Photo-Catalytic Activity of Different Thicknesses $\text{TiO}_2/\text{SnO}_2$ Double Layer Nano Composite Thin Films

Hsuan-Jen Wang*¹ and Shih-Chin Lee*²

Department of Materials Science and Engineering, National Cheng Kung University, 701 Tainan, Taiwan, R. O. China

TiO_2 thin films were deposited on rutile SnO_2 films by reactive radio frequency magnetron sputtering. The effect of thickness of TiO_2 layer, on the microstructure and chemical states of the $\text{TiO}_2/\text{SnO}_2$ thin films, was investigated in detail. With the increase of TiO_2 film thickness deposited on SnO_2 film, the crystallization of TiO_2 film becomes more perfect, and more Ti atoms are bonding in forms of stoichiometric TiO_2 . There is a thickness of TiO_2 film (150 nm) deposited on SnO_2 substrate that yields the best photo-induced superhydrophilicity and surface wettability. [doi:10.2320/matertrans.M2009154]

(Received April 27, 2009; Accepted July 6, 2009; Published August 25, 2009)

Keywords: titanium dioxide, photo-catalyst, contact angle

1. Introduction

In recent years, titanium dioxide (TiO_2) has been the most popular semiconductor because of its photo-catalytic capability.¹⁻³ When TiO_2 is illuminated by ultraviolet (UV) light with higher energy than its band-gap, electron and hole pairs are generated to reduce and oxidize adsorbates on the surface, respectively. It produces some radical species such as $\cdot\text{O}_2\text{H}$ and $\cdot\text{OH}$ that can decompose the majority of organic compounds adsorbed on the TiO_2 surface.^{4,5} Therefore, many studies have focused on the application of water purification.^{6,7} Besides, the photo-induced hydrophilicity of rutile or anatase TiO_2 whose water contact angle decreases to almost 0° from its surface with UV illumination in air, was also reported.⁸⁻¹⁰ The cause of hydrophilicity was oxygen vacancies generated by defection of bridging oxygen with UV irradiation; these oxygen vacancies on the surface could interact with water.¹¹ Such excellent photo-catalytic properties gave rise to extensive researches like self-cleaning glasses, antibacterial tiles, deodorant fibers, and antifogging windows.^{12,13}

Various deposition methods, including: plasma beam deposition, ion-assisted deposition, chemical vapor deposition, sol-gel, dip-coating, and sputtering techniques have been used to prepare TiO_2 thin film. For depositing the rutile or anatase structure of TiO_2 films, reactive radio frequency (rf) magnetron sputtering has proven to be an effective method. By controlling the sputtering condition, the desired thickness, roughness, and crystalline structure of the TiO_2 films can be obtained for increasing the photo-catalytic efficiency. In addition, Reactive rf magnetron sputtering deposition can be adapted to large-area coatings and its high deposition rate also gives a larger rugged surface, thereby creating a more interactive area to produce more radical species.

Recently, Semiconductor hetero-junction systems have been studied in order to improve photo-catalytic efficiency;¹⁴ these researches discussed the charge separation in different types of semiconductors which might suppress the recombina-

tion of photo-generated charge carriers. Various types of $\text{TiO}_2/\text{SnO}_2$ hetero-junction systems, such as: particle, composite film, stacks, and so on, have been deeply investigated, and have indeed achieved higher levels of efficiency of charge separation than pure TiO_2 systems.¹⁵ The band-gaps of SnO_2 and TiO_2 are 3.8 and 3.2 eV, respectively, and the conduction band of SnO_2 is approximately 0.5 V higher than that of TiO_2 .¹⁶ When combining these two materials with UV irradiation, both become excited. In this case, a high concentration of electrons (e^-) is obtained in the conduction band of SnO_2 , and holes (h^+) generated on the SnO_2 valence band. These holes from SnO_2 could be easily transferred to the valence band of the TiO_2 , hence increasing the probability of charge separation in TiO_2 . So hetero-junction systems like $\text{TiO}_2/\text{SnO}_2$ have been proven to enhance efficiency of charge separation for photo-catalytic applications.¹⁷

