ENGINEERING JOURNAL

Article

Total Pressure and Annealing Temperature Effects on Structure and Photo-induce Hydrophilicity of Reactive DC Sputtered TiO_2 Thin Films

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Abstract. Nano-crystalline Titanium dioxide (TiO_2) has been well-known as a one of the most useful semiconductor material for application in self-cleaning coating which contains hydrophilic property. In this research, the films were deposited on un-heated silicon and glass slide substrates by home-made reactive unbalance magnetron sputtering system at various total gas pressures of $3.0x10^{-3}$, $5.0x10^{-3}$ and $7.0x10^{-3}$ mbar. The as deposited thin films at $7.0x10^{-3}$ mbar annealed in the ambient air at 100^{O}C, 300 ^{O}C and 500^{O}C, respectively. The effect of total pressure and annealing temperatures on structure, surface morphology and hydrophilic properties were characterized by X-ray Diffraction (XRD), Atomic Force Microscope (AFM) and contact angle meter under UV illumination. The results reveal that the crystal structure, surface morphology and photo-induce hydrophilicity were strongly influence by total pressure and annealing temperature. The films showed mixed phase of rutile and anatase. The phase transition from rutile to mixed phase of anatase/rutile was observed with increase total pressure. In addition, the roughness of the films deposited at different total pressure increased from 2.1 to 5.3 nm which give a greater hydrophicity. The enhancement of crystallinity and hydrophilic properties were obtained by varied the annealing temperature. The phase mixture of anatase/rutite and annealed temperature of 300^{o}C show that the contact angle of thin film became 0^{o} after UV light irradiation which exhibited clearly superhydrohilic property.

Keywords: Hydrophilicity, TiO_2 thin films, reactive DC sputtered.

ENGINEERING JOURNAL Volume 16 Issue 3
Received 20 November 2012
Accepted 15 March 2012
Published 1 July 2012
Online at http://www.engj.org/
DOI:10.4186/ej.2012.16.3.79

This paper is based on the poster presentation at the German-Thai Symposium on Nanoscience and Nanotechnology 2011—Green Nanotechnology of the Future, GTSNN 2011, in Nakhon Ratchasima, Thailand, 13-16 September 2011.

DOI:10.4186/ej.2012.16.3.79

1. Introduction

Nano-crystalline Titanium dioxide (TiO_2) has been well-known as a one of the most useful semiconductor material for application in optical coatings [1, 2], microelectronic devices [3], and protective layers [4]. In the past decade, titanium dioxide has also attracted a great deal of interest due to its photo-induce behavior which turns the surface easy to clean the organic compound or called "self-cleaning". These properties are composes of photocatalytic and hydrophilic properties, the photocatalytic decomposition of organic material has been carefully studied [5-7] and the hydrophilic properties which have been intensive investigated by scientific research [8-10]. The mechanism of hydrophilic occur when the TiO_2 were illuminated by ultraviolet (UV) light with higher energy than the TiO_2 band-gap, inter-band transition can be induced resulting in the generation of electron–hole pairs. Such excited electrons or holes can diffuse to the TiO_2 surface and generate some kinds of radicals or ions which made TiO_2 surface able to absorbed water [11]. According of these properties, TiO_2 hydrophilicity has been applied in various fields, in which the self-cleaning and anti-fogging activities should be quite attractive for the application in architectural or automobile windows [12]. Furthermore, the photo-induced hydrophilicity was reported on amorphous, anatase and rutile phases of TiO_2 surfaces where water contact angle decreased after the UV illumination in air [13-15].

