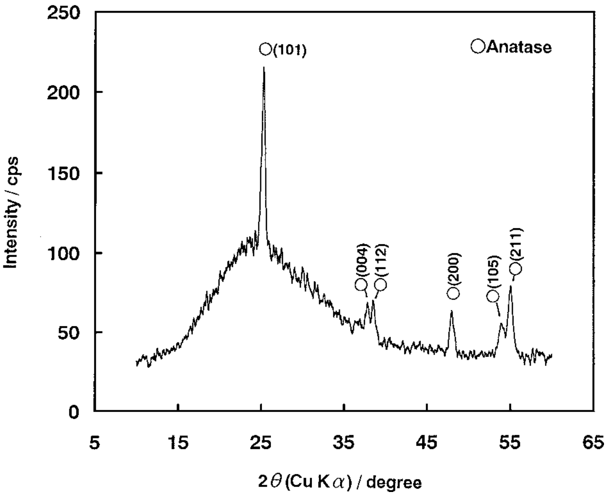

Figure 1 X-ray diffraction pattern of the TiO_2 film prepared by an electron beam vapor deposition method. Film was deposited at 240 nm in thickness on SiO_2 coated glass substrate at a temperature of 330°C.

In Fig. 4, the relationship between the set thickness and the measured thickness of the SiO_2 overlayer is shown. The relationship can be regarded as linear and the discrepancy between them is small. The stoichiometric ratios of the SiO_2-overlaid films ranging from 10 to 70 nm in thickness, determined by O 1s/Si 2p of the XPS measurements, indicated that the chemical formulas of the overlayers were between $SiO_{2.1}$ and $SiO_{2.3}$.

3.2. Photo-induced hydrophilicity and the self-cleaning effect of the films

Changes in the water contact angle on the TiO_2 film and SiO_2/TiO_2 multilayer films, induced by the UV light irradiation, are shown in Fig. 5. The films with the SiO_2 overlayer ranging from 0 to 50 nm in thickness indicated the decrease of the water contact angle by the UV light irradiation, which is recognized as photo-induced hydrophilicity of the films. Significant changes of the water contact angle were exhibited the films with the SiO_2 overlayer less than 30 nm in thickness. Remarkably, the multilayer films with 10 and 20 nm-thick overlayer showed lower water contact angle than 10 degree, which may be recognized as an enhanced photo-induced hydrophilicity.

The data obtained by XPS measurements on the surface of the SiO_2 (20 nm in thickness)/TiO_2 multilayer film illustrated in Fig. 6 shows the self-cleaning effect of the photo-catalytic film. Disappearance of C 1s peak of the XPS spectrum obtained from the surface of the multilayer film by the UV light irradiation is obvious. This result indicates that the organic substances existing as contaminants on the surface of the multilayer film, which showed the significant photo-induced hydrophilicity, were extremely removed by the UV light irradiation. In Fig. 7, the dependence of the photo-induced changes of C 1s/(Si 2p + Ti 2p) on the thickness of the SiO_2 overlayer in the multilayer films is shown in semi-logarithmic plot. The dependency resembles that of the photo-induced hydrophilicity, shown in Fig. 5, which suggests that the photo-induced hydrophilicity of the film closely relates to the photo-catalytic removal of organic substances from the film surface.

To evaluate the photo-catalytic activity of the multilayer film compared with the TiO_2 film, the UV light irradiations onto the films were carried out for 1, 2 and 4 hours by the irradiation condition as is remarked in experimental section. Fig. 8 shows the decreases of the organic contaminants on the TiO_2 film and the SiO_2 (20 nm in thickness)/TiO_2 multilayer film induced by the photo-catalytic activity, which curves are almost linear in semi-logarithmic plot. It is considered that both of the films indicated first-order kinetics of the photo-catalytic activity. It is also clear from the figure that the

