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Structures and Optical Properties of TiO_2 Thin Films Deposited on Unheated Substrate by DC Reactive Magnetron Sputtering

Nirun Witit-anun[1]*, Prasertsak Kasemanankul[1], Surasing Chaiyakun[2] and Pichet Limsuwan[1]

ABSTRACT

Titanium dioxide thin films (TiO_2) were deposited on unheated substrate on a glass slide and Si-wafer by the DC reactive magnetron sputtering method at different total pressures. The crystal structure, surface morphology and optical transmittance were characterized by X-ray diffractometer, atomic force microscopy and UV-VIS-NIR spectrophotometer, respectively. The deposited films were transparent and the thickness was about 133-168 nm. XRD results showed that all samples possessed a polycrystalline structure and changed from the mixed phase of anatase and rutile, to rutile phases, as the total pressure decreased. An increase in the film's roughness was observed with increasing sputtering pressure. The optical transmission measurements revealed that the mixed phases of anatase and rutile had higher transmittance than the pure rutile phase. The refractive index, in the visible spectrum was relatively high, while the energy band gap was found to be 3.25 eV.

Key words: TiO_2 films, anatase, rutile, optical constant, reactive sputtering

INTRODUCTION

Titanium dioxide, TiO_2, has been attracting much interest for a wide range of applications, such as photocatalysts (Fujishima and Honda, 1971; Fujishima and Honda, 1972), dye-sensitized solar cells (Hagfelt and Gratzel, 1995) and capacitors for large-scale integrated devices (Lee, 1998). Many TiO_2 applications require a high refractive index and/or high dielectric constant. TiO_2 films are also used as optical materials, such as antireflective coatings, high-reflectance films and wavelength-selective films (Fan, 1981). Moreover, TiO_2 has also been extensively studied for photo-assisted degradation of organic molecules.

In the natural environment, TiO_2 has three polymorphs, including rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile is a thermodynamically stable phase, while anatase and brookite exist as metastable phases below 800°C and can transform to rutile above this temperature. Each crystalline form is utilized for a different purpose. While rutile is mainly desirable for optical applications, anatase has more efficient photocatalytic properties (Fukushima *et al.,* 1999). It is formed during the deposition of TiO_2 thin films, depending on the deposition technique, the deposition parameters and the deposition configuration.

Reactive sputtering is one of the most-utilized methods for obtaining uniform and dense

[1] King Mongkut's University of Technology Thonburi, Bangmod, Bangkok 10140, Thailand.

[2] Burapha University, Muang, Chonburi 20131, Thailand.

* Corresponding author, e-mail: nirun_w65@hotmail.com

TiO_2 films, with well-controlled stoichiometry, strong adhesion and high purity. However, substrate heating and/or post annealing at high temperatures (Suhail *et al.*,1992; Martin *et al.*, 1997) are always necessary to get well-crystallized TiO_2 films, which no doubt limits the application of the TiO_2 films in many aspects. On the other hand, sputtering and ion beam assisted deposition, which are methods characterized by higher particle energies, can produce both amorphous and crystalline TiO_2 films below 200°C. However, the published results of experimental studies using these deposition methods are different and in some cases show contradictory results. For instance, Meng and Santos (1993) reported only the anatase structure for a wide range of working pressures, while Okimura *et al.* (1995) observed the phase transition with increasing pressure. Furthermore, the lower processing temperature can allow for a material with a low melting point to be used as the substrate, preventing harmful film–substrate interactions (Yamada *et al.,* 2000; Wang *et al.,* 2002; Liu *et al.,* 2005). Nowadays, considerable attention has been placed on fabricating crystalline TiO_2 films with a particular phase at low substrate temperatures (Ding *et al.,* 2000; Asanuma *et al.,* 2004). In order to produce crystalline TiO_2 films using sputtering methods, the deposition parameters need to be well controlled. High sputtering power, long sputtering time and short target substrate distance are mandatory (Okimura *et al.,* 1995; Zheng *et al.,* 2001). Due to the plasma heating effect, the substrate temperature will increase gradually from room temperature to a relatively high temperature, which equates to substrate heating and thus affects the crystallinity, structure and properties of the films deposited.

