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Oxygen Partial Pressure Dependence of the Properties of TiO_2 Thin Films Deposited by DC Reactive Magnetron Sputtering

M. Horprathum[a*], P. Eiamchai[a], P. Chindaudom[a], A. Pokaipisit[b,c*], P. Limsuwan[b,c]

[a]Optical Thin-Film Laboratory, National Electronics and Computer Technology Center, Pathumthani 12120, Thailand
[b]Department of Physics, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[c]Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok 10400, Thailand

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Abstract

Thin films of TiO_2 have been deposited on glass and silicon wafers (100) substrates by DC reactive magnetron sputtering from a 99.995% pure titanium target. The influence of the oxygen partial pressure on the optical, crystallinity, surface morphology and UV-induced hydrophilic properties has been studied. The films were characterized by UV-VIS spectrophotometer, X-ray diffractometer, atomic force microscopy and scanning electron microscope. The UV-induced hydrophilicity of the films was measured by the contact angle variation. The results showed that the crystalline anatase, anatase/rutile or rutile films can be successfully deposited on unheated substrate. The best hydrophilicity was obtained on the well-crystallized anatase TiO_2 thin film deposition with 5.0×10^{-3} mbar oxygen partial pressure. The optical band gap of TiO_2 thin films increased with increasing oxygen partial pressure, from 3.21 to 3.28 eV, with film thickness of 135 nm.

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Keywords: Hydrophilic; Oxygen partial pressure; Sputtering; TiO_2

1. Introduction

TiO_2 thin films are extensively used in a wide range of applications such as antireflective coating, gas sensor, and the photocatalysts due to remarkable optical, electrical and chemical properties [1-3]. Three major crystalline phases have been detected in TiO_2 thin films: rutile (tetragonal with a=0.4594 nm,

* Corresponding author. Tel.: +66 2872 5253; fax: +66 2872 5254.
E-mail address: opticslaser@yahoo.com.

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c=0.2958 nm); anatase (tetragonal with *a*=0.3785 nm, *c*=0.9514 nm); and brookite (orthorhombic with *a*=0.9184 nm, *c*=0.5145 nm) [4]. Many different techniques can be used for the fabrication such as sol-gel [2], spray pyrolysis [5], chemical vapor deposition [6], electron-beam evaporation [4] and sputtering [7].

Reactive sputtering is widely used to prepare Ti compound thin films such as TiO_2 and TiN. Generally, high flows of the reactive gases such as oxygen and nitrogen are required for formation of Ti compound films during reactive sputtering of Ti metal. The pressure of reactive gases and substrate temperature has been the main parameters used to influence the packing density of the films, the film crystallinity and the optical properties [8].

It well knows recently that TiO_2 films have an amphiphilic surface induced by UV irradiation. The mechanism of the conversion from hydrophobic to hydrophilic under UV illumination was explained by assuming that surface Ti^{4+} sites were reduce to the Ti^{3+} states via the photogenerated electrons, and oxygen vacancies were generated through the oxidation of the bridging O^{2-} species to oxygen via the photogenerated holes. In comparison to the other crystalline phase of TiO_2, such as rutile and brookite, the most photoactive phase of TiO_2 is anatase. The relations between the structure of the films by dc reactive magnetron sputtering technique and the corresponding hydrophilic properties have yet been well investigated. Hence, the purpose of this study is to investigate the variations of the hydrophilic properties induce by the surface and structures following the oxygen pressure.

2. Experimental

2.1. Preparation of TiO_2 thin films

Titanium dioxide transparent films were prepared using a dc magnetron sputtering system. A 3 inch diameter titanium disc of 99.995% purity was use as the target. All samples were reactively sputtered in a mixture of 99.999% argon and 99.999% pure oxygen. The based pressure of the deposition chamber was about 10^{-5} mbar. The discharge was generated at a constant DC power of 100 W. The flow rate of Ar was kept at constant value of 5.5 sccm. The glass and silicon wafers (100) substrates were prepared by ultrasonic washer with acetone, before loaded into the deposition chamber. During the deposition the substrates were not heat. The deposition time was fixed at 90 min.

2.2. Characterization

The film crystalline structures were also examined by X-ray diffractometer (XRD), Bruker D8 Advance, operating with Cu-$K_{\alpha 1}$, operated at 40 kV and 40 mA. The surface morphology of the films was examined using atomic force microscope (AFM), Seiko instrument model SPI-4000.

