

Full Length Research Paper

Persistent hydrophilicity for Titanium oxide (TiO₂) thin films by Silicon oxide (SiO₂) over nanolayers

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SiO₂ thin layers in thicknesses (1, 5, 10, 18 nm) on TiO₂ thin layer in thickness 79 nm deposited by reactive RF sputtering technique. The deposited films were heat treated at temperatures (200, 400, 500, 600°C). The surface properties of thin films by atomic force microscopy (AFM), surface chemical composition by X-ray photoelectron spectroscopy (XPS) and self-cleaning effect in bi layers, were studied. In addition, enhanced hydrophilicity property in the films under the effect of annealed temperature and persistence without UV light illumination were evaluated.

Key words: Nanolayers, X-ray photoelectron spectroscopy (XPS), hydrophilicity, annealed temperature.

INTRODUCTION

Titanium oxide exhibits hydrophilicity and self-cleaning properties as exposed to UV. As TiO₂ surface is exposed to UV radiation, electron/hole pairs are created inducing an oxide-reduction reaction. To maintain the status of surface oxygen vacancies by OH groups that exist in atmospheric water, superhydrophilicity property (that is, water contact angle of near zero with surface) on the surface is generated (Wang et al., 1999; Sakai et al., 2001). However, a superhydrophilic surface is converted to an hydrophobic surface in the absence of UV illumination due to replacement of OH groups with atmospheric oxygen. As reported by other researchers (Machida et al., 1999; Ren et al., 2004; Guan, 2005; Lee et al., 2004; Maeda and Yamasaki, 2003; Yu et al., 2002) the addition of SiO₂ to TiO₂ enhances the hydrophilicity and it is maintained in dark without UV light radiation. According to X-ray photoelectron spectroscopy experiments, the formation of Ti-O-Si bond at the TiO₂-SiO₂ interface led to important changes in the electronic

structure of over layer (Sanz et al., 1998). This changes enhanced the acid property of surface and result in improving hydroxyl groups at the surface of film (Guan et al., 2003, 2005), which led to increasing hydrophilicity and the surface of film maintained. In this work, SiO₂ was more physical and chemically stable than TiO₂ and also Si-OH surface bond was more stable than Ti-OH; also, bi-layer films was deposited with SiO₂(top)/TiO₂(under) (Komatsu et al., 1998; Guan et al., 2004). More recently, it was observed that SiO₂-TiO₂ interface is formed in the sufficiently high annealed temperatures (Permpoon et al., 2008). It was found that the thickness of SiO₂ on TiO₂ layer had important effect on increasing of hydrophilicity property (Hattori et al., 2000). In other researches, enhanced natural superhydrophilicity and its conservation in TiO₂-SiO₂ composite thin films or bi-layer films deposited in method of sol-gel at special temperatures and thickness have been investigated (Houmard et al., 2007; Liu et al., 2009). In this study, we deposited the

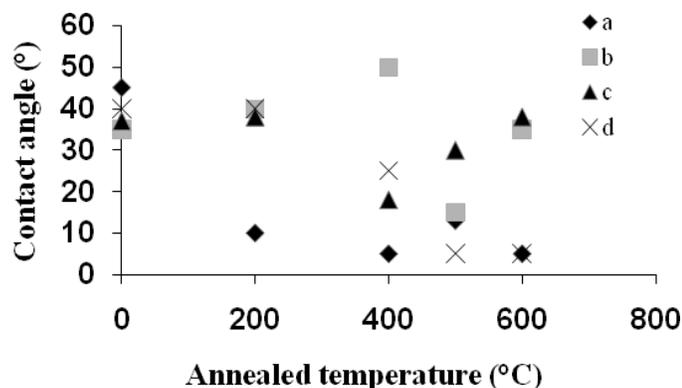


Figure 1. Water contact angle on surface of the as-deposited and annealed SiO₂/TiO₂ bilayer films in the absence of UV irradiation at room temperature for various thicknesses of the SiO₂ layer: a) 1, b) 5, c) 10, and d) 18 nm.