The structure and properties of TiO_2 films prepared by magnetron sputtering can be modified and controlled via the process parameters of sputtering pressure, sputtering power and oxygen partial pressure. In this paper, polycrystalline TiO_2 films were deposited at different sputtering pressures on unheated substrate using DC unbalanced magnetron sputtering. The sputtering pressure had an obvious influence on both the structure and optical properties of the TiO_2 films.

MATERIALS AND METHODS

TiO_2 thin films were deposited onto well-cleaned glass slides and silicon wafer substrates by the homemade, DC unbalanced magnetron sputter deposition system illustrated in Figure 1. cylindrical stainless steel vacuum chamber was 310 mm in diameter and 370 mm in height. The target used was metallic titanium (purity 99.97%) with a diameter of 54 mm and a thickness of 3 mm. High-purity Ar (99.999%) and O_2 (99.999%) gases were used as the sputtering and reactive gases, respectively. The flow rate ratio of Ar and O_2 was always kept at a constant value of 1:4, which was controlled by a mass flow controller (MKS type 247D). Before each deposition, the chamber was evacuated by diffusion pump to a base pressure of less than 3×10^{-5} mbar. The target was pre-sputtered in an Ar atmosphere for 10 min, in order to remove the surface oxide layer of the target. Sputtering pressures (P_{tot}) of 5×10^{-3}, 7×10^{-3} and 9×10^{-3} mbar were investigated. The sputtering power was fixed at 210 W. The distance

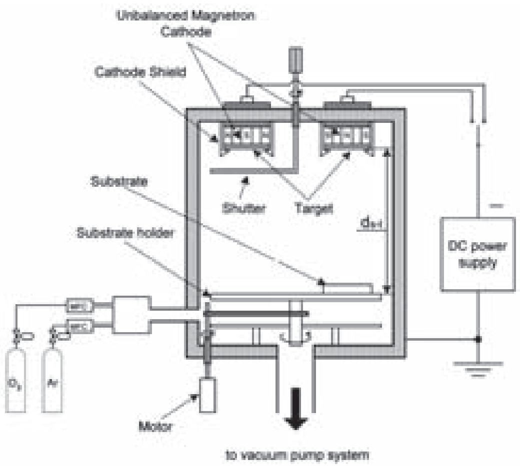

Figure 1 Homemade DC unbalanced magnetron sputtering.

between the target and substrate was kept at 120 mm and each film was deposited for 3 h.

The silicon substrates were analyzed by XRD (Rigaku RINT2000) to determine the crystallographic phase. The XRD patterns were measured at a glancing angle of 3° using CuKα radiation (λ = 1.54059 Å) at 40kV and 40 mA with a pattern recoded from 20° to 65° of 2θ at a scan rate of 2° min^{-1}. The evolution of the surface morphology and thickness of the samples were investigated by AFM (Nanoscope IV, Veeco Instrument Inc.). The UV-VIS transmission spectroscopy of the films was measured with the UV-VIS-NIR spectrophotometer system (Shimadzu MPC-31000) in the range of 200 nm to 2000 nm. Swanepoel's envelope method was used to determine the optical constant of the films (Swanepoel, 1983).

RESULTS AND DISCUSSION

Figure 2 shows that the XRD patterns of the films were deposited at different P_{tot} on the Si-wafer. The anatase phase was observed on the films by increasing the P_{tot} to 7×10^{-3} mbar, while the rutile phase was stable at all P_{tot}. Moreover, the single phase of rutile film was deposited at P_{tot} of 5×10^{-3} mbar. Shibata *et al.,* (1993) reported that the anatase phase resulted from the reaction between neutral Ti and neutral O_2 and O_2^-, with the rutile being a result of the reaction between decelerated Ti^+ or activated Ti and O_2^-. In this work, the sputtering was installed with two cathodes but during the deposition of the TiO_2 films, only one cathode was used. However, the magnetic field of the unused magnetron could influence the plasma structure, which in turn would increase the number of electrons. The electrons in the plasma could bombard the Ti atom into Ti^+ or activated Ti (Kasemanankul *et al.,* 2009). Moreover, at high total pressure (P_{tot}), the Ti^+ or activated Ti decreased due to a decrease in the ionization energy by collisions between Ti^+ species (Okimura *et al.,* 1995).