There are several reports to fabricate transparent TiO_2 thin films which have been mainly prepared by various methods such as sol–gel method [16], cathodic electrodeposition [9], plasma enhanced chemical vapor deposition (PECVD) [17], vacuum arc plasma evaporation [18] and sputtering [19-21]. In comparison with other methods, sputter depositions is one of the most widely techniques for large-area uniform coatings with high packing density and strong adhesion [22]. In addition, this method is easily to apply in industry and to accomplish thin film which has good quality in the large area [23-24]. The reactive sputtering technique for coating nanocrystalline TiO_2 thin film are mainly use as radio frequency (RF) and direct current (DC). The reactive dc sputtering technique provide a wide range to vary the sputtering parameters such as total pressure, partial pressure ratio, DC power or substrate temperature etc. [25]. It was well know that the crystal structure and properties of deposited thin film were varied with the modification of the sputtering parameters [26-28]. Therefore, some literatures have been published on the influence of post-annealing temperature which effect to the hydrophilic properties of TiO_2 films obtained by RF magnetron sputtering method [29-30], however, the studied of the relation between hydrophilicity and deposition parameter, especially the annealing temperature of DC magnetron sputtering deposited TiO_2 thin film were limited [25].

In this research, the TiO_2 thin films were deposited by DC magnetron sputtering under various total pressures on un-heated substrates with keeping the Ar to O_2 ratio constant. The objectives are to study the influence of the total pressure and post-annealing temperature on structure, surface morphology, hydrophilic property and established details in relation between the sputter deposition parameters and their hydrophilic property.

2. Experimental

TiO_2 thin films were deposited on glass slides and silicon wafer at room temperature by DC magnetron sputtering system without substrate heating during the sputtered process by using Titanium target (Ti disk of purity 99.97% with diameter of 54 mm) in a 200 W power of DC in a ratio of Ar to O_2 1:4 sccm mixed at various total pressure of 3.0×10^{-3}, 5.0×10^{-3} and 7.0×10^{-3} mbar. Figure 1. shows a diagram of home-made sputtering system, the cylindrical chamber of the magnetron with 31 cm in diameter and37 cm in height was connected to the vacuum pump system. The glass slides and silicon wafer substrates were cleaned by ultrasonic sequentially in the solutions of trichloroethylene (TCE), acetone and alcohol, respectively. First, the pressure of the vacuum chamber was kept below 10^{-5} mbar. Then Ar (purity 99.999%) and O_2 of purity (99.999%) was emit to the vacuum chamber which systematic controlled by mass flow controller (mks type 247D). Before deposition, the target was pre-sputtered for 10 min for surface cleaning and each film deposited for 3 hour. The substrate heating and biasing voltages are not use during the deposition. After that, the as deposited films were post-annealed at different temperature of 100^{O}C, 300^{O}C and 500 ^{O}C, respectively, and kept for 2 h each.

The crystal structure of the TiO_2 thin films was characterized by X-ray diffractrometer (Rint 2000, Rigaku corporation) with Cu Kα radiation. The surface morphology and thickness were evaluate by an atomic force microscope (Nanoscope IV, Veeco Instrument Inc.) and contact angle of water on TiO_2

surface measured by contact angle meter (Erma, Tokyo) before and after irradiation with ultraviolet light (Phillips CLEO COMPACT 15W) for 5 hour.

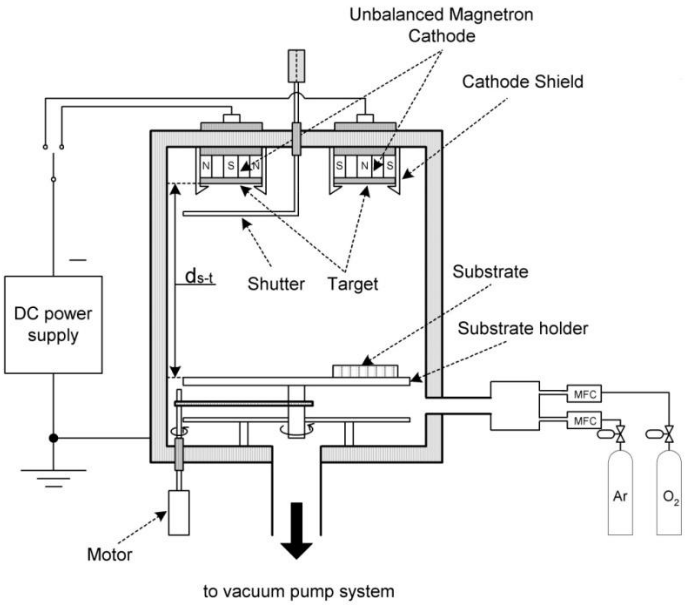


Fig. 1. Schematic diagram of the DC magnetron sputtering apparatus.

