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The Phase Evolution and Photocatalytic Properties of a Ti-TiO₂ Bilayer Thin Film Prepared Using Thermal Oxidation

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Abstract: Ti-TiO₂ bilayer thin films were successfully prepared onto a glass substrate using magnetron sputtering with different TiO₂ bottom layer conditions. These represent a lack of (as-deposited) and full oxygen content (annealed). Single-layer Ti was additionally used as a control. The influence of oxygen diffusion phenomena of the bottom layer of TiO₂ to the upper layer of Ti thin films at different oxidation temperatures on structural, optical, and photocatalytic performance was investigated. X-ray diffraction (XRD) results confirmed that the crystalline phases coexisting on thin-film samples oxidized at 450 °C were TiO, TiO_{1.4}, (bilayer, as-deposited TiO₂), anatase (bilayer, annealed TiO₂), and rutile (single and bilayer). This finding showed that the film's phase structure evolution is significantly affected by oxygen diffusion from the bottom layer. Further increasing the thermal oxidation temperature caused a notable decline in the amorphous zone in bilayer thin films based on TEM analysis. Bilayer thin films lead to higher degradation of methylene blue under UV light radiation (63%) than single-layer films (45%) oxidized at 450 °C. High photocatalytic activity performance was found in the bilayer annealed TiO₂-Ti thin-film sample. This study demonstrates that the bilayer modification strategy promotes the oxygen-induced bottom layer of TiO₂ bilayer thin films.

Keywords: TiO₂; bilayer thin films; photocatalytic; thermal oxidation

1. Introduction

Semiconductor-based photocatalytic reactions have been fascinating as a promising technology that relies on the interaction between light and solid semiconductor particles. Titanium dioxide (TiO_2) has been acknowledged as the most crucial photocatalyst that strongly resists chemical and photo-corrosion, is non-toxic, and has thermal stability [1]. Several methods have been introduced to synthesize TiO_2 thin films, such as the sol-gel method [2], the combustion method [3], the chemical vapor deposition (CVD) method [4], and the sputtering method [5]. The magnetron sputtering technique was approved for providing solid substrate adhesion and a large area with uniform thickness [6,7].

The high-power impulse magnetron sputtering (HiPIMS) technique has demonstrated significant potential in material processing. This technique enables accessing high-density



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). plasmas with excessive quantities of ionized species, high-energy transfer functions, and low duty cycles than direct current magnetron sputtering (DC-MS) [5,8,9]. Various studies have highlighted the favorable impact of reactive HiPIMS on thin-film performance, including denser microstructures, higher hardness, good film adhesion, a high degree of crystallinity, and extended phase stabilities or enhanced surface coverage complex-shaped substrate [10–12]. However, due to the excessive ions sputtered during deposition to the target, the HiPIMS approach is less efficient, which decreases the deposition rate [13]. One approach to addressing this issue uses another coating technology. The DC-MS technique generates coatings with a higher deposition rate than the HiPIMS technology. Therefore, the combined HiPIMS and DC-MS method has been suggested to increase deposition rates and improve physical, chemical, and functional properties [14–16].

Several studies have recently developed TiO₂ films using thermal oxidation from sputtered Ti metal films [17,18]. The thermal oxidation temperature plays a crucial role in the crystal structure, particle morphology, and various TiO₂ phases, such as anatase or rutile, and their mixed phases have distinct photocatalytic activity levels [19]. The layered structure of the deposited Ti layers changes from amorphous to crystalline at the anatase phase by thermal oxidation [20]. Oxygen transport plays a crucial role in developing oxide materials using the thermal oxidation technique. Oxygen diffusion in TiO₂ thin films has previously been intensively studied based on electrical conductivity measurement [21] and oxygen tracer experiments [22,23]. Several studies have suggested that the oxidation layer is grown during the initial oxidation stage and distributed in the substrate. When the oxygen penetrates the subsurface layer, it is then chemisorbed and formed onto the surface [24], resulting in forming an oxide layer with substantial thickness. However, if the film thickness is greater than 200 nm, it is difficult to obtain the mixed phase (rutile and anatase), because the titanium film does not entirely oxidize down to the inner layer [17]. In addition, increasing the temperatures (700 and 900 $^{\circ}$ C) to create high oxidation states in thick films results in decreased band gap energy due to oxygen defect formation in the thin films [25]. As a result, the thin-film photocatalytic performance decreases.