Figure 3 shows the AFM images of the TiO_2 films that were deposited on Si-wafers at different P_{tot}. The film thickness, which was analyzed using sectional analysis, was about 133 nm to 168 nm. The surfaces showed spherical, uniform nodules. For P_{tot} of 5×10^{-3} mbar (Figure 3a), the nodules were aggregated together and many deep valleys between these aggregates were observed. The diameter and height of the nodules increased significantly and the nodules seemed to be less coalescent; the mean roughness increased from 1.69 nm to 4.36 nm with an increase in P_{tot}

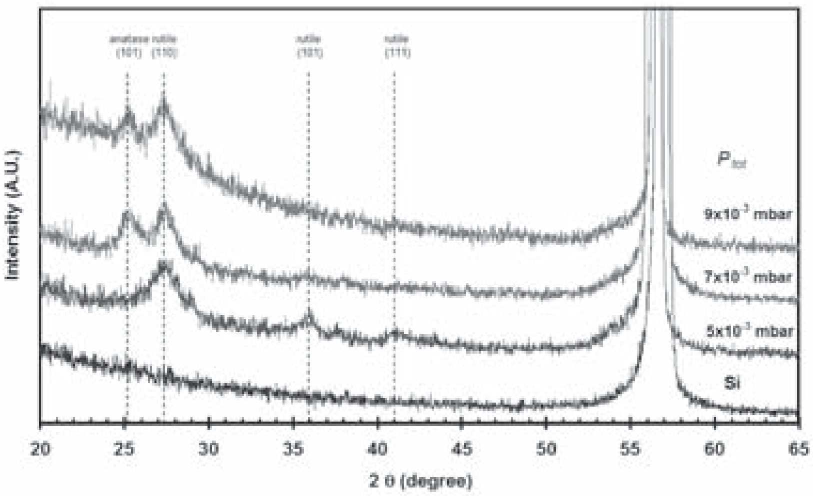

Figure 2 XRD patterns of TiO_2 films deposited on Si-wafers at different P_{tot} .