According to previous studies, rf magnetron sputtering would be a potential process to deposit $\text{TiO}_2/\text{SnO}_2$ double layers with large area. However, the effect of the sputtering condition on the characteristics of deposited TiO_2 anatase in the $\text{TiO}_2/\text{SnO}_2$ system is not clear. The hetero-junction system of $\text{TiO}_2/\text{SnO}_2$ thin film with different thicknesses of TiO_2 layers on a constant thickness of SnO_2 layer are studied in this work. The effects of SnO_2 layer and different TiO_2 layer thickness prepared by reactive rf magnetron sputtering on the structure, morphology and photo-catalytic properties of TiO_2 thin film are discussed. The aim of this paper is to present the minimum thickness of TiO_2 layer with anatase structure and to achieve the best photo-catalytic efficiency in a $\text{TiO}_2/\text{SnO}_2$ system. Besides, the photo-catalyst and wettability of $\text{TiO}_2/\text{SnO}_2$ bi-layer are also investigated in this work.

2. Experimental Procedure

N-type (100) Si wafers were used as substrates in this study. The substrates ($30 \times 30 \times 2 \text{ mm}^3$) were ultrasonically cleaned in acetone solution and de-ionized water to remove all of the organic contaminants, and chemically etched with diluted HF solution just prior to loading into the deposition chamber. SnO_2 thin polycrystalline films were deposited onto Si substrates by a reactive rf magnetron sputtering system

*1Graduate Student, National Cheng Kung University

*2Corresponding author, E-mail: pates@mail.mse.ncku.edu.tw

Fig. 1 Schematic of reactive magnetron sputter system.

with an Sn target (99.99%), as shown in Fig. 1. The target was pre-sputtered for 20 min to remove the oxide and any contamination. All depositions were carried out in 99.999% ultra high purity Ar/O₂ (1 : 3) ambient. The base pressure of the deposition chamber was evacuated to below 1.0×10^{-4} Pa and the working pressure was 1.5 Pa. The rf power applied to the Sn target was kept at 120 W and the substrate temperature was kept at 100°C. In order to gain the same thickness (120 nm), all SnO₂ film was deposited for 90 min.

Before TiO₂ deposition, the SnO₂ substrates were introduced into an ultra-high vacuum XPS system and cleaned by Ar⁺-ion bombardment (500 eV, 1 μ A cm⁻², 1 min) in order to remove surface impurities. TiO₂ thin film were deposited on SnO₂ substrates by using reactive rf magnetron sputtering method with a high purity (99.99%) Ti target. All of the sputtering conditions, such as Ar/O₂ ratio, substrate temperature etc., were the same as SnO₂ thin films deposited. The rf power was kept at 200 W, and deposition times were 30, 60, 90, 120, 150 min. TiO₂ thin film without SnO₂ layer was deposited for 270 min on Si substrate. (TiO₂ thin film deposition rate was 1 nm/min in this study).

The thickness of the films was measured using an alpha-step surface profiler (α -step). The crystalline structure of the films was evaluated by glancing incident angle X-ray diffraction (GIAXRD), X-ray photoelectron spectrometry (XPS) for chemical binding states, and scanning electron microscopy (SEM) for surface microstructure. The incident angle of GIAXRD was set at 5°. XPS measurements were carried out with monochromatized Mg K α radiation (1253.6 eV).

Surface wettability was evaluated by the water contact angle. The sessile drop method was used for Dataphysics OCA-20 contact angle analyzer. The contact angles were measured at four different points on the surface of the film at room temperature in air.

3. Results and Discussion

3.1 Structural characterization

The GIAXRD spectrum of the deposited TiO₂/SnO₂ double-layer thin films with various TiO₂ film thicknesses and TiO₂ thin film without SnO₂ layer is shown in Fig. 2. All five of the films show rutile phase SnO₂ diffraction peaks with various thicknesses of TiO₂ thin films coated and identified as SnO₂ (110), (101), (211) directions. The

Fig. 2 A typical GIAXRD spectrum of TiO₂/SnO₂ double layers and TiO₂ thin film without SnO₂ layer.

Fig. 3 Plain-view SEM micrographs and the thickness of TiO₂ film is (a) 30 nm, (b) 60 nm, (c) 90 nm, (d) 120 nm, (e) 150 nm, (f) 270 nm.

presence of an anatase phase in the film was identified. Accordingly, the TiO₂ films exhibit an amorphous-like structure with thicknesses less than 150 nm. The diffraction peaks of (101), (004), (211) of TiO₂ anatase are only observed in the 150 nm TiO₂ and the TiO₂ thin film without SnO₂ layer. The GIAXRD diffraction results reveal that the crystallization of TiO₂ is enhanced as the coating thickness is increased.

