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Research Article

Fabrication and Characterization of Hydrophilic TiO_2 Thin Films on Unheated Substrates Prepared by Pulsed DC Reactive Magnetron Sputtering

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TiO_2 thin films were deposited on unheated silicon wafers (100) and glass slides by a pulsed DC reactive magnetron sputtering in an ultrahigh vacuum (UHV) system. The effects of both an operating pressure and deposition time on film structure, surface morphology, and optical property were studied. The film structure and microstructure were characterized by grazing-incidence X-ray diffraction (GIXRD) technique and transmission electron microscopy (TEM). The surface morphology was investigated by field emission scanning electron microscopy (FE-SEM). The optical property of the TiO_2 thin films was determined by spectroscopic ellipsometry (SE). The water contact angle measurement was also used to determine hydrophilicity of the films after exposed to UV light. The results suggested that the TiO_2 thin film at less than 40 nm was amorphous. As the thickness was increased, the mixture of anatase and rutile phases of TiO_2 began to form. By reducing the operating pressure during the film deposition, the rutile phase component can also be enhanced. Both the increased film thickness and decrease operating pressure were the critical factors to improve the hydrophilicity of the TiO_2 thin films.

1. Introduction

Titanium dioxide (TiO_2) is a well-known photocatalyst with good chemical stability, high refractive index, and good mechanical hardness. Photocatalytic reactions proceed under UV-irradiation, with photon energy greater than the band gap energy of TiO_2 anatase phase (3.20 eV). The electron hole pairs generated by absorption of a photon play also a fundamental role at the photo-induced superhydrophilicity. The electrons reduce Ti^{4+} cation to Ti^{3+} and the holes oxidize oxygen anions near the surface. Thereby oxygen vacancies are created. These vacancies can be occupied by water molecules creating adsorbed OH groups [1–3]. Thus, the surface energy is minimized and the surface becomes hydrophilicity. For these unique properties, TiO_2 can be used for preparation of self-cleaning, antifogging, and antibacterial coating.

Such TiO_2 thin films can be prepared by many methods which include sol-gel [4, 5], metal-organic chemical vapor deposition (MOCVD) [6], molecular beam epitaxy (MBE) [7], ion-beam assisted deposition [8, 9], and sputtering technique [10–14]. Reactive magnetron sputtering has become a preferred technique because of its applications in large area coating on glass, such as architectural glass and exterior rear view mirrors of the cars. Several literatures suggest modifications of structure; the structure, optical, and photo-induced hydrophilic properties can be modified by changing the deposition conditions, for examples, sputtering power,

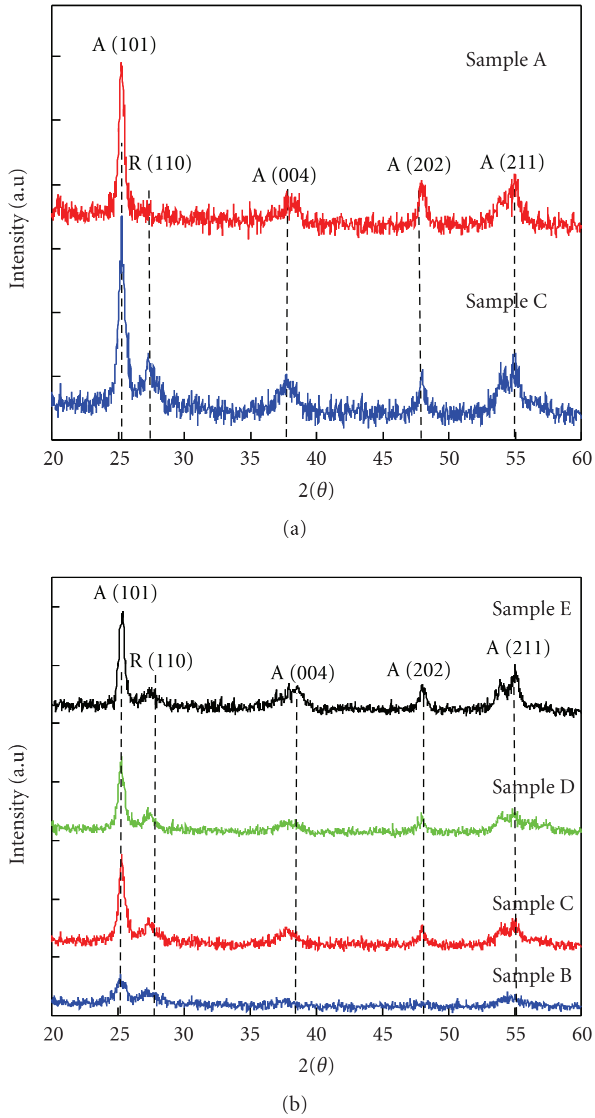

Figure 1: XRD patterns of TiO_2 thin films deposited on Si substrates at (a) two different operating pressures of 10 mTorr (sample A) and 3 mTorr (sample C), and (b) different deposition times of 30, 60, 90, and, 120 min (samples B, C, D, and E, resp.).

