

Photo-Catalytic and Photo-Conductive Properties of SiO₂/TiO₂ Multilayer Film Prepared by Vacuum-Deposition Method

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真空蒸着法により調製した SiO₂/TiO₂ 多層薄膜の光触媒特性と光伝導性

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To characterize a photo-catalytic SiO₂/TiO₂ multilayer film prepared by vacuum-deposition method, kinetic measurements of the photo-catalytic activity were carried out, and the interface structure and photo-conductivity of the film were also investigated. By the kinetic analyses of self-cleaning of stearic acid and de-colorization of methylene blue, it was proved that the SiO₂/TiO₂ multilayer film with the 20 nm set-thick SiO₂ overlayer exhibited an improved photo-catalytic activity as compared to the TiO₂ film. The multilayer film had a heterogeneous interface structure, whereas the photo-catalytic reaction seemed to occur on the photo-catalytically inactive SiO₂ surface. A sufficient overlying by the SiO₂ thin film on the TiO₂ film improved the photo-catalytic properties of the film. The multilayer film with improved photo-catalytic activity exhibited a significantly increased photocurrent compared to a TiO₂ film. Both improved photo-catalytic activity and photocurrent amplification of the multilayer film might be strongly correlated to an increase of photo-generated carriers at the interface of the film. A nanometer-sized insulating overlayer can synergistically form integration to improve photo-catalytic activity, an attractive function for photocurrent amplification of the multilayer film.

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1. Introduction

TiO₂ has been attractive as a useful photo-catalyst for resolving environmental and energy problems.¹⁾⁻⁵⁾ Although the TiO₂ powders have been greatly used as industrial materials, thin film and coating technologies are worthwhile in developing industrial applications of the materials. Some of attractive applications of TiO₂ film are photo-catalytic self-cleaning⁶⁾ and hydrophilicity,^{7),8)} which are useful for preparing clean and hydrophilic surface of materials, respectively. Those functions are applicable to optical products, medical parts, and electronic devices, etc., where clean surface preparations are required. On the other hand, TiO₂ composite photo-catalysts have been extensively investigated.⁹⁾⁻¹⁷⁾ Among these researches on the composite photo-catalysts, the TiO₂ photo-catalysts combined with SiO₂ have been investigated in the view of improved photo-catalytic activity, which is thought to be due to the adsorption ability of SiO₂^{14),15)} and the TiO₂-SiO₂ interface structure.¹⁶⁾ The TiO₂-SiO₂ composite photo-catalytic films prepared by sol-gel method have been developed as "super-hydrophilic film" contributing to the improved photo-induced hydrophilicity and its endurance,¹⁷⁾ which is applicable to anti-fogging mirror and glass. Machida et al.¹⁷⁾ concluded that the enhanced hydrophilicity was attributed to the increased capability of holding adsorbed water due to SiO₂. As for the photo-catalytic reaction on the SiO₂ in the composite films, Anderson and Bard¹⁴⁾ suggested the diffusion of photo-generated oxidants from TiO₂ domain onto the SiO₂ surface in the experiments of the photo-catalytic decomposition of rhodamine-6G by the sol-gel mixed TiO₂-SiO₂ composite. However, it was still unclear how the SiO₂ involved the photo-catalytic reaction. In order to clarify the

photo-catalytic activity on SiO₂ in TiO₂-SiO₂ composite system, we have designed the SiO₂/TiO₂ multilayer films, which are vacuum-deposited TiO₂ films overlaid with the thin SiO₂ films¹⁸⁾. The multilayer system made it possible to assess the photo-catalytic activity on the SiO₂ influenced by the TiO₂. In the experiments of photo-catalytic activity for hydrophilicity and self-cleaning, the multilayer film with ca. 10 to 20 nm set-thick SiO₂ overlayer exhibited the significantly enhanced photo-induced hydrophilicity and the improved photo-catalytic self-cleaning. Also, these photo-catalytic activities were exhibited even at the multilayer film with the 50 nm set-thick overlayer.¹⁸⁾ It was suggested that the photo-catalytic activity of the multilayer film occurred on the surface of the photo-catalytically inactive SiO₂ layer, where the TiO₂ film was thoroughly covered and might be heterogeneously separated by the overlayer.