Light transmission of the films was measured and considered by a double-beam ultraviolet-visible light (UV-VIS) spectrophotometer, PerkinElmer Lambda 950. The measurements were done from 200-860 nm.

The photoinduced hydrophilicity was evaluated by measurement of contact angles to pure water after UV illumination (black light lamp, 1.2 mW/cm^2) with the maximum intensity centered at 365 nm. Water contact angle measurement was performed at room temperature in ambient atmosphere using a contact angle meter (ramé-hart instrument model 250) with an experimental error less than 0.1°. The UV intensity was measured using a UV Integrating Radiometer.

3. Results and Discussion

3.1. Crystalline structure

The goal of this study is to deposit and analyze TiO_2 thin films with a oxygen partial pressure ranging from 4.8×10^{-4} to 5.0×10^{-3} mbar. Crystal structure of the films was examined by using XRD, as shown in Fig. 1. The XRD patterns of Fig. 1 indicate that the samples prepared at low oxygen partial pressure have rutile structure. From the results of XRD measurement, it can be noticed that rutile TiO_2 was obtained when the oxygen pressure is 4.8×10^{-4} mbar, and anatase TiO_2 was obtained when the partial oxygen pressure is 5.0×10^{-3} mbar. For the TiO_2 thin films with oxygen partial pressure 5.0×10^{-3} mbar, a low-intensity reflection line from rutile R(110) is also revealed. Thus, it is clear that the crystal formation is influenced by the oxygen partial pressure.

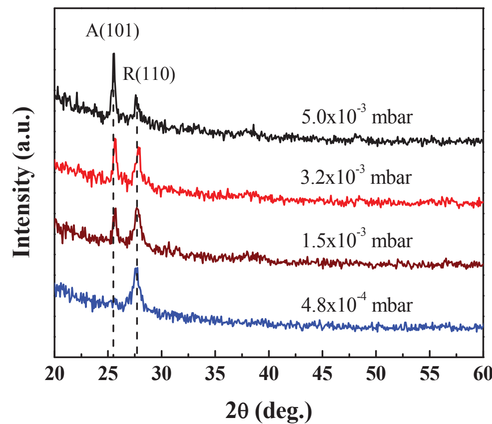

Fig. 1. XRD patterns of TiO_2 thin films deposited at different oxygen partial pressures

3.2. Surface morphologies observed by AFM and SEM

The surface morphologies of TiO_2 thin films deposited on silicon wafers were observed by AFM. Fig. 2 shows the AFM images of the films at different oxygen partial pressures. As can be seen from films at 4.8×10^{-4} mbar oxygen partial pressure, the surface morphology of TiO_2 thin films is smooth with roughness of 1.68 nm. At the low oxygen partial pressure, the sputtered adatoms (titanium atoms and oxygen atoms from reactive gas) have relatively high energy, therefore their mobility is high enough to from a smooth surface. As the oxygen partial pressure increases, the surface roughness increases. At the oxygen partial pressure of 5.0×10^{-3} mbar, for example, the roughness is 2.33 nm. The surface morphology of the film roughens because the energy of sputtered adatoms decreased, and consequently the capability of sputtered adatoms to move on the surface of substrate also decreases [9]. The cross-sectional of TiO_2 thin films deposited at oxygen partial pressure 1.5×10^{-3} mbar on silicon wafer is shown in Fig. 3. The film thickness of TiO_2 thin films is about 135 nm.