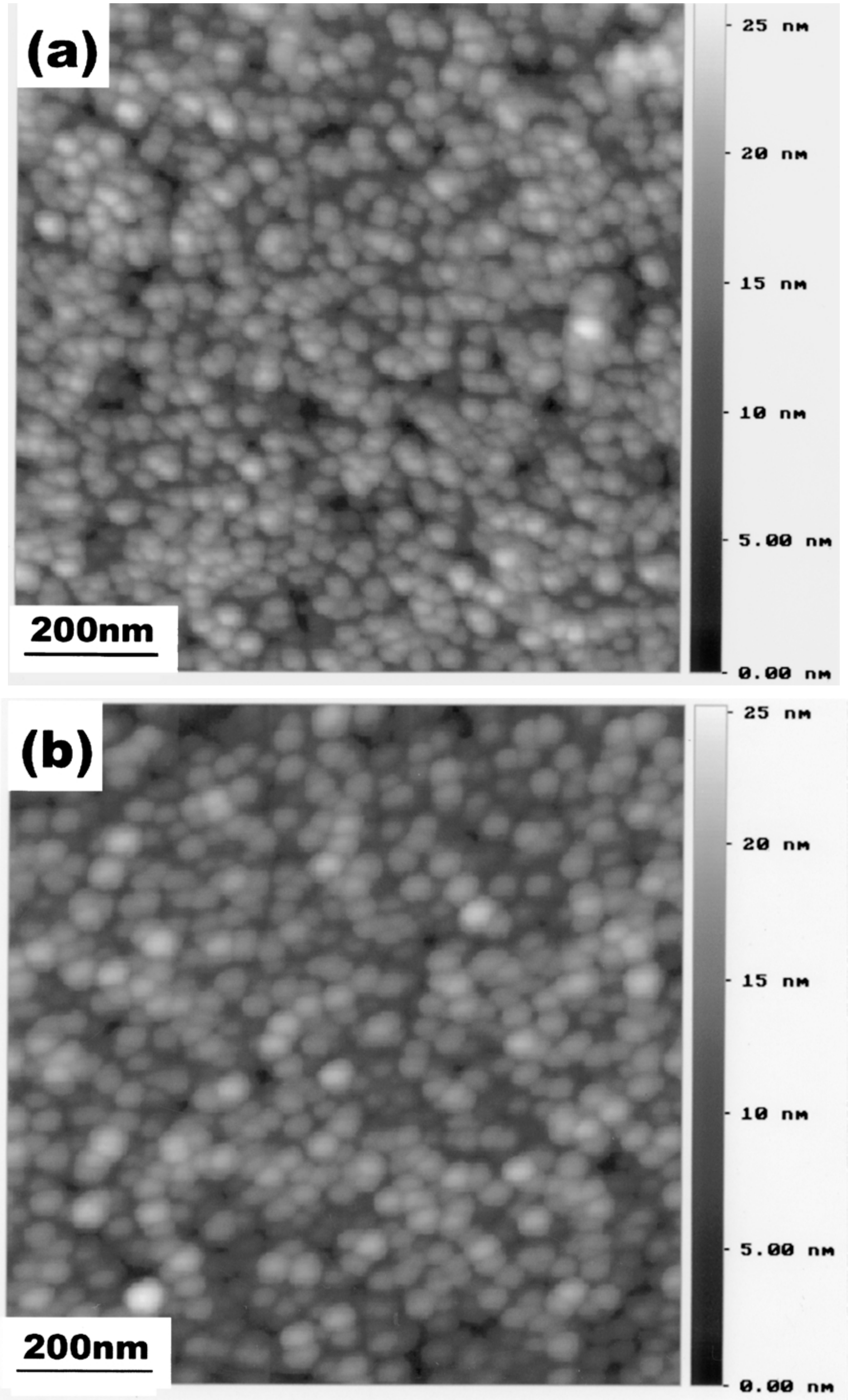

Figure 2 AFM images of (a) the TiO_2 film and (b) the SiO_2 (20 nm in thickness)/TiO_2 multilayer film prepared by the vapor deposition.