To elucidate this unique photo-catalytic activity of the multilayer film, we have performed the experiments obtaining spectrum response of the photo-catalytic activity of the films.¹⁹⁾ The results of photo-catalytic oxidation of polystyrene indicated that the photo-catalytic activity of the multilayer film was significantly increased at the light irradiation below 350 nm compared to that of the TiO₂ film alone. Furthermore, measurements of surface photoconductivity of the films showed that the multilayer film with increased photo-catalytic activity exhibited the photocurrent amplification at the light irradiation. The results of photo-conductivity suggested that the photo-generated carriers contributed to the photo-catalytic activity.¹⁹⁾ However, the photo-catalytic activities of the multilayer films have never been analyzed kinetically for particular substances, and the relationships between the photo-catalytic activities and pho-

to-conductivity of the multilayer films were not clarified yet. On the other hand, a report on the double-layered TiO₂/SnO₂ photo-catalytic film mentioned that the charge separation of photo-generated carriers at the hetero-junction interface of the catalyst might play important roles on the photo-catalytic activities.²⁰⁾ Therefore, it should be examined whether the multilayer film has such a heterogeneous interface structure (hetero-structure) to understand the photo-catalytic activity.

In this paper, in order to clarifying the photo-catalytic activity of the multilayer film, we kinetically analyzed the photo-catalytic properties of the multilayer films with overlayers of several thicknesses. The experiments were performed to measure the photo-catalytic elimination of stearic acid, which has been used for evaluating the self-cleaning,⁶⁾ and de-colorization of methylene blue (MB) in water solution. Relationships of the photo-catalytic properties and the photo-conductivity of the multilayer films were also examined, and synergistic effects caused at the interface of the multilayer film were discussed. To confirm the hetero-structure of the multilayer film, measurements of transmittance electron microscope (TEM) and X-ray photo-electron spectroscopy (XPS) were also carried out.

2. Experimental procedure

2.1 Preparation and characterization of the vacuum-deposited multilayer films

The vacuum-deposited multilayer films were prepared by an electron-beam vacuum-deposition method as previously described.¹⁸⁾ The substrate was prepared by the vacuum-deposition of SiO₂ (120 nm in set-thickness) on 2 mm-thick soda-lime glass plate and the photo-catalytic TiO₂ film (240 nm in set-thickness) was deposited on the substrate. Crystal structure of the TiO₂ film was determined as a polycrystalline anatase. The SiO₂/TiO₂ multilayer films used in this work were prepared by the SiO₂ deposition of 10, 20 and 50 nm in set-thickness over the TiO₂ film. Thickness of the deposition films was set by a double-chromatic photometer and estimated by XPS depth profile measurements, where the discrepancies between set-thickness and measured thickness were small.¹⁸⁾

Chemical elements on the surface of the films were measured by an X-ray photoelectron spectrometer (XPS; AXIS-HS, Kratos Analytical Ltd.) using a monochromatic X-ray source emitted from an Al anode at a power of 150 W. The XPS data were acquired at pass energy of 20 eV using a charge neutralizer to prevent deviation of spectra caused by X-ray irradiation. For the XPS experiments, samples were irradiated by UV light to prepare clean surface. To analyze the morphology and interface structure of the multilayer film at the cross section, a high resolution transmittance electron microscope (HR-TEM; model 002B, TOPCON) was used. Thin foil specimen for the HR-TEM was prepared by mechanical polishing with diamond polishing papers and then thin section was made by low-incident-angle Ar ion milling (Precision Ion Polishing System (PIPS), Gatan Inc.). XPS depth profile of atomic concentration of Ti and Si at the multilayer was obtained by Ar⁺ ion etching measurement.

2.2 Measurements of photo-catalytic activity

In the measurements of the photo-catalytic self-cleaning of stearic acid, the stearic acid was homogeneously cast-coated on the films from 5.5 mmol/l *n*-hexane solution and dried. Using an FT-IR spectrometer (Magna-IR 750, Nicolet Corp.), absorbance at 2917 cm⁻¹ (anti-symmetric stretching of -CH₂-) of aliphatic group of stearic acid on the films was monitored by transmittance mode during UV light irradiation. The UV light irradiation was carried out under an ambient condition (25°C, RH60%, in air) using a

commercial black light lamp (Toyostar Co., Ltd., FL20S BL-B, 23W), of which emission was centered at 360 nm. The light power was measured to be maintained at 1 mW/cm² on the films by an UV meter (Topcon UVR-1).