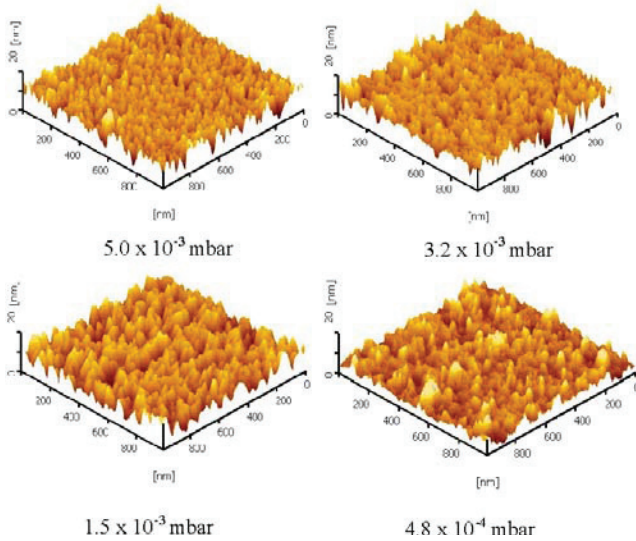

Fig. 2. AFM images of TiO_2 thin films at different oxygen partial pressures

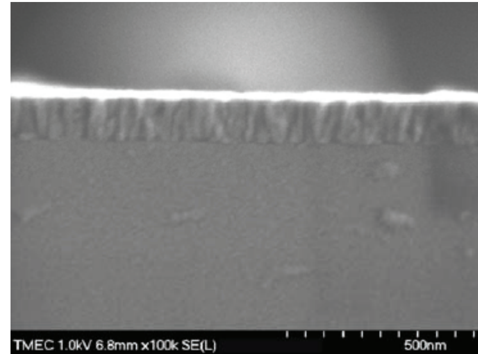

Fig. 3. Cross-section of SEM images of TiO_2 thin films at oxygen partial pressure of 1.5 x 10^{-3} mbar

3.3. Transmittance and Reflectance spectra of TiO_2

Fig. 4 shows the UV-VIS spectra of TiO_2 thin films at different oxygen partial pressures on glass slide substrates. The blank glass was again used as a reference, giving the highest transmittance percentage at all visible range. The films are lilac and highly transparent. The average transmittance of the sputtered film is ~ 80% in the visible region. The obtained spectra of the films are characterized by the typical semiconductor material with good optical quality. While, the films prepared at high oxygen partial pressure showed a relatively high transmittance.

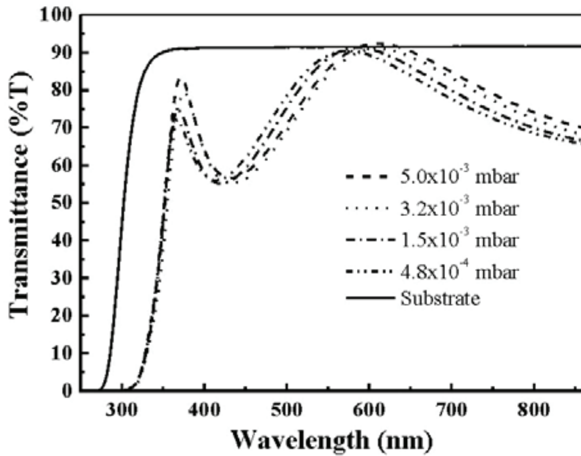

Fig. 4. Transmittance of TiO_2 thin films at different oxygen partial pressures

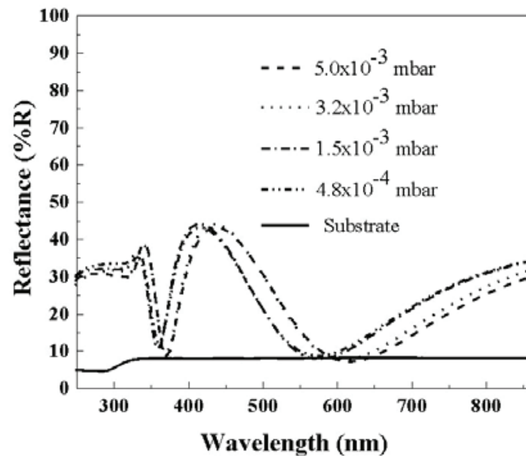

Fig. 5. Reflectance of TiO_2 thin films at different oxygen partial pressures

For the reflectance spectra, the angle of incident was set at 8° for the vertical plane of the films surface. Fig. 5 shows the decreasing reflectance of TiO_2 thin films deposited at difference oxygen partial pressures. The films deposited at high oxygen pressure of 5 x 10^{-3} mbar had the highest transmittance and the lowest reflectance.

3.4. Optical band gap

Transmittance spectra (Fig. 4) have been used to obtain the optical band gap of the studied thin films. The sharp decrease in the transparency of the TiO_2 thin films in the UV region results from the fundamental light absorption of the semiconductor.

The absorption coefficient α, which depends on the wavelength λ, can be obtained the following relationship: [10]

$$T = (1-R)^2 e^{-\alpha d} \tag{1}$$

where T is the transmittance, R is the reflectance, α is the absorption coefficient and d is the films thickness. Equation (1) is of course only valid close to the optical band gap of the material under the condition $exp(\alpha d) >> R^2$. When the scattering effect is neglected, the absorption coefficient may be expressed by [11]

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \tag{2}$$

where $h\nu$ is the photon energy, A is parameter independent of photon energy for respective transition and E_g is the optical band gap. Hence, at photon energies $h\nu > E_g$, TiO_2 material can absorb photons, while at $h\nu < E_g$, α=0 and the photons can not be absorbed.