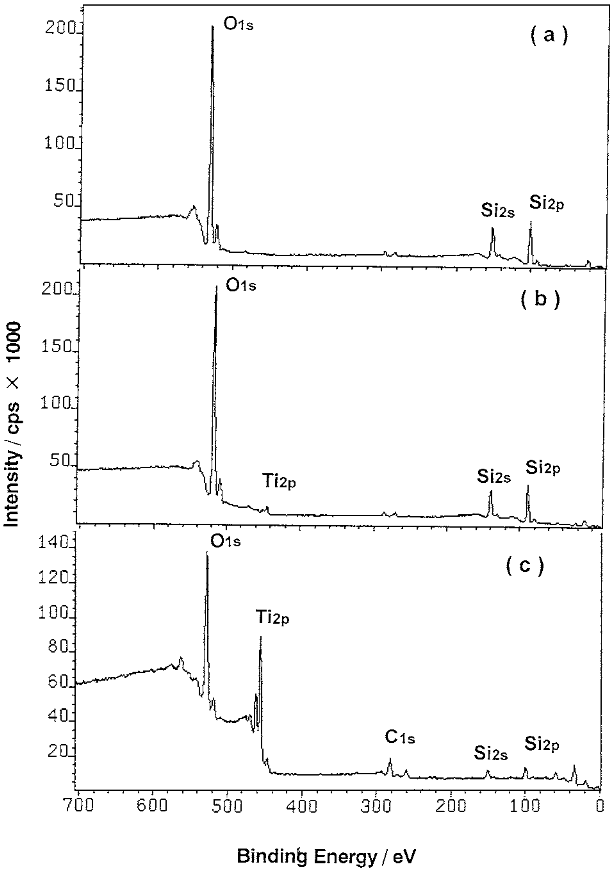

Figure 3 XPS survey spectra of the SiO_2/TiO_2 multilayer films using 90 degree of take-off angle of photoelectron, (a) 20 nm set-thickness of SiO_2 overlayer, (b) 10 nm set-thickness of SiO_2 overlayer, (c) 5 nm set-thickness of SiO_2 overlayer.

multilayer film showed a greater reaction rate and an improved photo-catalytic activity than the TiO_2 film.

3.3. Surface characterizations of the films using TOF-SIMS and ATR-FTIR

The characterization of chemical species and functional groups on the photo-catalytic film was important to understand the photo-induced hydrophilicity on the surface. The TOF-SIMS measurements revealed that the main cation fragments detected from the surface of the SiO_2 (20 nm in thickness)/TiO_2 multilayer film, which indicated the extreme photo-induced hydrophilicity, are $SiOH^+$ ($m/Z = 45$) and Si^+ ($m/Z = 28$). Depth profile curves of $SiOH^+/Si^+$ obtained by TOF-SIMS etching measurements are shown in Fig. 9 for the multilayer film. It is recognized that the content of the SiOH group significantly increases only in the uppermost surface (0 to 3 nm in depth) of the film after the UV light irradiation. This result suggests that the growth of SiOH group occurs only in the uppermost surface of the SiO_2 overlayer.

The ATR-FTIR spectra obtained from the surface of the multilayer film are shown in Fig. 10. Significant changes in the spectra due to the UV light irradiation occurred in the region from about 3600 cm^{-1} to 2800 cm^{-1} and around 1640 cm^{-1}, which bands are assigned to the OH group having strong hydrogen bond such as liquid water. These bands can be attributed to the water adsorbed on SiOH group, which was generated by the UV light irradiation on the surface of the multilayer film.

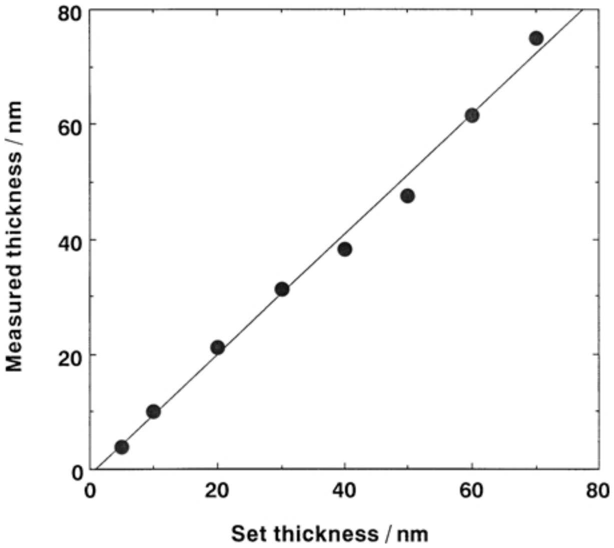

Figure 4 Relationship of the set thickness and measured thickness of the SiO_2 overlayer using XPS depth profile and surface step measurements. The measured thickness of the overlayers were calculated from the etching times of the XPS depth profile measurements, which were calibrated by the etched crater depth of the SiO_2 overlayer with set-thickness of 70 nm. The crater depth was measured by a surface step meter.