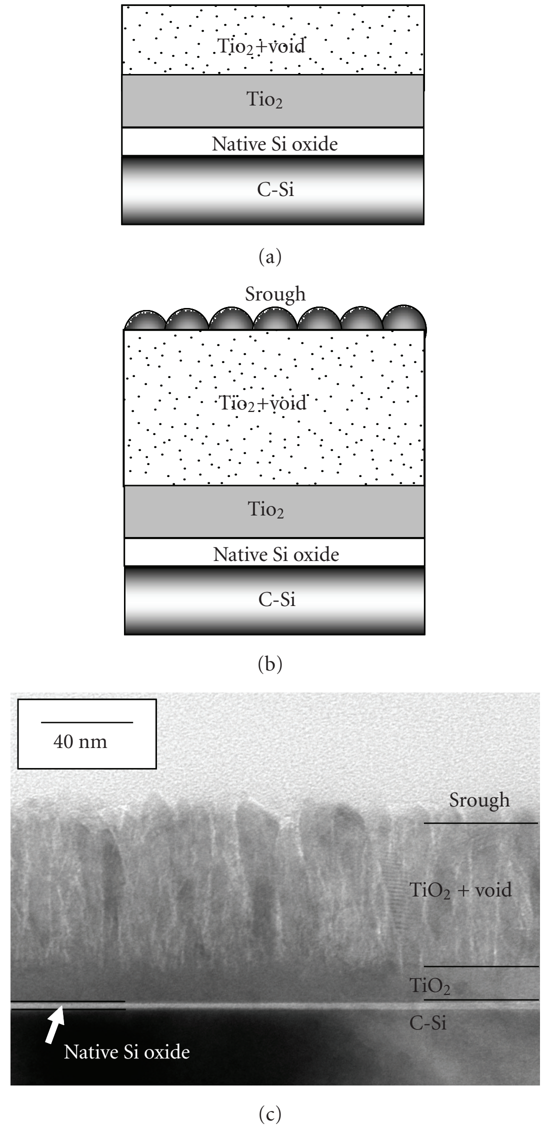

Figure 2: Ellipsometric model for TiO_2 thin films deposited on an Si substrate: (a) fitting model 1, (b) fitting model 2, and (c) cross-section TEM micrograph of TiO_2 thin film deposited at 10 mTorr (Sample A).

oxygen partial pressure, operating pressure, deposition time, substrate temperature, and postannealing treatment [13–19].

This work mainly focused on the effects of the operating pressure and the deposition time which critically affect the structural, optical, and hydrophilic properties of the TiO_2 thin films prepared by the pulsed DC reactive magnetron sputtering.

2. Experimental Details

Transparent TiO_2 films were deposited on unheated silicon wafers and glass slides using a commercial pulsed DC reactive magnetron sputtering system (AJA International, ATC 2000-F). Pure argon (99.999%) and oxygen (99.999%) were used as sputtering and reactive gas, respectively. Metallic titanium with purity of 99.995% and a diameter of 2 inch was used as a sputtering target. The base pressure of the deposition chamber was approximately 1×10^{-7} Torr. The pressures were monitored with Pirani, Baraton, and Penning pressure gauges when the flow rates of Ar and O_2 were controlled with mass flow meters (MKS). Both flow rates of Ar and O_2 were kept constant at 10 and 20 sccm, respectively. The pulsed DC power and frequency were kept constant at 400 W and 20 kHz, respectively. The deposition time, which directly affects the film thickness, and the operating pressure were selected as variable parameters. The operating pressure was controlled with a pressure control gate valve.