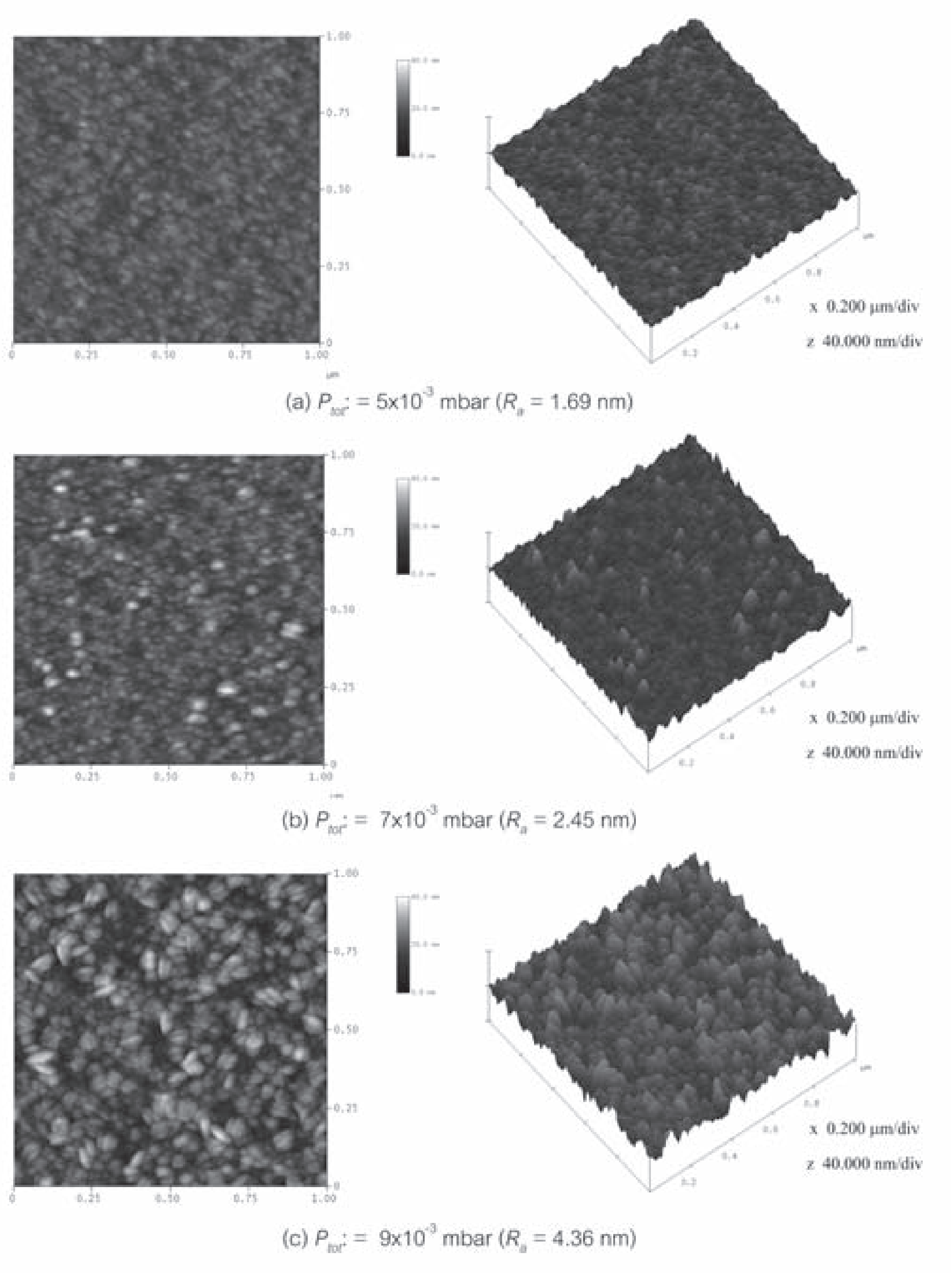

Figure 3 AFM images of TiO_2 films deposited on Si wafers at different P_{tot}: (a) P_{tot}: = 5x10^{-3} mbar (R_a = 1.69 nm); (b) P_{tot}: = 7x10^{-3} mbar (R_a = 2.45 nm); and (c) P_{tot}: = 9x10^{-3} mbar (R_a = 4.36 nm).

from 5×10^{-3} mbar to 9×10^{-3} mbar. This occurred because the film roughness correlated with the adatom mobility, which was governed by the energy of the impinging particles (Meng and Santos, 1993; Kim *et al.,* 2002). The energy of the impinging particles decreased with an increase in P_{tot}, owing to the increase in the collision probability of the particles. This might have resulted in a decrease in the mobility of the impinging particles, which in turn would result in an increase in the roughness of the films.

Figure 4 shows the transmission spectra of TiO_2 films deposited at different P_{tot}. The spectra of the films show wave forms (ripples), which are characteristic of the interference of light. The transmission spectra in the optical region are transparent. As a general feature, the films deposited at high P_{tot} have relatively higher transmittance maxima than those deposited at low P_{tot}. In other words, the films having mixed phases of anatase and rutile structures have higher transmittance than those with a rutile structure. The change in the optical transmittance may be correlated with the film thickness, the density of the films and the phase transformation (Mardare *et al.,* 2000). The refractive index of the films deposited at different P_{tot} was plotted as a function of wavelength as shown in Figure 5. The refractive index of the films was in the range of 2.42-2.51 at a wavelength of 550 nm, which corresponded to that reported by Amor *et al.,* (1997).

Due to the fundamental absorption in the vicinity of the band gap, the transmission decreased sharply as the wavelength reached that of ultraviolet radiation. The optical band gap E_g can be determined from the absorption coefficient α calculated as a function of incident photon energy $E\,(h\nu)$. Near the absorption edge, α can be expressed by Equation 1 (Asanuma *et al.,* 2004):

$$\alpha = \frac{-\ln(T)}{d} \qquad (1)$$

where, d is the film thickness.

The optical band gap E_g can be derived from Equation 2:

$$\alpha = (h\nu - E_g)^m \qquad (2)$$

where, m = 2 for indirect allowed transition.

The value of E_g is about 3.25 eV, which can be obtained by extrapolating the linear section to the photon energy axis, as shown in Figure 6.