Band gap was derived from $\alpha^{1/2}$ versus $h\nu$ curve by extrapolating the linear part of the curve. The calculated band gaps are plotted in Fig. 6. The optical band gap of TiO_2 thin films increased with increasing oxygen partial pressure, from 3.21 to 3.28 eV. The sample oxygen partial pressure of 5.0×10^{-3} mbar has a higher band gap (3.28 eV) than that oxygen partial pressure of 4.8×10^{-4} (3.24 eV). This behavior is probably due to the different contents of anatase and rutile phase, which have different band gaps. Anatase phase (3.20 eV) has higher band gap than rutile (3.00 eV) [12]. All values are larger than those bulks by about 10%. There are two possible reasons for a large band gap value of the films: (1) presumably due to an axial strain effect from lattice deformation as has been pointed out for ZnO films [13]; and (2) probably due to a change in the density of semiconductor carriers.

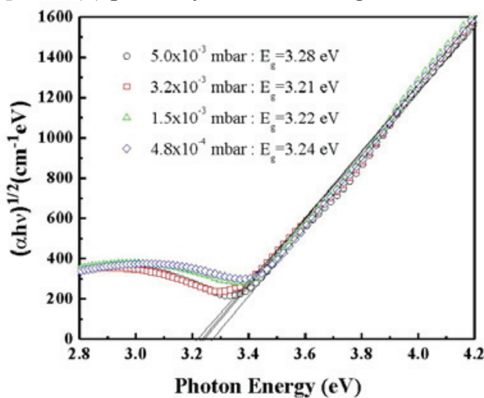

Fig. 6. $(\alpha h\nu)^{1/2}$ as a function of photon energy for the TiO_2 thin films at different oxygen partial pressures.

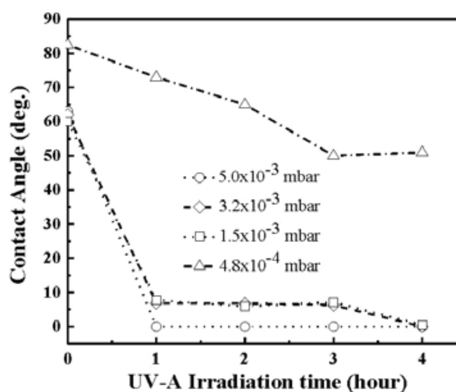

Fig. 7. Water contact angle variation following the UV illumination time for the films.

3.5. Hydrophilic properties

TiO_2 is outstanding photcatalytic material, hence, attracting many studies on the photocatalytic behavior on the TiO_2 thin films. In our study, water contact angle measurement was conducted to examine the UV-induced phenomena of the films. Fig. 7 shows the contact angle variation with respect to the time of UV illumination for the films at different oxygen partial pressures. Before UV light irradiation, the original contact angles of TiO_2 thin film were 82° 60° 62° and 63° for the films with the oxygen partial pressure of 4.8×10^{-4}, 1.5×10^{-3}, 3.2×10^{-3} and 5.0×10^{-3} mbar, respectively.

The TiO_2 is a hydrophilic material, which the contact angle of the flat dense TiO_2 layer is about 50-60° [14]. Therefore, it is reasonable to obtain a good hydrophilic TiO_2 thin film with a reactive sputtering process. After 1 hour of UV light irradiation at 1.2 mW/cm^2, all prepared TiO_2 thin films were photo-induced to become super-hydrophilic, except TiO_2 thin films prepared at oxygen partial pressures 4.8×10^{-4} mbar with rutile phase and smooth surface maintain a contact angle of about 51° under UV-irradiation. The contact angles were below 5° and revealed the good photocatalytic wettable property. Moreover, the rate of photo-induced super-hydrophilicity was proportion to the oxygen partial pressure.

There are two plausible mechanisms for the photo-induced superhydrophilicity of TiO_2. One is the increase of number of hydroxyl groups of the TiO_2 surfaces during UV light irradiation. The film thickness does not affect the hydrophlicity property because it is only related to the physical-chemical property of the film surface. The reason for this better photo-induced hydrophilic film are the well-crystallized and rough structure on the surface.