In the experiments of de-colorization of MB, absorption spectra of MB solution in water were measured by a UV-VIS spectrometer (UV-2400PC, Shimadzu Corp.) during the UV light irradiation. The 20 × 20 mm²-sized vacuum-deposited films were put into 10 ml of MB water-solution (0.01 mmol/l) in 50 ml volume-sized beakers and UV-VIS spectra were recorded during the UV light irradiation. The UV light was irradiated onto the films through the solution in the same manner as described in the experiment of photo-catalytic self-cleaning of stearic acid.

2.3 Measurements of surface photocurrent

Surface photo-conductivity was measured at room temperature using a 150 W Xe lamp as a light source. The light was aimed at the sample passing through the chopping disk and the monochromator with a 300 groove mm⁻¹ grating. In order to detect even the faint photocurrent, the amplitude of photocurrent is measured by inputting chopped light signal and the photocurrent to the lock-in amplifier. Spectra of the conductivity were recorded by irradiation of the monochromated light and have been corrected for the emission spectra of the lamp. Indium electrodes, which are supposed to form Ohmic contact at surface, were evaporated on the surface of the films using planer type mask with 0.1 mm of set-distance in-between electrodes. An electric field of 10⁴ V/cm was applied in-between the electrodes at the measurement.

3. Results and discussion

3.1 Overlayer coverage and interface structure

The TiO₂ film and SiO₂/TiO₂ multilayer films prepared by the vacuum-deposition method had smooth surface, and were transparent and slightly colored. Table 1 shows the chemical elements detected on the films and the atomic concentrations (AC%) obtained by XPS measurements using 90° of take-off angle of photoelectron. Ti element at the surface of the multilayer film with 20 and 50 nm set-thick SiO₂ overlayer was not detected. While, 0.6 AC% of Ti was detected at the multilayer film with 10 nm set-thick SiO₂ overlayer, although the Ti was not detected at the measurement using 20° of the take-off angle. The results indicated that the multilayer films with 20 and 50 nm set-thick SiO₂ overlayers were sufficiently covered by the overlayer, while the film

Table 1. Binding Energies (BE), Full Width of Half Maximums (FWHM), and Atomic Concentrations (AC%) of Chemical Elements Obtained from the Films by High Resolution XPS Measurements Using 90° of Take-Off Angle of Photoelectron

Film	Details	Ti2p _{3/2}	Si2p	O1s	C1s*
TiO ₂	BE (eV)	458.8	-----	530.0	285.0
	FWHM (eV)	1.02	-----	1.15	1.18
	AC%	25.9	-----	64.1	10.0
SiO ₂ (10 nm in set-thick.) /TiO ₂	BE (eV)	458.7	103.7	532.5	285.0
	FWHM (eV)	0.97	1.48	1.22	1.15
	AC%	0.6	24.2	69.0	6.2
SiO ₂ (20 nm in set-thick.) /TiO ₂	BE (eV)	-----	104.0	532.6	285.0
	FWHM (eV)	-----	1.45	1.27	1.44
	AC%	-----	26.5	71.0	2.5
SiO ₂ (50 nm in set-thick.) /TiO ₂	BE (eV)	-----	103.9	532.5	285.0
	FWHM (eV)	-----	1.50	1.31	1.36
	AC%	-----	26.0	70.2	3.8

* Binding energies of charge-neutralized XPS spectra were corrected by adjusting the C1s peak to 285.0 eV.

with 10 nm set-thick SiO₂ overlayer was barely covered.

As for the interface structure of the multilayer film, HR-TEM image of the SiO₂ (20 nm set-thickness)/TiO₂ multilayer film shows the morphology of the films (Fig. 1). As seen in the figure, the TiO₂ film consists of columnar grains of about 20 nm in diameter with high aspect ratios. It also shows that the TiO₂ film is sufficiently covered by the SiO₂ overlayer, where the overlayer thickness can be estimate as ca. 20 nm and the both TiO₂ and SiO₂ layers seem to be heterogeneously separated.