SiO₂/TiO₂ bi-layer films by using radio frequency reactive magnetron sputtering at different thicknesses of SiO₂ over layer and various annealed temperatures and evaluated the hydrophilicity and persistence in a dark place.

EXPERIMENTAL DETAILS

Fabrication of SiO₂/TiO₂ bilayer films

SiO₂/TiO₂ bilayer films were deposited on float glass substrates (Kaveh Glass Industry Group) by using radio frequency (RF) reactive magnetron sputtering. The base pressure of the sputtering chamber was $\sim 10^{-7}$ Torr (133322×10^{-10} Pa). To grow the TiO₂ (SiO₂) target (with purity of 99.9%) was reactively sputtered at pressure of 100 m Torr (13.3322 Pa) in an Ar/O₂ (60/40) discharge gas. Thickness of the as-deposited-beneath TiO₂ layer was considered 80 nm, while thickness of the as-deposited SiO₂ over layer was adjusted 1, 5, 10 or 18 nm. Thickness of the deposited films was measured by using an interferential optical technique. The as-deposited bilayer films were then annealed at 200, 400, 500, 600°C in air for 30 min.

Hydrophilicity and material characterizations

Surface hydrophilicity of the bi layer films was evaluated by measuring water contact angle on surface of the films. Experiments were performed under an ambient condition using a digital camera (with 2 mega pixel resolution) and suitable software (LB-ADSA). Before any experiment, surfaces of the films were washed with distilled water, acetic acid and ethanol. Then, a distilled water droplet was dropped on the film and water contact angle was measured with accuracy better than $\pm 5^\circ$. Then, the superhydrophilic samples (with the contact angle $< 5^\circ$) stored within plastic covers in dark to check any variation in the water contact angle of the films by elapsing the time (up to six weeks) under no UV irradiation. Super-hydrophilicity of the films was also studied by measuring the water contact angle under UV light illumination. In this work, a 6-W mercury (Philips) UV source with wavelengths ≥ 254 nm was used. To evaluate self cleaning effect, surface of the films was contaminated by the special oil and after exposure to UV

illumination. To study the surface topography of the films, a Park Scientific Model CP-Research (VEECO) atomic force microscopy (AFM) was utilized at a non-contact mode. To investigate the surface chemical states of the films, X-ray photoelectron spectroscopy (XPS) was used. The XPS data were acquired by using a hemispherical analyzer with an AL K α X-ray source operating at energy of 1486.6 eV and a vacuum better than 10^{-7} Pa. The binding energy of the XPS peaks was calibrated by fixing the C(1s) peak to 285 eV. SDP Ver. 4.0 software was applied to deconvolute and analyze the XPS peaks. The peaks were deconvoluted by using Gaussian-Lorentzian components (90 to 10%) with a constant FWHM for each component after a Shirley background subtraction. The elemental compositions of the films were determined using area ratio of the deconvoluted XPS peaks and the sensitivity factor (SF) of each element in XPS.

RESULTS AND DISCUSSION

Hydrophilicity and self-cleaning

Figure 1 shows hydrophilicity of the SiO₂/TiO₂ thin films (with various thicknesses of the SiO₂ nanolayer ranging from 1 to 18 nm) annealed at the different temperatures of 200, 400, 500, 600°C, as compared to that of the as-deposited film, in the absence of UV irradiation. The as-deposited films in all thicknesses of SiO₂ nanolayer showed contact angles $> 35^\circ$. In case of the SiO₂/TiO₂ with thickness of 1 nm, very good hydrophilicity with contact angle $\sim 5^\circ$ at annealed temperatures of 400, 600°C and also thickness of 18 nm at annealed temperatures of 500, 600°C was observed. With regard to the above results, the annealing temperature in SiO₂ various thicknesses play an important role in enhanced hydrophilic property without UV irradiation.