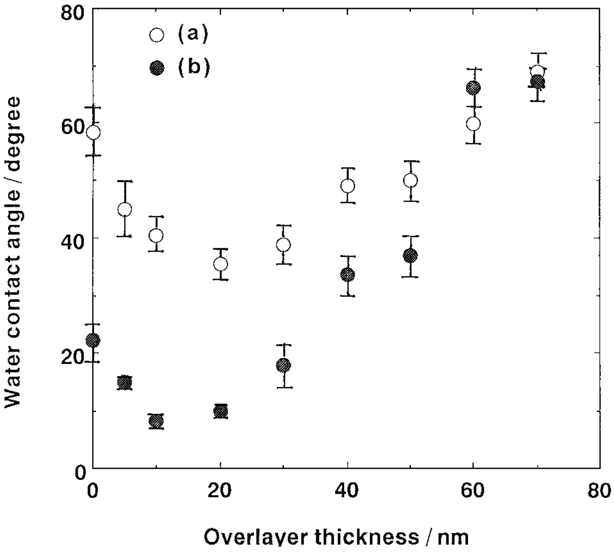

Figure 5 Dependence of changes in water contact angle on the thickness of the SiO_2 overlayer in the SiO_2/TiO_2 multilayer film induced by UV light irradiation of a commercial black light lamp (FL20S, BL-B, 23 W) at an ambient condition (25 °C, RH 60%, in air atmosphere) for 4 hours, (a) before light irradiation, (b) after light irradiation. The light power on the films was maintained at 1 mW/cm^2.

3.4. Sustained efficiency of the hydrophilicity of films

The photo-induced hydrophilic SiO_2/TiO_2 multilayer films possessed another significant property. Fig. 11 shows the sustained efficiency of hydrophilicity of the photo-induced hydrophilic films during storage in a dark room for one week. Water contact angle of the TiO_2 film started to increase right away after storing in a dark room (Fig. 11a). However, as shown in Fig. 11b and

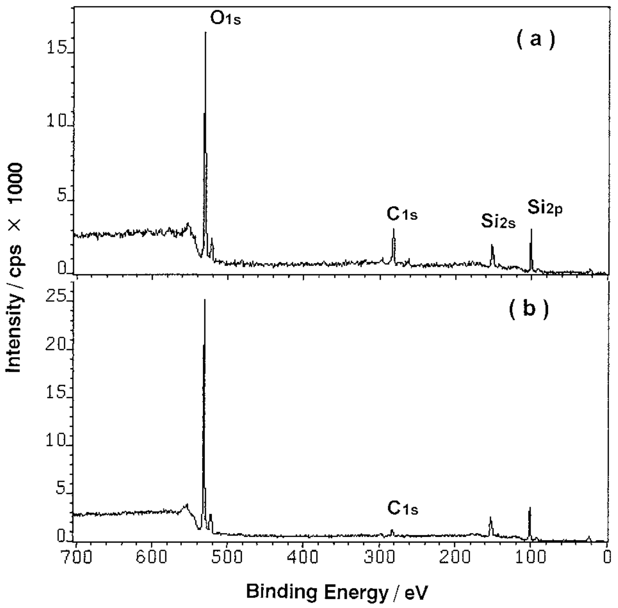

Figure 6 Changes of XPS survey spectra on the surface of the SiO_2 (20 nm in thickness)/TiO_2 multilayer film by the UV light irradiation (as the same conditions as remarked in Fig. 5, (a) before light irradiation, (b) after light irradiation.