The silicon wafer (100) and glass substrates were cleaned by an ultrasonic washer with isopropanol and acetone

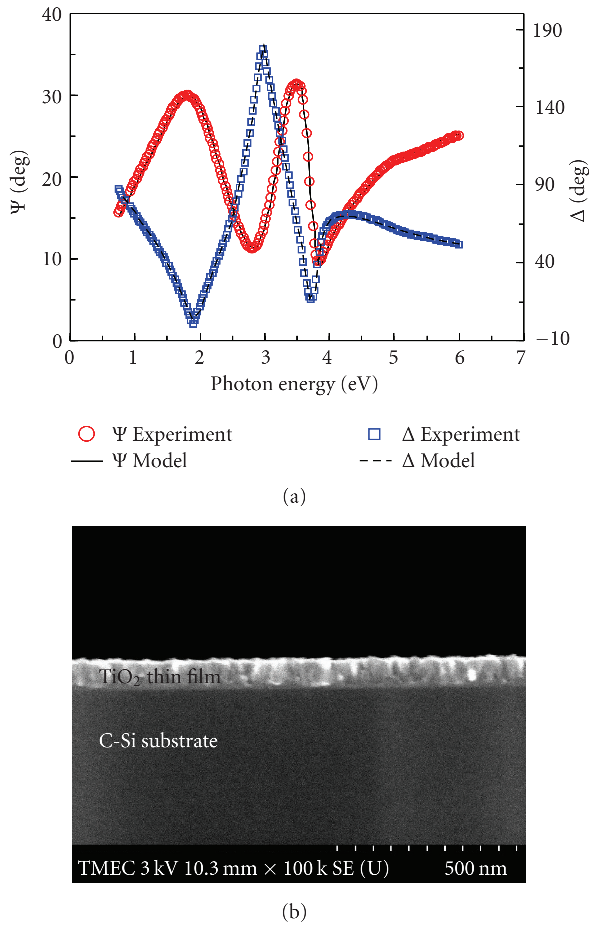

FIGURE 3: (a) Spectroscopic ellipsometry measurement and (b) FE-SEM cross-section image of an as grown TiO_2 thin film deposited on a Si substrate at an operating pressure of 10 mTorr.

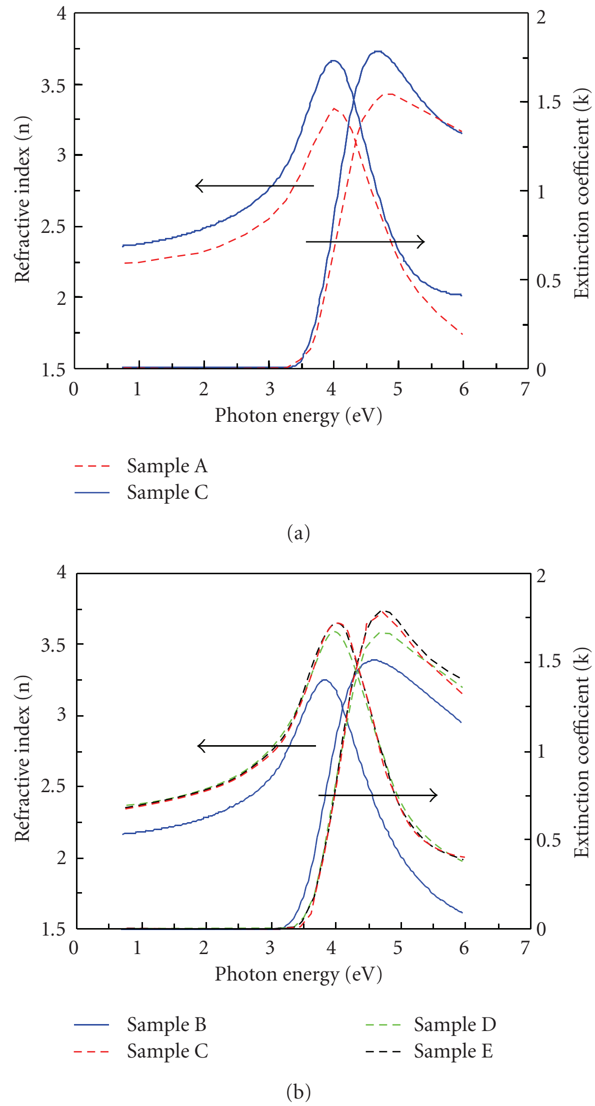

FIGURE 4: The variation of optical constants as a function of photon energy for TiO_2 thin films deposited on Si substrates: (a) two different operating pressures and (b) different film thicknesses.

successively, and dried in nitrogen atmosphere before being loaded into the deposition chamber. Prior to the deposition, the substrates and target were cleaned in argon plasma at 5 mTorr for 5 min in order to remove surface contamination and top oxide layer surface. All silicon and glass substrates were placed at 90 mm from the target. The TiO_2 thin films were deposited simultaneously on silicon and glass substrates at two operating pressures of 3 and 10 mTorr, respectively, with different deposition times of 30, 60, 90, and 120 min as shown in Table 1.