To check the self-cleaning property of the bilayer films, we selected the films which initially presented a hydrophilic property with the water contact angle $< 20^\circ$ in the absence of UV irradiation (based on the results of Figure 1). Then, the films were contaminated by the oil layer and exposed to the UV irradiation for 4 h. Table 1 shows water contact angle on surface of the contaminated SiO₂/TiO₂ bilayers before and after UV irradiation. It is seen that the oil contamination resulted in increasing the water contact angle of the films from $> 5^\circ$ around 30° , indicating disappearing of the superhydrophilic property of the films. However, after 4 h UV irradiation the films showed their natural superhydrophilic property, indicating the role of the beneath TiO₂ layer as an effective photocatalyst for removing the oil contamination layer.

In order to study persistence of the superhydrophilicity of the film photocatalytically under UV irradiation, the water contact angles were measured in one week time intervals as shown in Figure 2. The SiO₂(5 nm)/TiO₂ annealed at 500°C was the longest superhydrophilicity (up to six weeks) among the samples. It should be noted that the superhydrophilicity of these films reappeared

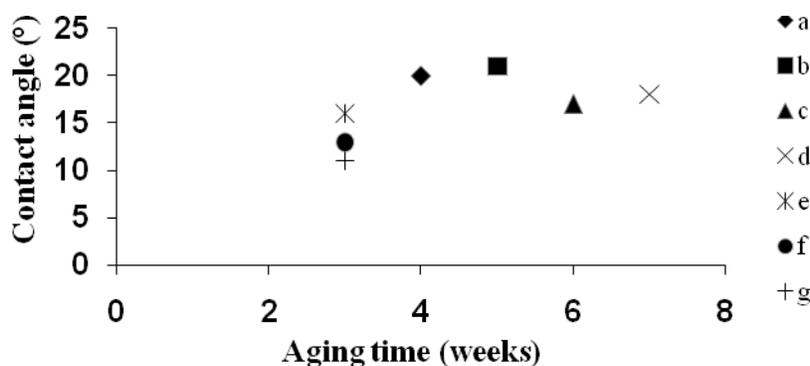


Figure 2. Persistence of water contact angle on surface of $\text{SiO}_2/\text{TiO}_2$ bilayers with the SiO_2 thickness (at the annealing temperature) of: a) 1 nm (400°C), b) 1 nm (500°C), c) 1 nm (600°C), d) 5 nm (500°C), e) 10 nm (400°C), f) 18 nm (500°C), and g) 18 nm (600°C).

Table 1. Results of the self-cleaning experiments.

SiO ₂ thickness	Water contact angle (°)	
	Oil contaminated state	UV irradiation time (4 h)
1 nm (400°C)	38	5
1 nm (500°C)	33	5
1 nm (600°C)	35	5
5 nm (500°C)	30	5
10 nm (400°C)	30	5
18 nm (500°C)	33	5
18 nm (600°C)	35	5

after a simple rinsing, as similarly reported by Houmar et al. (2011).

In Figure 2, the water contact angles with surface of the films were represented at the time of removing of the superhydrophilicity property and the contact angles were measured 5° at the times of before.

AFM analysis

To investigate the effects of heat treatment on surface topography and consequently on the hydrophilicity of the films morphology, AFM was utilized. Figure 3 shows AFM image of the $\text{SiO}_2(5 \text{ nm})/\text{TiO}_2$ films (the films with the longest superhydrophilicity) before and after annealing at 500° .

For evaluating the effect of surface roughness on the hydrophilicity of the thin films, the water contact angles measured on surfaces of the $\text{SiO}_2(5 \text{ nm})/\text{TiO}_2$ films were compared with the water contact angles modified through Wenzel's equation (Wenzel, 1949) (the contact angles in which the effect of surface roughness was eliminated), as shown in Figure 4. It is seen that although surface

roughness could be partially effective in decreasing the measured contact angle especially at annealing temperatures $\geq 400^\circ\text{C}$, it was not the main parameter describing the superhydrophilicity of films and its variation. In fact, surface chemical composition can be considered as one of the important parameters in this regard, as discussed in the following.