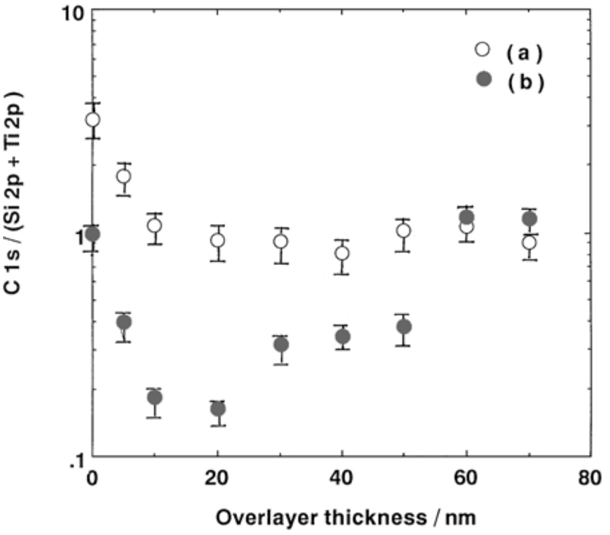

Figure 7 Dependence of the photo-induced changes in C1s/(Si2p + Ti2p) calculated by the XPS spectra on the thickness of the SiO_2 overlayer in the SiO_2/TiO_2 multilayer film, (a) before light irradiation, (b) after light irradiation. The UV light irradiation was carried out as the same conditions as remarked in Fig. 5.

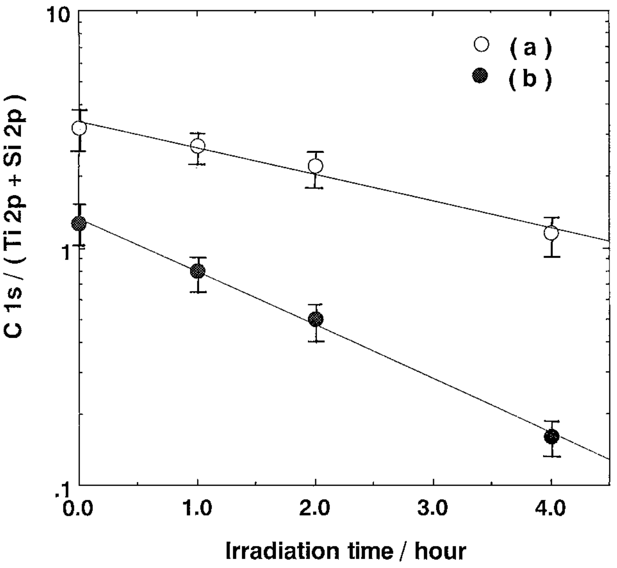

Figure 8 Plots of the decrease in C1s/(Si2p + Ti2p) calculated by the XPS spectra on (a) the TiO2 film and (b) the SiO2 (20 nm in thickness)/TiO2 multilayer film vs. UV irradiation time (as the conditions remarked in Fig. 5).

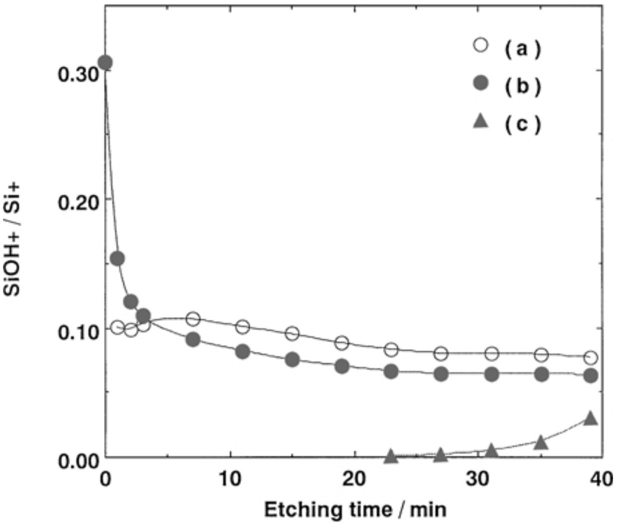

Figure 9 Depth profile plots of the $SiOH^+/Si^+$ obtained by the TOF-SIMS etching measurements, (a) before light irradiation, (b) after light irradiation, (c) $^{46}Ti^+/Si^+$ to show the interface between the SiO_2 and the TiO_2 layers, plotted in the same vertical axis of $SiOH^+/Si^+$. The UV light irradiation was carried out as the same conditions as remarked in Fig. 5.