The structure of the films was characterized by an X-ray diffractometer (Rigaku, Ttrax III) operating with Cu-$K_{\alpha 1}$. The measurements were conducted at grazing incidence from 20–60°. The microstructure of the films was characterized by a transmission electron microscope (TEM, Jeol, JEM-2010). The morphology of the films was investigated by a field emission scanning electron microscope (FE-SEM, Hitachi, S-4700). The optical parameters, that is, the index of refraction and the extinction coefficient, were extracted from ellipsometric measurements using a variable-angle spectroscopic ellipsometer (VASE, J.A. Woollam). The VASE measurements, which also grave the film thickness, were performed at 70° incident angle, in the photon energy range 0.75–6.0 eV. The surface hydrophilicity was evaluated by the water contact angle measurement, using a commercial contact angle meter (Ramé-Hart Instrument, 250) with an experimental error less than 0.1°. The UV illumination was carried out using a black-light lamp with a power density of 1.2 mW/cm^2 and a maximum intensity centered at 365 nm as measured by a UV integrating radiometer. The water contact angle measurement was performed at room temperature in ambient atmosphere.

3. Results and discussion

3.1. Film Crystallinity by X-Ray Diffraction. First, the structures of TiO_2 thin films deposited at two different operating pressures and at equal thickness were compared. From

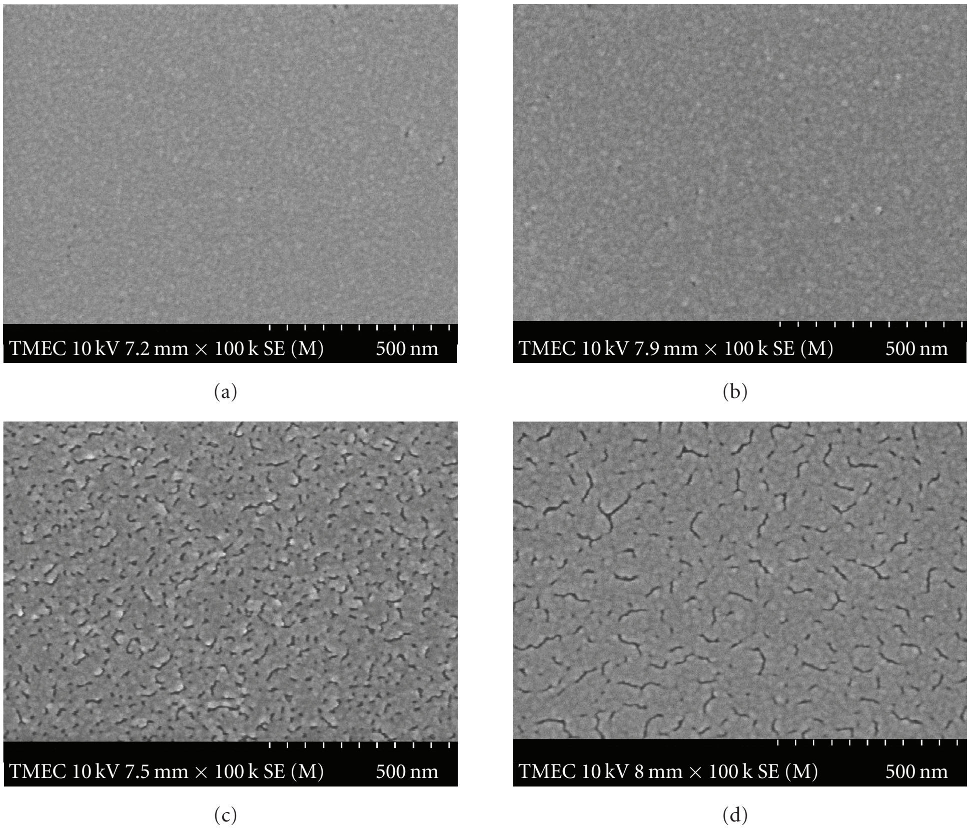

Figure 5: FE-SEM surface images of TiO_2 films deposited on Si substrates at different thicknesses (a) 40, (b) 85, (c) 120, and (d) 150 nm (samples B–E).