XPS analyses

To determine the chemical state and surface stoichiometry of the layers, the samples were analyzed by XPS. The survey scans of the $\text{SiO}_2/\text{TiO}_2$ thin films (with the SiO_2 thicknesses of 1 and 5 nm annealed at 500° and 600°C , respectively) are presented in Figure 5. The survey spectra show the presence of Si, Ti, O, Na, C on surface of the films. In the XPS survey scans, Silicon related to the SiO_2 overlayer was obvious clearly. Also, Titanium obtained from the TiO_2 underlayer was observed on the surface of the films and therefore can be an expected possibility of the mixed oxide (Ti-O-Si) on the surface of the films. In this case, we will discuss it in

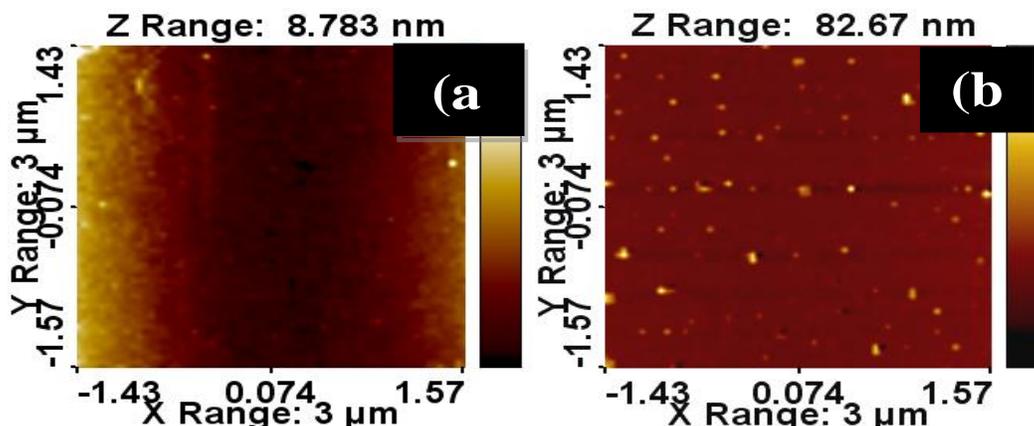


Figure 3. 2D AFM images of SiO₂(5 nm)/TiO₂ films a) before and b) after annealing at 500°C.

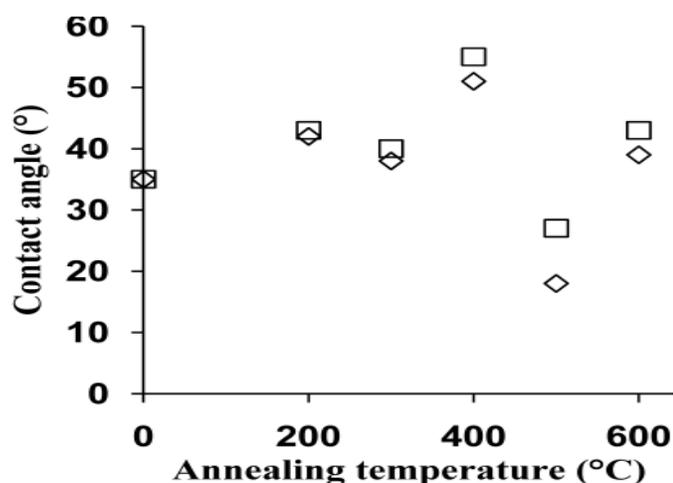


Figure 4. □) Measured and ◇) calculated contact angles (based on Wenzel's equation) on surface of the SiO₂(5 nm)/TiO₂ films annealed at the different temperatures.

the deconvoluted O (1 s) peaks. The existence of Na ion indicates the migration of Na related to the glass on the surface. The carbon peak shows the contamination of the surface on the films.

The Ti(2p) peaks of the as-deposited and annealed SiO₂(5 nm)/TiO₂ thin films are shown in Figure 6. There are two peaks corresponding to the Ti(2p_{3/2}) and Ti(2p_{1/2}) components at binding energies of 458.58 and 464.18 eV, respectively. Deconvolutions of the Ti(2p_{3/2}) peaks indicated that the as-deposited films contained a slight amount of Ti³⁺ chemical state (with Ti³⁺/Ti⁴⁺ ratio of 0.003), while after annealing at 500°C, no significant trace relating to the presence of Ti³⁺ was found. The binding energies relating to the Ti³⁺ and Ti⁴⁺ (as the predominant chemical state of the films) were considered at 456.7 and 458.5 eV, respectively (Kumar et al., 2000).