CONCLUSIONS

The influence of sputtering pressure on the surface morphology, structure and optical properties was studied. It was found that with a

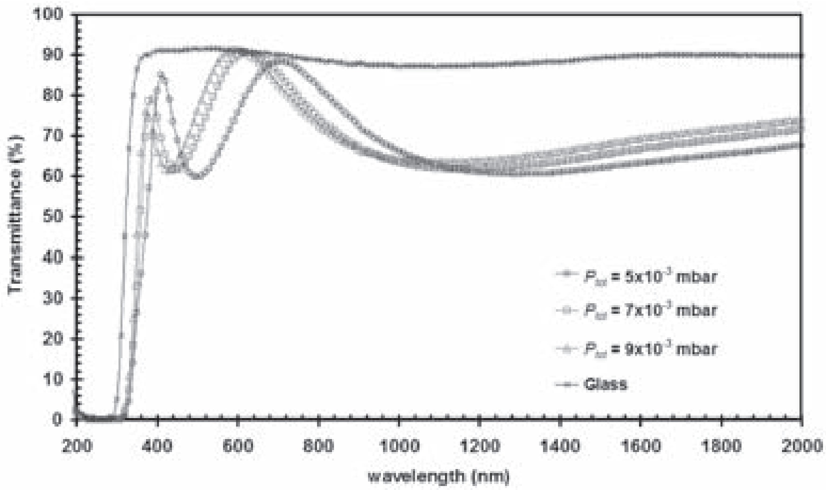

Figure 4 Transmission spectra of the TiO_2 films deposited on glass substrate at different P_{tot}.

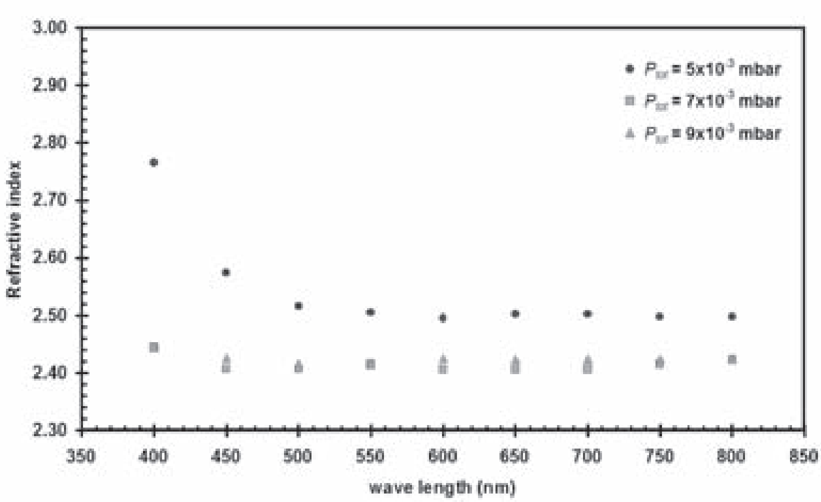

Figure 5 Refractive index of TiO_2 films as a function of wavelength deposited on glass substrate at different P_{tot}.

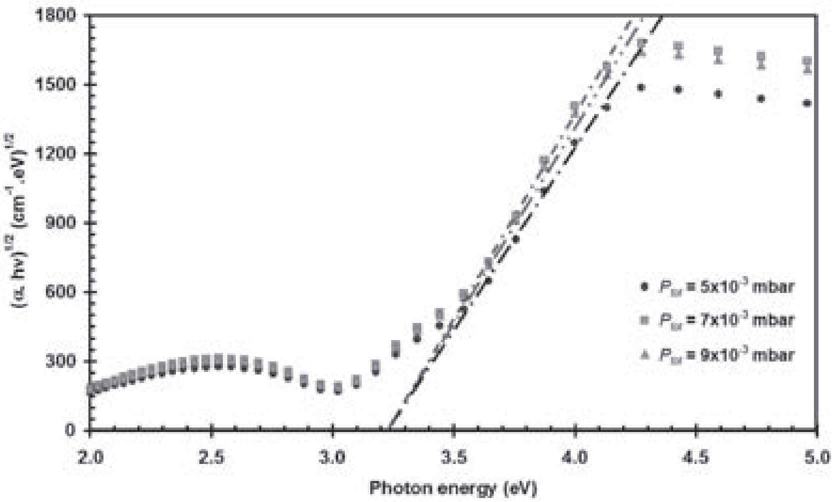

Figure 6 Dependence of (*ahÌ*)$^{1/2}$ on photon energy for TiO_2 films deposited on glass substrate at different P_{tot}.

decrease in the P_{tot}, the films changed from mixed phases of anatase and rutile to the pure rutile phase. The plasma structure effect is a factor that should be considered when depositing crystalline TiO_2 films by sputtering. For TiO_2 films, the refractive index in the visible spectrum was relatively high. In addition, the energy band gap was found to be 3.25 eV.

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