3. Results and Discussions

3.1. The Crystallization of TiO_2 Thin Films

3.1.1. The Influence of Total Pressures on Crystallization

Figure 2. show XRD patterns of TiO_2 thin films deposited at different total pressures. The results show that the films deposited at total pressure of 3.0×10^{-3} mbar exhibited only polycrystalline rutile structure which diffractive angles 2θ of the samples are 25.3^o, 27.5^o, 36^o, 56.5^o and 41.3^o are attributed to rutile (110), rutile (101), silicon (100) and rutile (111) planes, respectively. The XRD pattern of TiO_2 films deposited at 5.0×10^{-3} and 7.0×10^{-3} mbar composed mixed of anatase and rutile phases at diffractive angles 2θ of 25.3^o and 27.5^o corresponded to anatase (101) and rutile (110) however the intensity of rutile structure has a higher than anatase.

In case of TiO_2 films deposited at low total pressure, we found that the TiO_2 films have only polycrystalline rutile structure. When total pressure increase anatase phase was appeared also attributed to Zeman and Takabayashi [19] reported that the "anatase phase exhibit for higher total pressure, XRD intensity decreased and board peak appeared with total pressure which corresponding to decrease crystal structure of TiO_2 thin films". The phase evolution of TiO_2 structure was attributed to the sputtered energy of atom during the deposition process which depended on deposition parameters. In this research, the total pressure has a stronger effect on the phase evolution and the crystallinity of the TiO_2 films. The energies of sputtered particles that reflected fast neutrals at the target, ejected secondary electrons and finally deposited particles seem to be crucial factors in determining which phase is formed on the substrate. An increase in the total pressure increases the density of gas particles in the chamber and decreases the cathode potential, which influences the probability of collisions and the acceleration of particles and consequently the particle energy [19]. The relation between total pressures and phase evolution were discussed. The rutile structure is a high temperature phase which preferable form at high energy bombardment given by low total pressure deposition whereas when an increase in the total pressure will reduce the mean free path of particle, the decreased of deposited atom energy with enhancement of low activation energy for the phase formation resulting the mixed phase of anatase and rutile structure were observed.

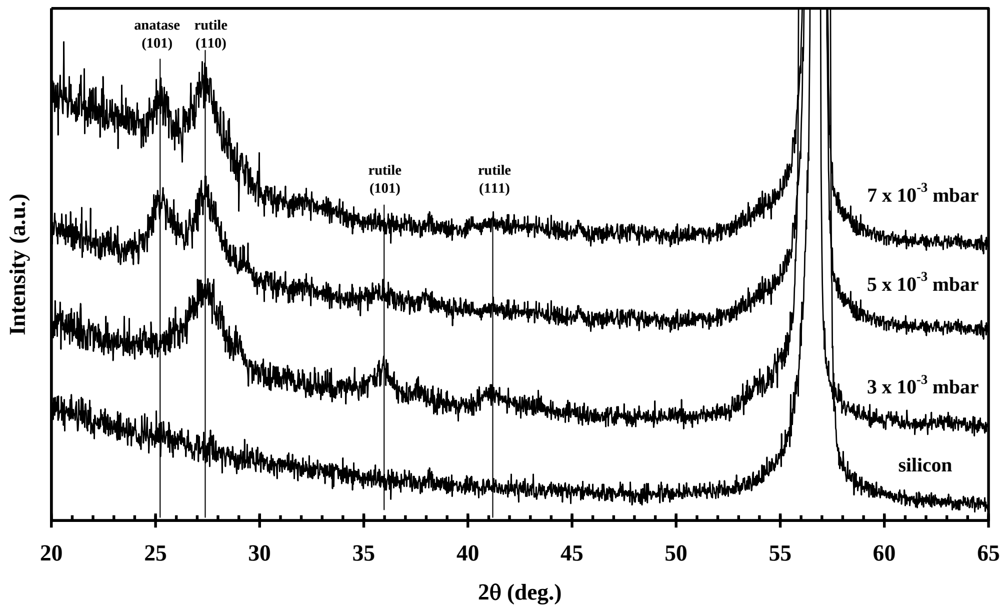


Fig. 2. XRD patterns of TiO_2 thin films deposited at various total pressures.