Result of XPS depth profile measurement showed the depth-directed distribution of atomic concentrations of Ti and Si at the cross section (Fig. 2). The profile also showed that the multilayer film was sufficiently covered by the overlayer. The Si-Ti mixed region of the profile in the figure may be due to the surface roughness of the film, etching damages, effective measuring depth determined by the mean free path of photoelectron, and Ti-O-Si cross-linked layer²¹⁾ at the interface of the film. To estimate the existence of the Ti-O-Si layer, XPS details of the multilayer film with 10 nm set-thick SiO₂ overlayer are useful. As seen in Table 1, binding energy (458.7 eV) of Ti2p_{3/2} of the multilayer film with 10 nm set-thick SiO₂ overlayer almost cor-

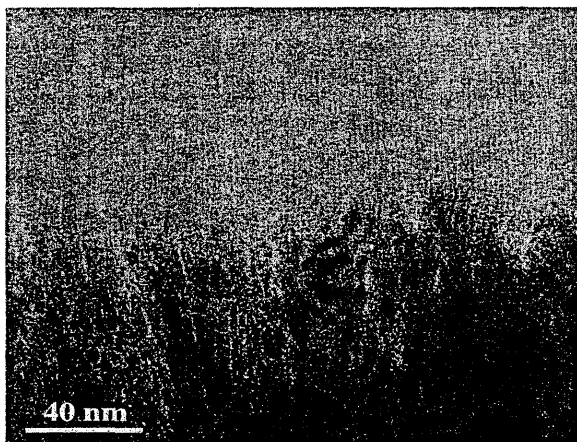


Fig. 1. TEM images of the cross section of SiO₂(20 nm in set-thickness)/TiO₂ multilayer film

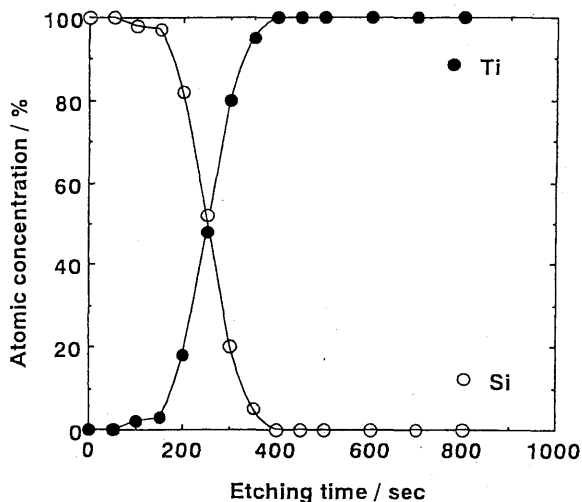


Fig. 2. Depth profile of atomic concentration of Ti and Si of the SiO₂(20 nm in set-thickness)/TiO₂ multilayer film obtained by XPS measurements using an argon ion etching method.

responds to that (458.8 eV) of the TiO₂ film alone, whereas the Ti-O-Si layer may possess the binding energy of Ti2p_{3/2} at 459.5 eV.²¹⁾ Furthermore, full width of half maximum (FWHM) of the multilayer film (0.97 eV) is not larger than that (1.02 eV) of the TiO₂ film alone, which means that the state of Ti⁴⁺ at the interface is not any more complex than that of the TiO₂ film alone. These results indicate that the Ti-O-Si layer, even if it exists between the TiO₂ and SiO₂ layers, must be quite thinner than the mean free path of photoelectron and the SiO₂ overlayer is heterogeneously separated from the TiO₂ layer.

3.2 Photo-catalytic activity of the films

In the FT-IR measurements of photo-catalytic self-cleaning of stearic acid on the films, absorbance of the characteristic band of the aliphatic group at 2917 cm⁻¹ decreased during the UV light irradiation, while broad band of adsorbed water ranging from about 3700 to 2700 cm⁻¹ grew. Figure 3 shows decrease in the absorbance at 2917 cm⁻¹ of stearic acid on the films during the UV light irradiation, where the absorbance was corrected by the subtraction of the absorbance due to adsorbed water. The decrease curves seem to consist of two lines with different gradient, i.e. the line at early stage (0 to about 10 min of the irradiation time) and that at later stage (about 10 to 30 min). The curves showed significant decrease at the later stage region and were almost linear in semi-logarithmic plot. At the later stage, the stearic acid might have proper concentration to react homogeneously on the photo-catalytic films, and the photo-catalytic films exhibited first-order kinetics of the self-cleaning elimination of stearic acid. The reaction rate constants of the photo-catalytic activities are listed in Table 2. It was found from the table that the SiO₂ (20 nm in set-thickness)/TiO₂ multilayer film exhibited a greater reaction rates and an improved photo-catalytic activity than the TiO₂ and other multilayer films.