Table 1: Deposition conditions of TiO_2 thin films.

Sample	Operating pressure (mTorr)	Deposition time (min)	Thickness (nm)		Surface roughness (nm)
			FE-SEM	SE	SE
A	10	90	95	89	2.8
B	3	30	45	41	—
C	3	60	79	85	3.2
D	3	90	120	123	4.7
E	3	120	153	151	5.2

Table 1, the TiO_2 thin films deposited at 10 and 3 mTorr, denoted as samples A and C, respectively, had almost equal thickness of about 85 nm. The XRD patterns of both samples show that sample A deposited at high operating pressure exhibited a pure anatase phase and sample C deposited at low operating pressure showed a mixture of anatase and rutile phases. The formation of rutile phase of TiO_2 thin films on unheated substrate at low operating pressure is due to higher energy of the particles impinging on the growing film surface [12, 13]. Figure 1(b) compares the XRD patterns of the TiO_2thin films which were prepared at 30, 60, 90, and 120 min, and denoted as samples B, C, D, and E, respectively. It can be seen that all samples showed a mixture of anatase and rutile phases. Their relative intensities were gradually increased with increased deposition time, or increased films thickness [14]. However, sample B displays very low X-ray diffraction peak.

3.2. Spectroscopic Ellipsometry, FE-SEM, and TEM Characterization. In this work, the layer thickness was determined by spectroscopic ellipsometry (SE). The fitting of measured parameters of Δ and Ψ by SE was carried out by using a model as shown in Figure 2. An interfacial layer of native silicon oxide with an assumed thickness of 2 nm was incorporated because the Si substrates were not etched by hydrofluoric acid before deposition. A physical model was constructed in order to describe physically possible TiO_2 thin films. Generally, inhomogeneity was particularly considered for the island film growth which optically represented a mixture of dense material and void [20]. Chindaudom

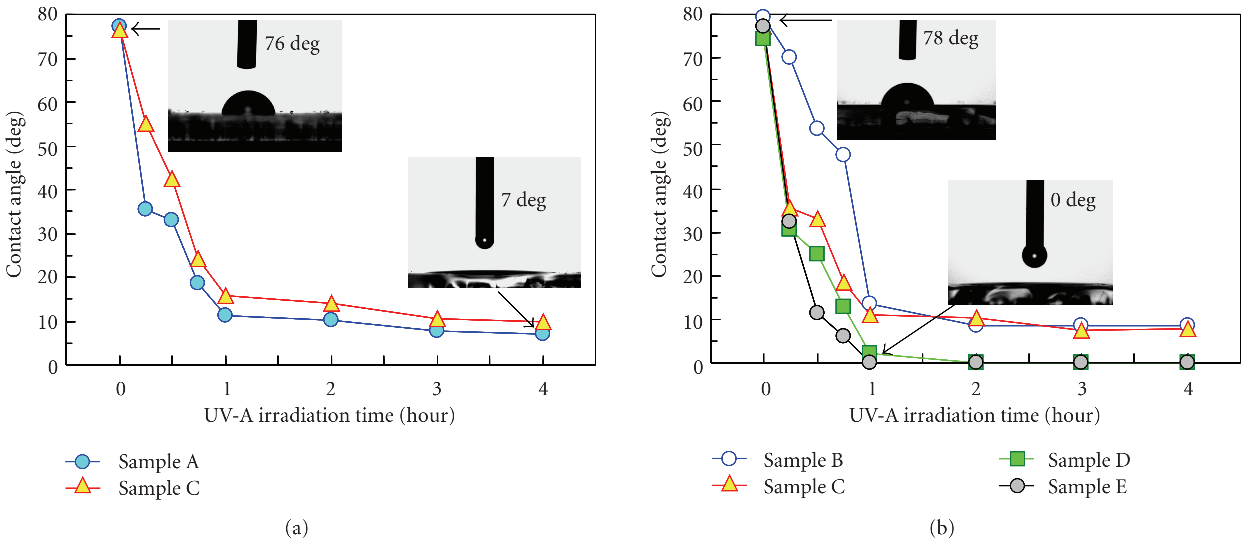

FIGURE 6: Water contact angle variation following the UV illumination time for the TiO_2 thin films deposited on glass slides at: (a) two different operating pressures and (b) different film thicknesses.