3.1.2. The Effect of Annealing Temperature on the Crystallization

The XRD patterns of TiO_2 thin films deposited at room temperature (7.0 x 10^{-3} mbar) were annealed at various temperatures of 100, 300 and 500 ^{o}C. Figure 3 shows that all samples posses of characteristic peaks mixed with anatase and rutile structure, suggesting that the film have polycrystalline structures. The diffractive angles 2θ of the samples at room temperature and anneal at the temperature range from 100 ^{o}C to 500 ^{o}C are 25.3^{o}, 27.5^{o}, 36.2^{o}, 41.2^{o} and 54.6^{o} which are attributed to anatase (101), rutile (110), rutile (101), rutile (111) and rutile (220), respectively, demonstrating that the films possess combined anatase and rutile structures. It was found that the all TiO_2 films have high crystallinity, a board peak appeared and highly XRD intensity with annealing temperatures which are corresponding to improve crystal structure of TiO_2 thin films by heat treatment. The results are also to be consistent of many researcher whom reported that "thin films show higher crystallinity with increase temperature [25, 29-31]". It was revealed that the XRD intensity of rutile (110) plane higher compare than that of anatase (101) plane for all samples. As the further increase annealing temperature, the dramatically increase rutile (110) intensity of were observed at the temperature of 500^{o}C which related to the high-temperature formation of rutile stable phase.

These investigations show that the substrate temperatures as well as the annealing temperature strongly influence the crystallographic structure of TiO_2 thin films. When the substrates were annealed after deposition, the modifications of crystallinity may be explained according to the increase of the adatom mobility at the substrate surface which effects their atom diffusion to more stable thermodynamically sites corresponding to well define structural arrangement [31]. Furthermore, the energy transferred to the atoms are provide more energy for surface diffusion resulting improve the crystallinity of the anatase (101) plane and much enhances prefer orientation of rutile (110) plane because of the rutile structure were formed by high energy formation process, were clearly shown in Fig. 3.