For studying the chemical state of the Si in thin films,

the Si(2p) peaks was recorded and deconvoluted, as shown in Figure 7. Each peak was deconvoluted into two components (2p_{3/2}, 2p_{1/2}) with separation energy of 0.6 eV and area ratio of 2 which is calculated from the splitting theory of 2p levels. Figure 7 shows the Si(2p) spectra of the as-deposited and annealed SiO₂(5 nm)/TiO₂ films. Taking into consideration the binding energy 103.2 eV for pure SiO₂ and in comparison with the binding energy values at our samples, compound structure of SiO₂ thin layer was concluded (Netterfield et al., 1989; Babapour et al., 2006). As shown in Figure 7 and Table 2 with increasing of the annealing temperature, the binding energy values of Si(2p) enhanced to the higher energy values. This shift in the Si(2p) binding energy indicates forming of a mixture oxide (Netterfield et al., 1989; Tachibana, 2000). The results of our XPS analysis for the Ti(2p) and Si(2p) peaks were summarized in Table 2.

The O(1s) spectra of the as-deposited and annealed SiO₂(5 nm)/TiO₂ bi-layer films are presented in Figure 8. The O(1s) peak of the as-deposited sample was deconvoluted into two components at binding energies of 530.88 and 532.71 eV. The two deconvoluted peaks were assigned to formation of Ti-O-Ti (peak A) and Si-O-Si (peak B). However, another peak (peak C) was found in the deconvoluted O(1s) peak of the film annealed at 500°C at the binding energy of 531.32 eV which was assigned to formation of Ti-O-Si bond in the annealed film, consistent with the previous reports (Permpoon et al., 2006; Yamashita et al., 1998; Lassaletta et al., 1995; Lin et al., 2002; Gallas et al., 2002; Almeida, 1998). Our results demonstrated that the naturally superhydrophilicity of the annealed films in the absence of UV irradiation and the persistence of the superhydrophilicity can be assigned to formation of this bond (Ti-O-Si bond) in the SiO₂-TiO₂ nanocomposite. Our XPS analysis also showed that the heat treatment resulted in increasing the concentration of Ti on surface of the films (Table 2), and consequently, increasing the

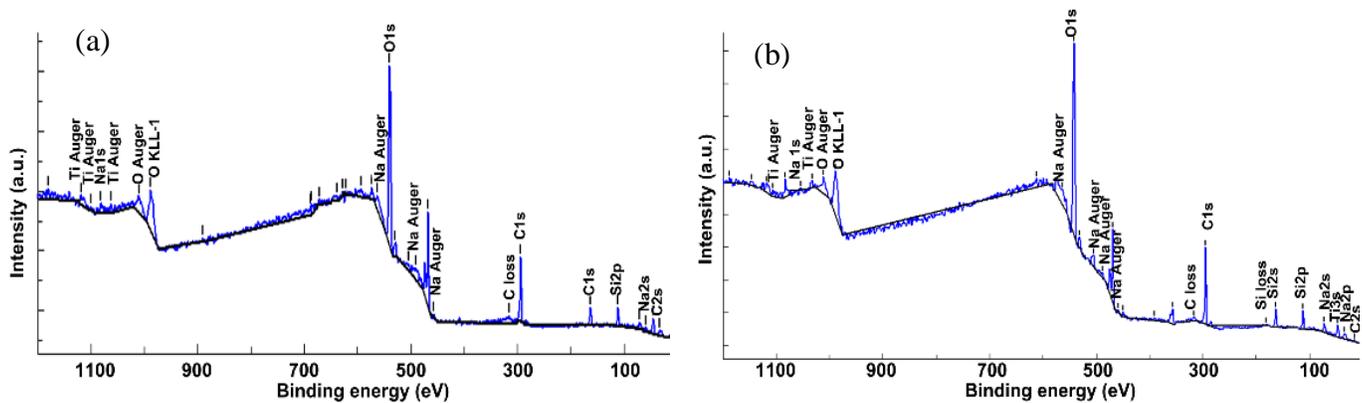


Figure 5. XPS survey spectra of a) as-deposited SiO_2 (5 nm)/ TiO_2 and b) SiO_2 (5 nm)/ TiO_2 at 500°C .