In the de-colorization measurements of MB, absorbance of the recorded spectra ranging from 200 to 800 nm decreased during the UV light irradiation with scarce change of the spectral shape. Decrease in maximum absorbance at 663 nm of MB in the water solution are plotted versus the irradiation time as shown in Fig. 4. As resulted in

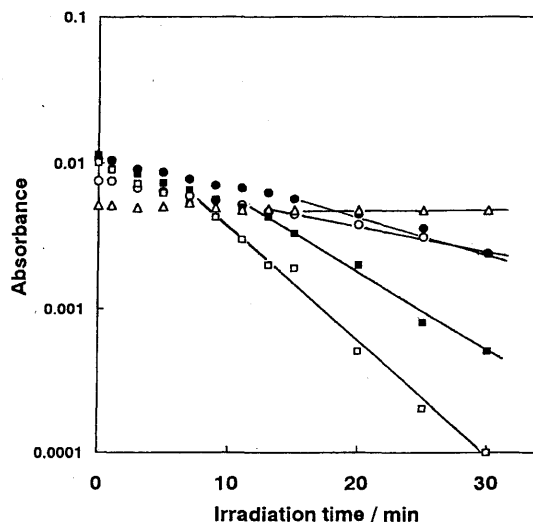


Fig. 3. Dependence of absorbance at 2917 cm⁻¹ of stearic acid on the UV light irradiation time measured by the FT-IR spectrometer. (Δ) SiO₂ (120 nm in set-thick.)-coated substrate, (○) TiO₂ (240 nm in set-thick.) film, (●) SiO₂ (10 nm in set-thick.) / TiO₂ film, (□) SiO₂ (20 nm in set-thick.) / TiO₂ film, (■) SiO₂ (50 nm in set-thick.) / TiO₂ film.

Table 2. Apparent Reaction Rate Constants of the Photo-Catalytic Activity for Self-Cleaning Elimination of Stearic Acid and de-colorization of Methylene Blue

Film	Rate constant	
	Stearic acid ($10^{-3} \cdot \text{min}^{-1}$)	Methylene blue ($10^{-3} \cdot \text{h}^{-1}$)
TiO ₂	16.9	34.6
SiO ₂ (10 nm in set-thick.)/TiO ₂	22.0	42.9
SiO ₂ (20 nm in set-thick.)/TiO ₂	80.6	78.4
SiO ₂ (50 nm in set-thick.)/TiO ₂	52.9	59.0
SiO ₂ -coated substrate	0.5	5.9

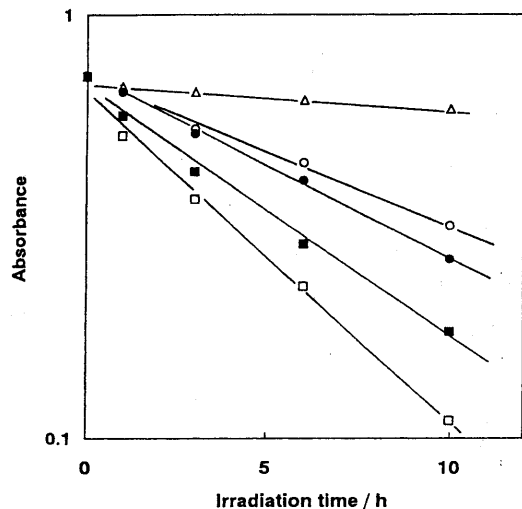


Fig. 4. Dependence of absorbance at 663 nm of methylene blue (MB) in water solution on the UV light irradiation time measured by the UV-VIS spectrometer. (Δ) SiO₂ (120 nm in set-thick.)-coated substrate, (\circ) TiO₂ (240 nm in set-thick.) film, (\bullet) SiO₂ (10 nm in set-thick.)/TiO₂ film, (\square) SiO₂ (20 nm in set-thick.)/TiO₂ film, (\blacksquare) SiO₂ (50 nm in set-thick.)/TiO₂ film.

the photo-catalytic elimination of stearic acid, the SiO₂ (20 nm in set-thickness)/TiO₂ multilayer film exhibited the greatest de-colorization of MB. The apparent reaction rate constants of the de-colorization obtained by first-order kinetic analysis are also listed in Table 2. The reaction rate constants of both elimination of stearic acid and MB show the similar tendency for photo-catalytic films in spite that they were obtained in the different measuring systems.