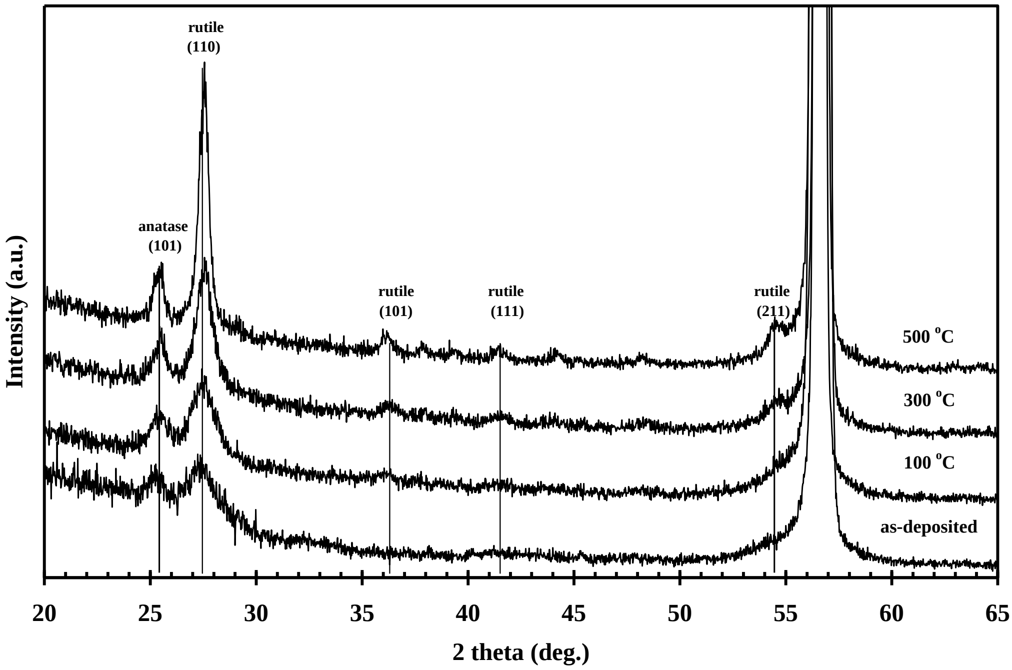


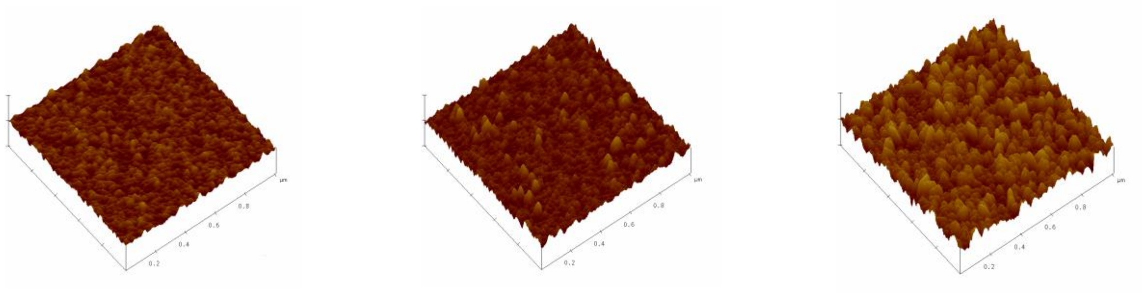
Fig. 3. XRD patterns of TiO_2 thin films at different annealing temperatures.

3.2. The Surface Morphology of TiO_2 Thin Films

3.2.1. The Effect of Total Pressure on the Surface Morphology of TiO_2 Thin Films

In Fig. 4, surface morphologies of the as-deposited TiO_2 thin films for three values of total pressure are displayed. The surface morphology at total pressure of 3.0×10^{-3} mbar as-deposited thin films (Fig. 4(a)) is mainly composed of individual small grain which has same size. Some of grains deposited at total pressure of 5.0×10^{-3} mbar were bigger than 3.0×10^{-3} mbar, as shown in Fig. 4(b). At total pressure 7.0×10^{-3} mbar (Fig. 4(c)) exhibited a much large grain size spread across its surface. When the total pressure increase, the surface morphology will be changed, grain size became bigger were proposed by Yamakishi et al. [11] and film thickness was decreased from 168.67 nm to 138.67 nm with increase of total pressure which according to Sirghi et al. [8] reported that the thickness decreased with total pressure. The total pressures varied from 3.0×10^{-3} to 7.0×10^{-3} mbar are crucial factors which influenced to the thickness and surface roughness of the films summarized, as shown in Fig. 5. The gradually increase of rms roughness value were observed from Fig. 5, confirmed by the previous study of Tölke et al. indicated the same trend of roughness which determine in terms of surface area varied with increase the total pressure [25].

It can be conclude that the total pressure play as an importance role to the film thickness and surface morphology. From the AFM measurements show that the thickness decreased strongly by the increase of the total pressure. It can be explained by the influence of the gas pressure on the sputtering rate that decreasing the mean free path between sputtered atoms with increased the total pressure. Therefore, high probability of the scattering collisions between the sputtered atoms and the atoms of the background gas which decreased the deposition rate resulting the decreased of film thicknesses. The morphological features of films change accordingly to the low energy scattered sputtered atoms induced low adatom mobility on surface yielding the aggregation of adatom were confined, thus the rough and valley between individual grains were obtain at highest total pressure, compare to high packing energy of smooth morphology deposited at low pressure.



(a) (b) (c)

Fig. 4. Surface morphology of TiO_2 thin films deposited at various total pressure: (a) 3.0×10^{-3} mbar, (b) 5.0×10^{-3} mbar and (c) 7.0×10^{-3} mbar.