3.2 Surface morphology

The surface topography and the cross-sectional microstructure of the coatings were examined by scanning electron microscopy. Figure 3 shows SEM micrographs of the different thicknesses of TiO₂ films deposited on SnO₂ substrate and the TiO₂ film without SnO₂ layer. The surface of TiO₂/SnO₂ bi-layer films, with TiO₂ thicknesses less than 150 nm, has a granular-like morphology, as shown in Figs. 3(a)–(d). A special rice-like morphology was clearly observed for the

Fig. 4 Cross-section SEM micrographs and the thickness of TiO₂ film is (a) 30 nm, (b) 60 nm, (c) 90 nm, (d) 120 nm, (e) 150 nm, (f) 270 nm.

TiO₂ film with 150 nm thickness and TiO₂ film without SnO₂ layer, as presented in Figs. 3(e)–(f). The surface, characterized by relatively dense-packed surface particles resembling an array of different polygons, is TiO₂ anatase surface morphology. The particles have a symmetrical or elongated shape with a size between 50 and 80 nm. The boundaries between particles are clearly seen and these surface particles seem to be the ends of individual columns. Not all surface particles are in close contact and they form blocks with a higher density. Such a special surface is characterized by a larger surface area and high roughness.

Cross-section SEM images revealed the thicknesses of all of the TiO₂/SnO₂ films, as shown in Fig. 4. Obviously, it was hard to observe the SEM cross-sections' considerable columnar structures, as shown in Figs. 4(a)–(d), because the TiO₂ films' amorphous-like structure with thicknesses less than 150 nm. Figure 4(e) displays a TiO₂ anatase columnar structure of the TiO₂ film with thickness of 150 nm, suggesting that further increasing the deposition time would cause an apparent increase in thickness, and enhance the aggregation of TiO₂ anatase grains on the SnO₂ substrate surface to improve photo-catalytic activity.^{18,19)} TiO₂ film without SnO₂ layer was observed anatase columnar structure because of the crystallization, as shown in Fig. 4(f).

3.3 Surface chemical binding states

X-ray photoelectron spectrometry (XPS) is a highly sensitive technique employed in surface analysis, and an effective method for investigating the surface composition and chemical states of all kinds of solid samples. The chemical binding states on the surfaces of TiO₂/SnO₂ films with different thickness of TiO₂ layers and TiO₂ film without SnO₂ layer were examined by XPS, and the spectra for O 1s and Ti 2p core levels are shown in Fig. 5. The binding energy scales are calibrated by shifting the peak of the adventitious surface carbon to 284.6 eV. The XPS peaks' positions are close to Ti 2p_{3/2} (458.6 eV) and Ti 2p_{1/2} (464.3 eV), demonstrating that the main chemical state of Ti in the TiO₂ film is +4 valance according to method principles and handbook of the XPS instrument,²⁰⁾ as shown in Fig. 5(a). However, the peaks slightly shifted toward the low-energy region as the thicknesses of TiO₂ decreased to 30 nm, perhaps due to the complex composition of the amorphous-like structure, diffusion of Sn atoms and Ti ions in other oxidation states.^{21,22)}

Figure 5(b) shows the XPS spectra of O 1s. The O 1s peaks are centered at 530.3 eV, and the values are close to the published data on binding energies for O 1s levels in bulk TiO₂, which is 530.3 eV.²³⁾ On account of the similarity

Fig. 5 XPS spectra of: (a) Ti 2p; (b) O 1s core levels for $\text{TiO}_2/\text{SnO}_2$ films with different thickness of TiO_2 layer and TiO_2 thin film without SnO_2 layer.

Fig. 6 The morphology between pure water and $\text{TiO}_2/\text{SnO}_2$ thin films with different thickness of TiO_2 layer and TiO_2 thin film without SnO_2 layer.

of the spectra, the binding states of O atoms, as well as the electronic structures of all the films, should be comparable among the samples. All O 1s XPS peaks are wide and asymmetric, with a slight broadening at the high-energy side observed, demonstrating that there are at least two kinds of O chemical states according to the binding energy range from about 528 to 533 eV, including crystal lattice oxygen

(O_L) and hydroxyl oxygen (O_H) with increasing binding energy.^{24–26} The O_L XPS signal is attributed to the contribution of Ti-O in the TiO_x lattice and Sn-O in SnO_2 lattice. The O_H XPS signal depends upon the hydroxyl groups (OH^-) resulting mainly from the presence of residual hydrogen in the processing chamber and the chemisorbed water.