c, the multilayer films exhibiting the enhanced photo-induced hydrophilicity, showed greater sustained efficiency of the hydrophilicity than the TiO_2 film without SiO_2 overlayer. Furthermore, the SiO_2 (20 nm in thickness)/TiO2 multilayer film scarcely changed the water contact angle during the dark room storage, which indicated greater sustained efficiency of the hydrophilicity than the SiO_2 (5nm in thickness)/TiO_2 multilayer film. It was demonstrated that thorough coverage of TiO_2 film by SiO_2 overlayer greatly improved the sustained efficiency of the hydrophilicity. This is another advantage of the multilayer film to develop practical hydrophilic films. Considering the bonding dissociation energy, SiOH (Si-O: 795 kJ/mol) is thought to be more stable than TiOH (Ti-O: 668 kJ/mol). This might be the reason why the multilayer film has a more stable hydrophilicity than the TiO_2 film.

4. Discussion

The enhanced photo-induced hydrophilicity of the surface of the SiO_2/TiO_2 multilayer films can be explained as follows: (1) the self-cleaning of the films by the improved photo-catalytic activity, (2) the growth of stable OH group (SiOH) in the uppermost surface and (3) the adsorption of water on the surface attracted by the OH group.

Among the results given above, attention should be paid to the fact that the SiO_2 overlayer as thick as 50 nm still showed the photo-induced hydrophilicity

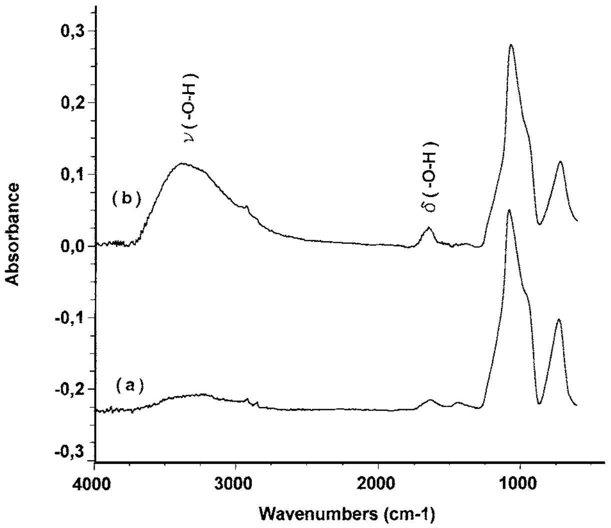

Figure 10 Change of the ATR-FTIR spectrum on the surface of the SiO_2 (20 nm in thickness)/TiO_2 multilayer film induced by UV light irradiation, (a) before light irradiation, (b) after light irradiation. The UV light irradiation was carried out as the same conditions as remarked in Fig. 5.

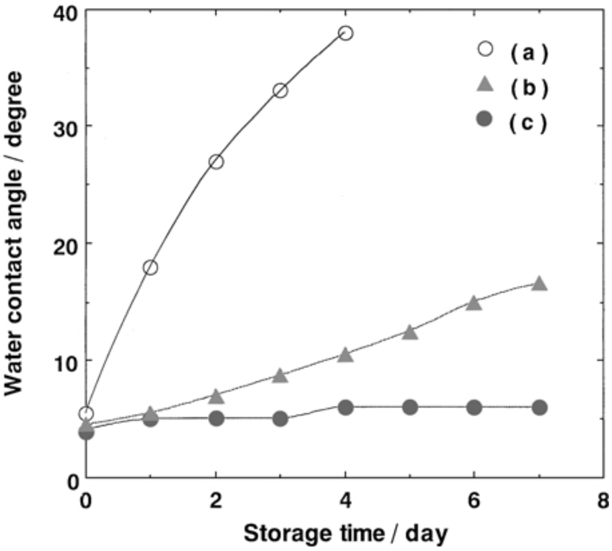

Figure 11 Sustained efficiency of the photo-induced hydrophilicity of (a) the TiO_2 film, (b) the SiO_2 (5 nm in thickness)/TiO_2 and (c) the SiO_2 (20 nm in thickness)/TiO_2 multilayer films, during a storage in a dark room. The films were prepared to be hydrophilic (about 5 degree of water contact angle) by UV light irradiation before the measurements.