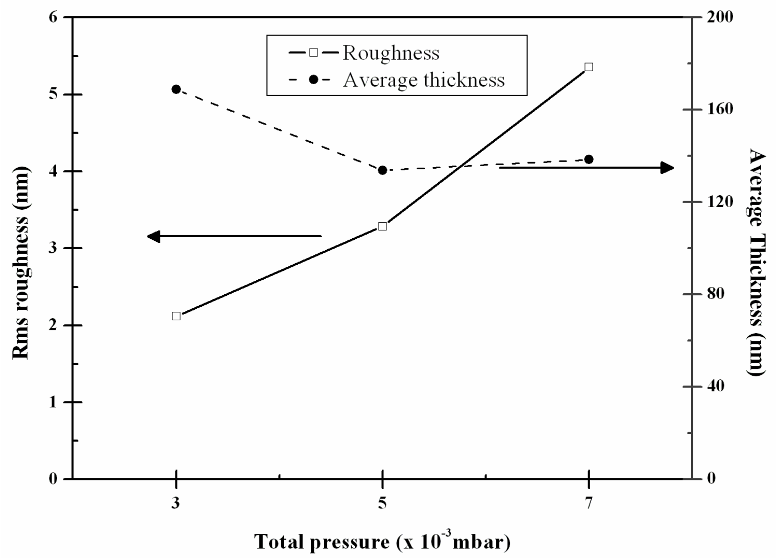
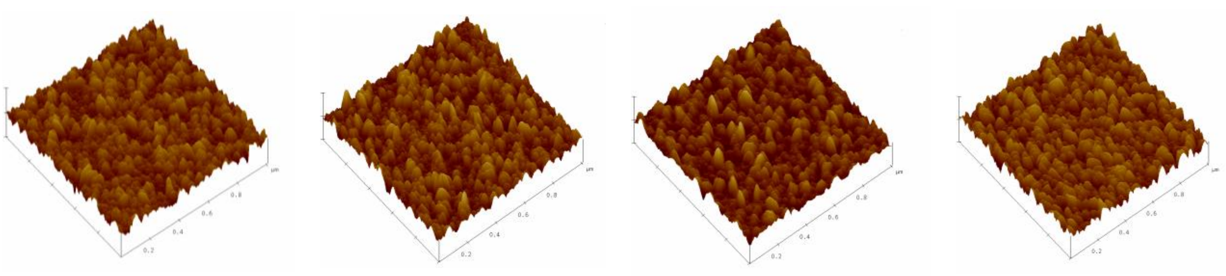


Fig. 5. The thickness and surface morphology of TiO_2 thin films deposited at various total pressures.

3.2.2. The Effect of Annealing Temperature on the Surface Morphology of TiO_2 Thin Films

The surface morphologies of the as-deposited (7.0 x 10^{-3} mbar) TiO_2 thin films with annealed from 100 °C to 500 °C are shown in Fig. 6. From AFM images, it was found that as-deposited thin films (Fig. 6(a)) are composed of different grain sizes, surface morphologies are different with and without substrate annealing. The grain size of the crystalline becomes bigger (Fig. 6(b), 6(c), and 6(d)) and film thickness was decreased from 138.4 nm to 121.9 nm, whereas rms roughness was almost constant as increasing annealing temperature. These surface morphologies were summarized in the Table 2.



(a) (b) (c) (d)

Fig. 6. AFM images of TiO_2 thin films (a) as-deposited and post-annealed at (b) 100°C, (c) 300°C, and (d) 500°C.

Table 1. Surface morphology of sputtered TiO_2 at different post-annealing temperatures.

Annealing temperature (°C)	**As-deposited**	**100**	**300**	**500**
Rms roughness (nm)	5.3	5.0	4.9	5.7
Average thickness (nm)	138.4	138.8	134.9	121.9

3.3. The Hydrophilic Property of TiO_2 Thin Films

3.3.1. The Effect of Total Pressure on Hydrophilic Property of TiO_2 Thin Films

The as-deposited TiO_2 thin films at various total pressures were performed hydrophilic property under UV irradiation. Figure 7 shows the change in the contact angle as a function of the UV irradiation time of the TiO_2 thin films deposited under total pressure of 3.0×10^{-3}, 5.0×10^{-3} and 7.0×10^{-3} mbar. When the films were irradiated by UV light, contact angle of water will decrease. It was revealed that the water contact angle of thin films deposited at 3.0×10^{-3} and 5.0×10^{-3} mbar decrease slowly, where as the decrease speed was faster and contact angle become 0° for film deposited at 7.0×10^{-3} mbar which exhibited clearly superhydrohilic property.