and Vedam [21] were able to determine inhomogeneous of transparent films by applying the effective medium approximation for describing the refractive indices by the Sellmerier dispersion equation. In present work, we used two models in analyzing the ellipsometric data. The first model, Figure 2(a), was used for deposited film with deposition time of less than 30 min. This model consisted of a dense TiO_2 layer, and a mixture of TiO_2 and void. The second model, Figure 2(b), was applied to the film with the deposition time of more than 30 min. This model consisted of a dense TiO_2 layer, a mixture layer, and surface roughness (Srough). The second model was confirmed by cross-section TEM micrograph of the film structure as shown in Figure 2(c). The columnar structure of TiO_2 layer was estimated at about 84 nm grown on approximately 2 nm thick native Si oxide. Bruggeman effective medium approximation (BEMA) was used to determine the optical parameters of the composition. The proposed optical dispersion model was a Cody-Lorentz oscillator in order to deduce optical band gap and exploit band-to-band transition regions between the band edge and the Urbach tail [9, 22–24].

Figure 3(a) shows the typical good fitting of the measured SE data of TiO_2 thin films for sample A and calculated values from the model as described above. The thickness and surface roughness of TiO_2 thin films for all samples (A–E), obtained from SE data, are shown in Table 1. The cross-section of the films for samples A–E was also observed by FE-SEM, as shown in Table 1. The results showed that the film thicknesses determined by SE agreed with those obtained by FE-SEM. It is seen that samples A and C, deposited at 10 and 3 mTorr, respectively, have almost equal thickness of about 85 nm. Therefore, it can be concluded that the deposition rate was decreased with the increased operating pressure.

Figure 4(a) shows the refractive index and the extinction coefficient of samples A and C. It can be seen that the refractive index of sample C was higher than that of sample A. Since it has been known that the refractive index of rutile was much higher than that of anatase, hence, the mixed anatase and rutile phases of sample C had higher refractive index than that of the pure anatase phase of sample A. Thus, the SE results agreed well with those of XRD results. The refractive index of TiO_2 films deposited at an operating pressure of 3 mTorr and different deposition times is shown in Figure 4(b). It was clearly seen that the refractive index of the films increased with increased deposition time or film thickness. The increase of film thickness resulted in the increase of film density.

FE-SEM micrographs of the TiO_2 thin films on silicon wafer at various deposition times are shown in Figure 5. It can be seen that the surface of TiO_2 films varied with deposition time or film thickness. Samples B and C showed quite smooth surfaces due to the smaller grain size. Samples D and E showed the larger grain size as the film thickness increases.

3.3. Photo-Induced Hydrophilic Activity. The hydrophilicity of the TiO_2 thin films was investigated by measurement of the water contact angle. Figure 6(a) shows the change of contact angle as a function of the UV-A illumination time of samples A and C deposited at 10 and 3 mTorr, respectively. The initial water contact angle was 77° for sample A and 76° for sample C. After the film surface was illuminated by UV-A light, the water contact angle started to decrease, that is, photo-induced hydrophilicity increases. Both samples had low water contact angle of about 7° after 4 hour of irradiation, which indicated good photo-induced hydrophilicity of these films. The comparison of photo-induced hydrophilic activity of TiO_2 thin films with the different thicknesses was shown in Figure 6(b). All films exhibited hydrophilic behaviors after irradiation for 4 hours. Among the thin films, the superhydrophilic activity was achieved from the films thickness of 120 and 150 nm on the samples D and E, respectively.

4. Conclusions

Pulsed DC reactive magnetron sputtering deposition without the external substrate heating has been successfully used for the growth of the crystalline TiO_2 films with the photo-induced hydrophilic activity. The XRD patterns of the films deposited at operating pressures of 3 and 10 mTorr showed the anatase phase, and the mixture of anatase and rutile phases, respectively. The strong effect of the operating pressure on the structure of deposited films was due to the plasma particle bombardment on the growing films. The effect of deposition time on the structure showed that, for a short deposition time, the structure was of pure anatase. The structure of the TiO_2 thin films became a mixture phase when the film thickness was increased. From the ellipsometric measurement, the refractive index of the films was found to increase with decreased operating pressure.

It is clearly seen that the photo-induced hydrophilic activity was also increased with the decrease of the operating pressure during the film deposition. On the other hand, the TiO_2 thin film with a thickness of 150 nm (sample E) deposited at an operating pressure of 3 mTorr showed a very good photo-induced superhydrophilic activity. Such results from the obtained this films can be utilized in many fields, such as self-cleaning and antifogging glasses.

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