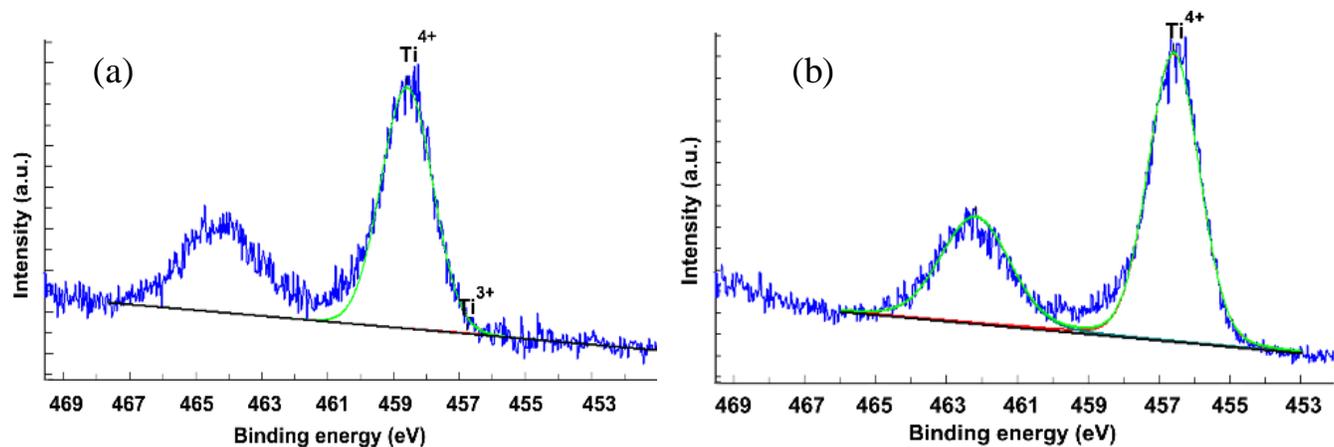


Figure 6. Ti(2p) XPS spectra of a) as-deposited SiO_2 (5 nm)/ TiO_2 film and b) SiO_2 (5 nm)/ TiO_2 annealed at 500°C .