It was concluded that the total pressures are strongly effect on hydrophilic property of TiO_2 thin films. When increase total pressure, the water contact angle decrease fast and showed super hydrophilic property which contributed to improve hydrophilic property by increased total pressure [11, 20]. The reason of high total pressure perform photo-induce superhydrophilic property are describe by the phase formation and surface roughness. It was not only an pure anatase phase of TiO_2 thin film is generally preferred use for superhydrophilicity coating according to perform excellent photo-induce hydrophilic activity [25, 29] but in our work, the mixture anatase/rutile phase obtained by home-made sputtering system can be also clearly show the superhydrophilic properties. In addition, the rougher surface, bigger grain size contain many internal voids separated the grain boundaries will give a greater surface area to explore the UV irradiation for photo-induce mechanism were observed in Fig. 4., corresponding to Du et al. [32] indicated that the "rough surface also enhanced the hydrophicity".

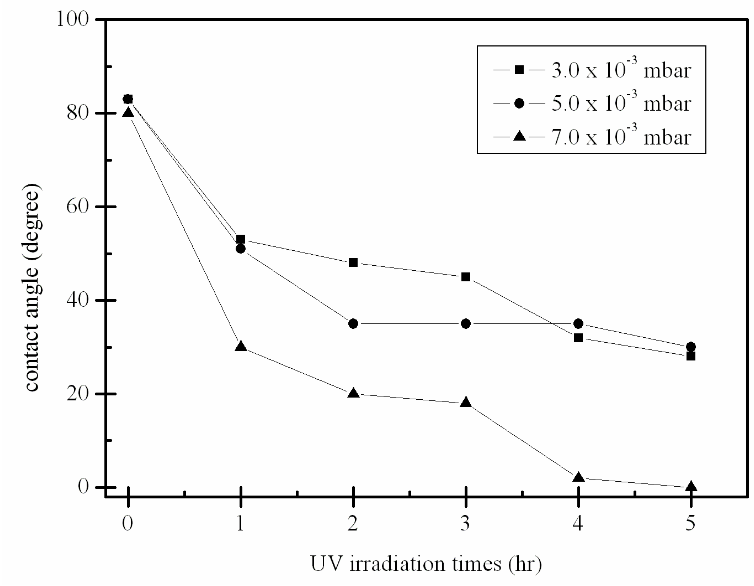


Fig. 7. Water contact angle of TiO_2 thin films deposited at different total pressure under UV irradiation time.

3.3.2. The Effect of Annealing Temperature on Hydrophilic Property of TiO_2 Thin Films

From Fig. 8 we revealed the relation between the hydrophilic properties of the TiO_2 thin film deposited at 7.0×10^{-3} mbar and annealing temperature. The measurement obtained from contact angle of dropped water on the films surface by contact angle meter during UV-irradiation. All films showed hydrophilic properties, It can seen that contact angle remarkably change when the annealing temperature increase to 300°C was contributed to and contact angle related to zero for the film annealed at 300°C is shorter than that at room temperature and 100°C, respectively. However, when the annealing temperature reaches to 500°C, the contact angle after UV irradiation increases a little bit which according to Ye et al. [29].