Layers completely consisting of anatase-rutile phase shows a fast drop of the contact angle than rutile layers. The different photo-induced hydrophicity can be interpreted by the different structure of anatase and rutile. Therefore, anatase has a bigger reducting power than rutile. Hence, anatase layers can easily formed oxygen vacancies on the surface, which affect the superhydrophilicity [15]. In contrast to Fig. 1 from Fig. 7, it is clear that the main factor affecting the photo-induced superhydrophilicity is the crystallinity. Our results show that the water contact angel is also decreased with increasing surface roughness.

4. Conclusions

DC reactive magnetron sputtering process without an external substrate heating has been successfully used for the deposition of crystalline anatase TiO_2 thin films with the hydrophilic activity. We obtained rutile crystal structure when the partial oxygen pressure was 4.8×10^{-4} mbar, and anatase structure crystal when the partial oxygen pressures was 5.0×10^{-3} mbar. Well-crystalline anatase TiO_2 thin films obtained in the optimal oxygen partial pressure at 5.0×10^{-3} mbar exhibits the best UV-induce hydrophilicity. The rough TiO_2 thin film exhibited a good original hydrophilic and was easily rendered to be super-hydrophilic after short period of UV light irradiation. Layers that contain a significant amount of the anatase phase show better photo-induced super-hydrophilicity than layers containing only the rutile phase. All of TiO_2 thin films show the optical band gap at 3.21-3.28 eV. The experiments demonstrated that magnetron sputtering is convenient technique for the deposition of UV-induce hydrophilic TiO_2 thin films.

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References

[1] Richards BS. Single-material TiO_2 double-layer antireflection coatings. *Sol Energy Mater So Cells* 2003;**79**:369-390.

[2] Yu J, Zhao X. Effect of substrates on the photocatalytic activity of nanometer TiO_2 thin films. *Mater Res Bull* 2000;**35**:1293-1301.

[3] Karunagaran B, Uthirakumar P, Chung SJ, Velumani S, Suh EK. TiO_2 thin film gas sensor for monitoring ammonia. *Mater Characterization* 2007;**58**:680-684.

[4] Wang YL, Zhang KY. Study of the growth morphology of TiO_2 thin films by AFM and TEM. *Surf Coat Technol* 2001;**140:**155-160.

[5] Deshmukh HP, Shinde PS, Patil PS. Structural, optical and electrical characterization of spray-deposited TiO_2 thin films. *Mater Sci Eng B* 2006;**130**:220-227.

[6] Nakamura M, Makino K, Sirghi L, Aoki T, Hatanaka Y. Hydrophilic properties of hydro-oxygenated TiO_x films prepared by plasma enhanced chemical vapor deposition. *Surf Coat Technol* 2003;**169-170**:699-702.

[7] Ye Q, Liu PY, Tang ZF, Zhai L. Hydrophilic properties of nano-TiO_2 thin films deposited by RF magnetron sputtering. *Vacuum* 2007;**81**:627-631.

[8] Heo CH, Lee SB, Boo JH. Deposition of TiO_2 thin films using RF magnetron sputtering method and study of their surface characteristics. *Thin Solid Films* 2005;**475**:183-188.

[9] Syarif DG, Miyashita A, Yamaki T, Sumita T, Choi Y, Itoh H. Preparation of anatase and rutile thin films by controlling oxygen partial pressure. *Appl Surf Sci* 2002;**193**:287-292.

[10] Martin N, Rousselot C, Rondot D, Palmino F, Mercier R. Microstructure modification of amorphous titanium oxide thin films during annealing treatment. *Thin Solid Films* 1997;**300**:113-121.

[11] Tauc J. *Optical Properties of Solids*. Amsterdam:North-Holland; 1972.

[12] Tang H, Prasad K, Sanjine R, Schmid PE, Lévy F. Electrical and optical properties of TiO_2 anatase thin films. *J Appl Phys* 1994;**75**:2042-2047.

[13] Ong HC, Zhu AX. Dependence of the excitonic transition energies and mosaicity on residual strain in ZnO thin films. *Appl Phys Lett* 2002;**80**:941-943.

[14] Dohshi S, Anpo M, Okuda S, Kojima T. Effect of gamma-ray irradiation on the wettability of TiO_2 single crystals. *Topic Catal* 2005;**35**:327-330.

[15] Wang R, Sakai N, Fujishima A, Watanabe T, Hashimoto K. Studies of Surface Wettability Conversion on TiO_2 Single-Crystal Surfaces. *J. Phys. Chem. B* 1999;**103**:2188-2194.