Fig. 7 The morphology between pure water and thin films with different thickness of TiO₂ layer after 180 min of UV irradiation.

Table 1 Atomic ratio calculated from the integrated area of XPS O 1s and Ti 2p_{3/2} singles, and the binding energy of Ti 2p_{3/2} and O 1s.

Samples	Atomic ratio (O/Ti)	Binding energy (eV)	
		Ti 2p _{3/2}	O 1s
TiO ₂ (30 nm)/SnO ₂ (120 nm)	1.523	458.48	530.34
TiO ₂ (60 nm)/SnO ₂ (120 nm)	1.597	458.36	530.30
TiO ₂ (90 nm)/SnO ₂ (120 nm)	1.727	458.26	530.46
TiO ₂ (120 nm)/SnO ₂ (120 nm)	1.830	458.08	530.22
TiO ₂ (150 nm)/SnO ₂ (120 nm)	1.923	458.04	530.18

Table 1 lists the $\frac{O}{Ti}$ atomic ratio in the TiO₂/SnO₂ films, calculated from the signal-integrated area and normalized with element sensitivity factors. It is clear that the $\frac{O}{Ti}$ ratio increases with the increasing thickness of TiO₂. The increase of the $\frac{O}{Ti}$ ratio suggests that more Ti atoms are bonding in forms of stoichiometric TiO₂ which is nearly defect-free, to suppress the recombination of photo-generated charge carriers.

3.4 Surface wettability

The surface wettability was evaluated by examining the contact angle for pure water of TiO₂/SnO₂ thin films with

various TiO₂ thicknesses and TiO₂ film without SnO₂ layer. It can be seen in Fig. 6 that the contact angles decrease with increasing TiO₂ film thickness. Owing to the surface roughness having increased when the TiO₂ film became crystalline, the contact angle decreased;²⁷⁾ this specific property is attributed to surface strain energy, which is generally higher in nano crystalline thin films than in amorphous.²⁸⁾

It was found that the contact angles for pure water on TiO₂ films with various thicknesses and TiO₂ film without SnO₂ layer decreased after the UV illumination for 180 min, as shown in Fig. 7. The contact angles were measured at four different points on the surface of the film at room temperature in air under UV irradiation and each contact angle plotted in Fig. 8, is an average of the data taken from four different locations. Based on Fig. 8, the order of photo-induced superhydrophilicity is TiO₂(150 nm) > TiO₂(270 nm) without SnO₂ layer > TiO₂(120 nm) > TiO₂(90 nm) > TiO₂(60 nm) > TiO₂(30 nm). The photo-induced superhydrophilicity of TiO₂/SnO₂ films increased in correlation to the thickness. The relationship of the photo-induced superhydrophilicity with the thickness of TiO₂ for TiO₂/SnO₂ films can be explained by analyzing both the crystallization and light-harvesting efficiency of TiO₂ films. On the one hand, with the increased TiO₂ film

Fig. 8 Time dependence of water contact angles of thin films with different thickness of TiO_2 layer under UV illumination.

thickness, the crystallization of TiO_2 film became more perfect (Fig. 2); on the other hand, the light-harvesting capacity of TiO_2 film increased, resulting in an increased number of photo-generated carriers (e^- and h^+)²⁹ which were transferred to the TiO_2 film surface and contributed to the photo-induced superhydrophilicity. These two factors increased the photo-induced superhydrophilicity. Furthermore, when the total thickness of films is the same, the photo-induced superhydrophilicity of $\text{TiO}_2(150\text{ nm})/\text{SnO}_2(120\text{ nm})$ film is higher than $\text{TiO}_2(270\text{ nm})$ film. This also confirms that a better charge separation is occurring in the coupled film.

4. Conclusion

With the increased TiO_2 film thickness deposited on SnO_2 film by using reactive rf magnetron sputtering method, the crystallization of TiO_2 film becomes more perfect, and more Ti atoms bond in forms of stoichiometric TiO_2 . There is a thickness of TiO_2 film (150 nm) deposited on SnO_2 substrate that yields the best photo-induced superhydrophilicity and surface wettability.