and photo-catalytic activity (Figs 5 and 7). Tada *et al.* [22] have explained on the improved photo-catalytic activity with SiO_x monolayer coverage of TiO_2 particles that the phenomenon could be attributed to the increase in the electrostatic attraction of adsorbates to the surface, which was caused by the interfacial charge transfer through the tunneling effect. The thickness of 50 nm of SiO_2 overlayer on TiO_2 film is much more than a monolayer, and seems too thick to exhibit the tunneling effect. Anderson *et al.* [19, 20] have reported that the photo-catalytic activity of TiO_2 is improved by mixing with SiO_2. They explained the effect by the increased adsorption of adsorbates on SiO_2 sites and the diffusion of photo-generated intermediates such as hydroxyl radicals from TiO_2 to SiO_2 surface. If the porosity of the SiO_2 overlayer is large enough to let water molecules into the SiO_2 layer, the hydroxyl radical, which is generated by UV light irradiation, in the interface between SiO_2 and TiO_2 layers would diffuse in the SiO_2 layer to the uppermost surface. However, the result of TOF-SIMS depth profile measurement shown in Fig. 9 indicates the growth of the SiOH group appeared in only the uppermost surface of the SiO_2 overlayer. This does not support the idea that water or hydroxyl radical diffuses into the SiO_2 overlayer. The hydroxyl radical, which will produce SiOH group, must be generated only in the uppermost surface of the SiO_2 overlayer by UV light irradiation. Considering that SiO_2 itself does not have any photo-catalytic activity, photo-generated species such as hole created in the TiO_2 layer might transmit the SiO_2 layer to uppermost surface. As we know from semiconductor thin film technology, defected or imperfect chemical bonds of SiO_2 make the hole easier to move thorough the SiO_2 film. However, it is necessary to evaluate the imperfect chemical bonds and structure of SiO_2 in the overlaid film for the further discussion.

The facts that the most enhanced photo-induced hydrophilicity and photo-catalytic activity of the multilayer films were observed for the films with the SiO_2 overlayer ranging from 10 to 20 nm in thickness are also an interesting phenomenon. To achieve enough photo-catalytic effect, photo-catalytic substances such as TiO_2 are supposed to need to form a charge space layer on the surface, which is thought to separate a pair of photoelectron and hole away, and decrease the rate of recombination of the pair [1–3]. The SiO_2 overlayer could enlarge the charge space layer in the interface between TiO_2 and SiO_2 layers to keep holes longer. The photo-catalytic activity and photo-induced hydrophilicity seem to be realized by the hydroxyl radicals originated from the holes in the uppermost surface. The photo-catalytic activity of the multilayer film could be improved by the enlargement of charge space layer and the efficiency of hole to reach the uppermost surface. In conclusion, the enhanced photo-induced hydrophilicity of the films can be assigned to the synergetic effect of the improved photo-catalytic activity and stable hydrophilicity of SiO_2 itself.

5. Conclusions

Extreme photo-induced hydrophilicity of the surface was observed in the photo-catalytic SiO_2/TiO_2 multilayer films with the SiO_2 overlayer ranging from 10 to 20 nm in thickness. The improved photo-catalytic activity was also exhibited in the multilayer films. The enhanced photo-induced hydrophilicity of the films is considered to be the result of the synergetic effect of the improved photo-catalytic activity of the multilayer film and the stable hydrophilicity of SiO_2 itself. Complete coverage of the SiO_2 overlayer on the photo-catalytic TiO_2 film is necessary to achieve the greater photo-catalytic activity. These enhancements are thought to be strongly related to the interfacial state of the SiO_2/TiO_2 multilayer films. Photo-generated reactive species such as hole, which are localized in the interface of the multilayer film, are supposed to transmit the SiO_2 layer efficiently.

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