3.3 Photo-conductivity of the photo-catalytic films

In order to clarify the mechanism of improving photo-catalytic activity obtained by SiO₂ overlayer, it is important to reveal the behavior of photo-generated carriers. The photoconductivity is regarded as a good measure for this purpose.^{22),23)} Figure 5 shows surface photoconductivity of the films. The photocurrent was detected at all of the photo-catalytic films, whereas it was not detected at the SiO₂-deposited glass substrate under the present measuring conditions. This result indicated that photo-generated carriers were produced at the photo-catalytic films, but not at the photo-catalytically inactive film. Among the photo-catalytic films, the multilayer film with the 20 nm set-thick SiO₂ overlayer exhibited the significantly increased photocurrent compared to the TiO₂ film, while the film with the 10 nm set-thick overlayer did not show the change so much. It should be noted that even the photo-catalytic multilayer film with as much as 50 nm set-thick SiO₂ overlayer exhibited the detectable photocurrent, indicating that the photo-generated

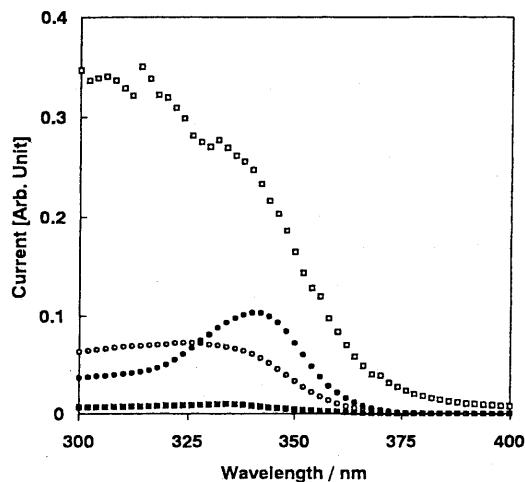


Fig. 5. Dependence of surface photocurrent on the wavelength of irradiation light at 10^4 V/cm of electric field in-between electrodes. (\circ) TiO₂ (240 nm in set-thick.) film, (\bullet) SiO₂ (10 nm in set-thick.)/TiO₂ film, (\square) SiO₂ (20 nm in set-thick.)/TiO₂ film, (\blacksquare) SiO₂ (50 nm in set-thick.)/TiO₂ film.

carriers were mobile in the 50 nm set-thick overlayer under the applied electric field. These results of the photo-conductivity are quite consistent with the tendency of photo-catalytic activities of the films.

Moreover, it is a noteworthy phenomenon that the photocurrent of the multilayer film with improved photo-catalytic activities was amplified more significantly at the shorter wavelength of the irradiation light. This result suggested that the photocurrent amplification of the films was correlated to the modified electronic states for the carriers due to the multilayer structure of the film, where the hetero-structure of the film might play key roles for the modification of the electronic states. As for the improved photo-catalyst with hetero-structure, Cao et al.²⁰⁾ reported the improved photo-catalytic activities of a double-layered TiO₂/SnO₂ photo-catalytic film with hetero-structure prepared by a chemical vapor deposition. They concluded that the surface hetero-structure promotes an increase in the charge separation of the photo-generated carriers leading to suppression of the carrier's recombination and improvement of the photo-catalytic activity. It is therefore expected that charge transfer at the interface of the SiO₂/TiO₂ multilayer film was caused during the irradiation. However, the double-layered photo-catalytic film consisting of SnO₂ under-layer and island-like TiO₂ particulate overlayer originally differed in the structure from our SiO₂/TiO₂ multilayer film with thorough coverage by the insulating overlayer.