It can be summarized that the post-annealing temperature influence strongly to the hydrophilic properties which able change the decreasing of water contact angle on TiO_2 surface by applied external to the films resulting improve the hydrophilic properties. This is called thermo-induce hydrophilicity. There are many researchers already clearly explain about the mechanism of UV-induce hydrophilic [6, 8, 16] whereas the different explanation in detail about thermo-induce hydrophilicity were discuss by various way of three aspects: (1) the cleansing effect, (2) the crystal phase transition and (3) the change of surface roughness [29, 30]. First, Ye et al. [29] revealed that the "annealing can remove superficial organic contaminants to expose the films to the adsorbent water molecules". Second, it is known the hydrophilic property depended on crystal phase and crystallinity of the films [30]. Figure 2 and 8 revealed that the films composed of mixtures anatase with rutile structure. The annealing temperature will induce the crystallinity, thus the hydrophilicity get a rapidly change. It was observed that the as deposited films exhibit poor hydrophilicity when annealing temperature elevated in the rage of 100 – 300°C, the contact angle remarkably decrease resulting turn to perform superhydrophilicity properties faster with 4 and 3 hour by UV explore, respectively. So, it can conclude that the hydrophilicity enhancement by increasing the crystallinity of anatase and rutile phases which given by annealing effect on the superficial cleaning. At annealing temperature of 500°C, the crystallinity of rutile phase were dramatically increase which can also exhibit the hydrophilicity, however poorer than 300°C due to the much highly crystallinity compare to anatase phase. Thus rutile decrease photo-induce hydrophilicity because of it is low hydrophilic activity than anatase TiO_2 [33]. The last aspect involve the surface roughness evolution, unfortunately the about constant of roughness value were observed in this work. The results from three aspects can be regard as crystal structure is a major factor in hydrophilic properties.

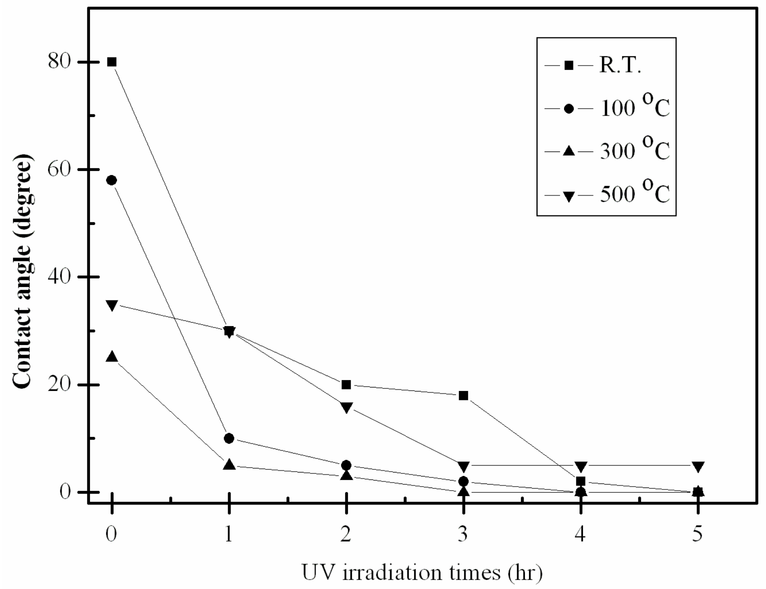


Fig. 8. Water contact angle of as- deposited TiO_2 thin films and annealed at various temperatures under UV irradiation time.

4. Conclusions

Nanocrystalline hydrophilicity TiO_2 thin films were successful deposited by home-made reactive unbalance magnetron sputtering system. The crystal structure, surface morphology and photo-induce hydrophilicity were depended strongly on values of the total pressure and annealing temperature. The XRD results show that the crystal phase of rutile transform to anatase/rutile with increase the total pressure, whereas annealing temperature will improve crystallinity. A larger grain size and rougher surface were observed with increased the total pressure. The rms roughness and thickness were in the range of 2.1-5.3 nm and 137.67 - 168.67 nm, respectively, but the decrease of thickness from 138.4 to 121.9 nm and almost constant of roughness value were indicated by AFM measurement. The films deposited at highest total pressure of 7.0×10^{-3} mbar perform superhydrophic property. The phase mixture of anatase/rutite with annealed temperature of 300°C exhibit best photo-induce hydrophilic activity. Moreover, the crystal structure is a key factor to the difference of their hydrophilicity.

Acknowledgement

This work was supported by Thailand Center of Excellence in Physics (ThEP), Commission on Higher Education, Ministry of Education, Thailand.

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