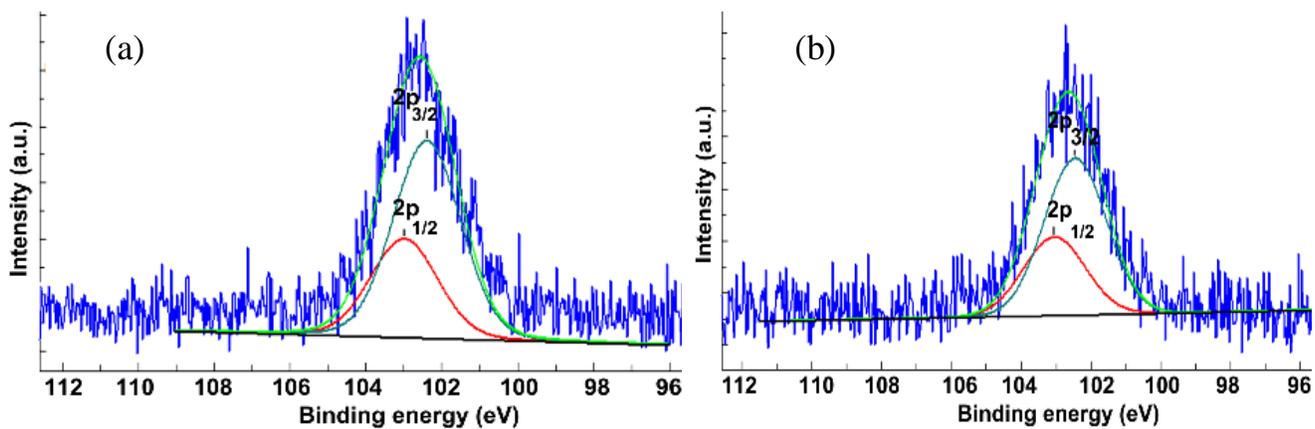


Figure 7. Si(2p) XPS spectra of a) as-deposited SiO_2 (5 nm)/ TiO_2 and b) SiO_2 (5 nm)/ TiO_2 annealed at 500°C .

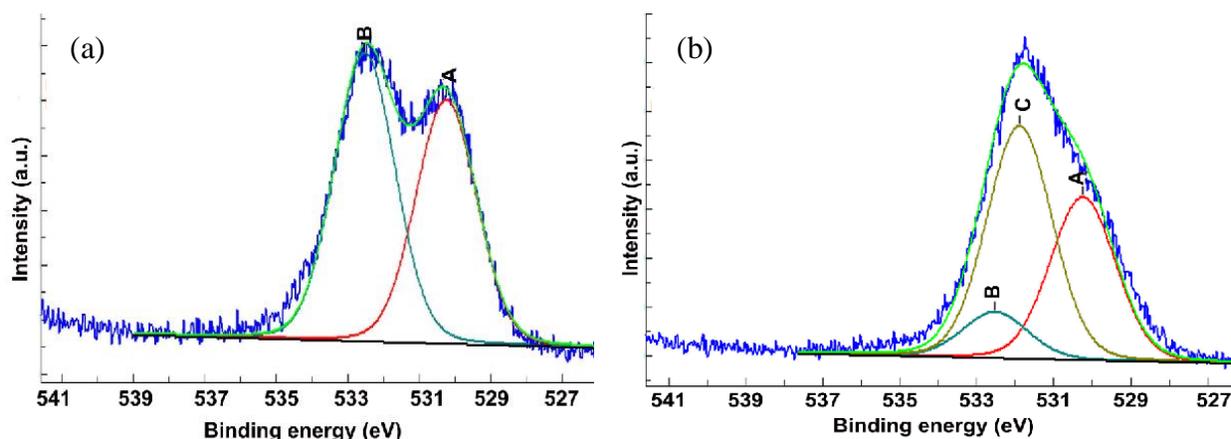
possibility of formation of the Ti-O-Si bond, consistent with some of the previous reports in this regard (for example, Mirshekari et al., 2010).

Conclusion

$\text{SiO}_2/\text{TiO}_2$ bi-layer films have been grown by RF reactive

Table 2. XPS data of the SiO₂/TiO₂ thin films for different temperatures.

Sample characterization	Annealed temperature (°C)	Ti(2p _{3/2}) (eV)	Si(2p _{3/2}) (eV)	Ti-O-Ti (eV)	Si-O-Si (eV)	Ti-O-Si (eV)	Ti/Si
SiO ₂ (5 nm)/TiO ₂	As deposited	458.58	102.39	530.24	532.62	-	0.84
SiO ₂ (5 nm)/TiO ₂	500	458.59	102.45	530.24	532.62	531.88	3.80

**Figure 8.** O(1s) XPS spectra of a) as-deposited SiO₂ (5 nm)/TiO₂ film and b) SiO₂ (5 nm)/TiO₂ film annealed at 500°C.

magnetron sputtering. XPS characterizations indicate that the annealing after deposition yield to the formation of Ti-O-Si bond at the films interfaces. On the other hand, this bond is never observed in deposited films without heat-treatment. The existence of Ti-O-Si bond enhances the surface acidity thus inducing hydrophilicity and it is maintained without UV light radiation. In our research, the best hydrophilic and persistent sample SiO₂(5 nm)/TiO₂ was evaluated at the annealed temperature 500°C. Finally, regenerable hydrophilic property of this film is observed after water rising operation without the requirement of UV light illumination.

Conflict of Interest

The authors have not declared any conflict of interest.

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