Concerning the photocurrent amplification at the multilayer films, there have been reported in the field of optoelectronic devices such as solar cells, photo-diodes²⁴⁾⁻²⁷⁾ and photo-sensors,²⁸⁾ where the interface structure between semiconductor layer and electrode played important roles. Among them, thin insulating layers such as SiN_x²⁷⁾ and SiO_x²⁸⁾ introduced in-between semiconductor layer and electrode promoted the photocurrent amplifications caused by avalanche-electron injection. The modified electronic structures at the interface, induced by nanometer-sized thin insulating layer, such as band-bending of valence and conduction bands, play important roles for the behavior of photo-generated carriers and photo-conductivity. Localized photo-generated carriers accumulated at the interface may form local electric field, which modifies the band structures and cause carrier-injection leading to increase of concentra-

tion and mobility of the carriers. It is, therefore, suggested that the photo-generated carriers increased at the multilayer film during the UV light irradiation, which were caused by the modified electronic structures at the interface of the film, and had enough lifetimes to reach the surface of the SiO₂ layer sufficiently. Both the improved photo-catalytic activity and photocurrent amplification of the multilayer film might strongly correlate to the increase of photo-generated carriers caused at the interface of the film.

On the other hand, it is of interest to elucidate the dependency of overlayer thickness on the photo-catalytic activity and photo-conductivity of multilayer films. Considering that the SiO₂ layer is photo-catalytically inactive, the photo-generated carriers contributing to photo-catalysis may be produced in the TiO₂ layer and transmit into the SiO₂ overlayer, which leads to the photo-catalytic reaction on the surface of SiO₂ overlayer. This is indicated from the fact that the photo-catalytic activities were sufficiently revealed even at the 50 nm set-thick SiO₂ overlayer. However, it is still difficult to explain the improvement of the photo-catalytic activity and photocurrent amplification at the 20 nm set-thick overlayer only by the idea that the photo-generated carriers transmit the SiO₂ overlayer. The 10 nm set-thick overlayer, which barely covered the TiO₂ film, scarcely improved the photo-catalytic activity as differed from the 20 nm set-thick overlayer. There is a question as to why the multilayer film with 10 nm set-thick SiO₂ overlayer did not show the changes so much compared to the TiO₂ film alone. Considering the structure of the 10 nm set-thick SiO₂, as shown in Table 1, the binding energy (103.7 eV) of Si2p of the 10 nm set-thick SiO₂ was different from that (104.0 eV) of Si2p of the 20 nm set-thick SiO₂. It is expected that the TiO₂ layer influence the growth of the 10 nm set-thick SiO₂ overlayer strongly, leading to inhomogeneous and imperfect structure of the SiO₂. The imperfect SiO₂ might be not electrically insulating enough, while the 20 nm set-thick SiO₂ might be insulating enough to keep the localized carriers at the interface of the multilayer film and lead to the photocurrent amplification. To confirm this assumption, it is necessary to characterize the electronic structures of the overlayers and carrier dynamics of the multilayer films.

Finally, it could be noted that the nanometer-sized insulating overlayer synergistically induced an attractive function of photocurrent amplification at the multilayer film, besides the functions of photo-catalysis. These properties suggest potential of the multilayer film for integrated functions such as photo-sensing, photo-etching and so on. The electronic structures and carrier dynamics of the films have been under investigation following by further characterizations of the static structures. The articles concerning the research will be submitted elsewhere.

4. Conclusion

It was kinetically proved that the SiO₂/TiO₂ multilayer film with the 20 nm set-thick SiO₂ overlayer exhibited the improved photo-catalytic activities compared to the TiO₂ film. The SiO₂ overlayer was mostly separated from the TiO₂ layer and the multilayer film had a heterogeneous interface structure, where the photo-catalytic reaction may occur on the photo-catalytically inactive SiO₂ surface. The sufficient overlaying by the SiO₂ thin film on the TiO₂ film improved the photo-catalytic properties of the film. The multilayer film with the improved photo-catalytic activity exhibited the significantly increased photocurrent compared to the TiO₂ film. Both the improved photo-catalytic activities and photocurrent amplification of the multilayer film might strongly correlate to the increase of photo-generated carriers caused at the interface of the film. The photo-generated carriers increased at the multilayer film with the im-

proved photo-catalytic properties during the UV light irradiation and might have enough lifetimes to reach the surface of the SiO₂ layer sufficiently. It is concluded that the nanometer-sized insulating overlayer can synergistically form integration of the improved photo-catalytic activities and an attractive function of photocurrent amplification at the multilayer film.

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