Acknowledgements

The authors would like to thank the Center for Micro/Nano Science and Technology, National Cheng Kung University, Taiwan for the provision of equipment and technical support.

REFERENCES

- 1) N. Negishi, T. Iyoda, K. Hashimoto and A. Fujishima: *Chem. Lett.* **9** (1955) 841.
- 2) A. J. Nozik and R. Memming: *J. Phys. Chem.* **100** (1996) 13061.
- 3) I. Sopyan, M. Watanabe and S. Murasawa: *Chem. Lett.* **1** (1996) 69.
- 4) T. Kawai and T. Sakata: *Nature* **286** (1980) 474.
- 5) I. Rosenberg, I. Brock and A. Heller: *J. Phys. Chem.* **96** (1992) 3523.
- 6) Y. Oosawa and M. Gratzel: *J. Phys. Chem.* **184** (1988) 197.
- 7) N. Negishi, K. Takeuchi and T. Ibusuki: *Appl. Surf. Sci.* **121** (1997) 417.
- 8) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni and E. Kojima: *Nature* **388** (1997) 431–432.
- 9) T. Watanabe, A. Nakajima, R. Wang, A. Fujishima and K. Hashimoto: *Thin Solid Films* **351** (1999) 260.
- 10) A. Nakajima, S. Koizumi, T. Watanabe and K. Hashimoto: *Langmuir* **16** (2000) 474.
- 11) R. Wang, N. Sakai, A. Fujishima, T. Watanabe and K. Hashimoto: *J. Phys. Chem. B* **103** (1999) 2188–2194.
- 12) K. Takagi, T. Makitomo, H. Hiraiwa and T. Negishi: *Vacuum Sci. Technol. A* **19** (2001) 2931.
- 13) D. Noguchi, Y. Kawamata and T. Nagatomo: *J. Electrochem. D* **124** (2005) 152.
- 14) P. Kamat: *Semiconductor Nanoclusters* **103** (1996) 237.
- 15) I. Bedja and P. Kamat: *J. Phys. Chem.* **99** (1995) 9182.
- 16) U. Stafford, K. Gray and P. Kamat: *Chem. Rev.* **3** (1996) 77.
- 17) P. Kamat and K. Vinodgopal: *Environmental photochemistry with semiconductor nanoparticles*, ed. by V. Ramamurthy, K. S. Schanze, Organic and Inorganic Photochemistry, (Marcel Dekker, New York, 1998).
- 18) P. Zeman and S. Takabayashi: *Surf. Coat. Technol.* **153** (2001) 97.
- 19) H. C. Yao, W. T. Wu and F. S. Shieu: *J. Electrochem. Soc.* **153** (2006) 241.
- 20) C. Wanger, L. Davis, J. Moulder and G. Muilenberg: *Handbook of X-ray photoelectron spectroscopy*, (Eden Prairie, Minn., Physical Electronics, 1995).
- 21) G. Song, H. Joly, E. Liu and T. Peng: *Appl. Surf. Sci.* **220** (2003) 165.
- 22) J. Liqiang, F. Honggang, W. Baiqi and W. Dejun: *Appl. Catal.* **62** (2006) 282.
- 23) N. McIntyre: *Practical surface analysis*, ed. by M. Seah, (Chichester, Wiley, c1990–c1992, New York).
- 24) C. Wanger: *Practical surface analysis*, ed. by M. Seah, (Chichester, Wiley, 1983, New York).
- 25) J. Yu, H. Yu, B. Cheng, X. Zhao and W. Ho: *J. Phys. Chem.* **107** (2003) 13871.
- 26) L. Jing, X. Sun, H. Hou, B. Xin, W. Cai and H. Fu: *J. Solid State Chem.* **177** (2004) 3375.
- 27) S. Kandlikar and M. Steinke: *Trans IChemE.* **79** (2001) 491.
- 28) B. Cuulity and S. Stock: *Elements of X-ray Diffraction*, third ed., (Prentice-Hall, Englewood Cliffs, 2000) p. 452.
- 29) Y. Tachibana, K. Hara, K. Sayama and H. Arakawa: *Chem. Mater.* **14** (2002) 2527.