Most researchers have focused on the development of thermal oxidation treatment for oxide surface growth and investigated the effects of temperature on the structural, microstructure, optical also Ti/O ratio in single-layer Ti films [25,26]. In contrast, developing a bilayer thin film to perform oxygen diffusion from the bottom to the upper layer has yet to be fully mastered. Therefore, it is necessary to investigate the oxygen diffusion phenomena from TiO₂ as the bottom layer, with different conditions representing a lack of and full oxygen content (as-deposited and annealed films, respectively), to the upper layer of Ti thin films. Furthermore, with further thermal oxidation, thin-film coupling between Ti and TiO₂ is predicted to contribute to the oxygen diffusion from the bottom to the upper layer, affecting several thin-film properties. In this study, three types of samples were prepared: a single layer of Ti, a bilayer of Ti-TiO₂ as a deposit, and a bilayer of annealed Ti-TiO₂. Different thermal oxidation temperatures were used to investigate the bottom-layer oxygen dependency on phase evolution, crystalline behavior, microstructures, and photocatalytic properties of Ti-TiO₂ bilayer thin films.

2. Materials and Methods

2.1. Preparation of TiO_2 Thin Films as a Bottom Layer

A titanium oxide (TiO₂) thin film as the bottom layer was deposited onto glass substrates ($26 \times 76 \text{ mm}^2$) using reactive HiPIMS. A pure titanium target (99.99% purity, Ultimate materials Technology Co., Ltd, Hsinchu, Taiwan) with $550 \times 125 \times 6 \text{ mm}^3$ dimensions was used to set the distance between target and substrate at 150 mm. The sputtering power was fixed at 2.5 kW, with a deposition rate of 15 (mm/s) × 2 passes. High-purity argon (99.99%) and oxygen (99.99%) gases were introduced into the vacuum chamber using a mass flow controller with gas flow rates of 200 and 5 sccm, respectively. The combination of oxygen gas flow and sputtering power to develop TiO₂ thin films has been observed in previous research. The working pressure was fixed at 2.7×10^{-3} Torr. The substrate temperature was controlled at 25 °C. The TiO₂ film bottom-layer thickness was controlled at about 40 nm. Both TiO₂ films, as-deposited and annealed (550 °C for 3 h in the air), were created to obtain different oxygen contents in the bottom layer. Several parameters, such as sputtering power, oxygen flow, and annealing temperature, used in this research to develop as-deposited and annealed TiO₂ were investigated as a preliminary study.

2.2. Ti-TiO₂ Bilayer Thin-Film Preparation

Pure Ti films were produced as an upper layer deposited using direct-current (DC) magnetron sputtering with a pure titanium target (99.99% purity, Ultimate materials Technology Co., Ltd., Hsinchu, Taiwan), 3 inches in diameter and 6 mm thick. The distance between target and substrate was set at 100 mm. The base pressure was controlled at 3.2×10^{-6} Torr, and the working pressure was 6.7×10^{-3} Torr. The argon (99.99%) gas flow was controlled at 30 sccm by a mass flow controller. The substrate holder was rotated at 24 revolutions per minute (rpm). Ti upper-layer films were deposited on a TiO₂ bottom-layer film at room temperature. The DC power was fixed at 125 W with a 12 min deposition time. The Ti film top-layer thickness was controlled at about 120 nm.

Three types of samples were prepared, as illustrated in Figure 1. Sample 1 was a single-layer Ti film deposited onto glass substrates (Figure 1a). Samples 2 and 3 were a bilayer thin film containing as-deposited TiO_2 (without annealing) (Figure 1b) and annealed TiO₂ (550 °C for 3 h) (Figure 1c) films as the bottom layer, respectively. Furthermore, the Ti film covered as the upper layer for both samples 2 and 3. Different oxidation temperatures (450 and 550 °C for 3 h) were used to evaluate the effects of the bottom-layer oxygen dependency of Ti-TiO₂ bilayer thin films on crystalline behavior, microstructures, optical, and photocatalytic properties.



Figure 1. Sample preparation: (**a**) sample 1, Ti films; (**b**) sample 2, bottom layer of TiO2 (as-deposited) + upper layer of Ti films; and (**c**) sample 3, bottom layer of TiO2 (annealed) + upper layer of Ti films, deposited onto a glass substrate.

2.3. Sample Characterization

Film crystallinity was analyzed with X-ray diffraction (XRD; Bruker D8 Advance-AXS Gmbh, Am Studio 2D, Berlin, Germany) using Monochromatic Cu K α radiation ($\lambda = 1.540598$). The machine was operated at 40 kV and 40 mA. The scanning angle 2 θ with a value range of $10^{\circ} \le 2\theta \le 80^{\circ}$ and a step size of 0.1° , measuring time at 5 s per step, was used. Microstructural and oxidation layer observations of the thin-film cross-sectional and plane-view morphology grown onto glass substrates were made with field-emission gun transmission electron microscopy (FEG-TEM; FEI E.O Tecnai F20, FEI Company—Thermo Fisher Scientific, Hillsboro, OR, USA) equipped with an energy-dispersive spectrophotometer at an acceleration voltage of 200 kV. Selected-area electron diffraction (SAED) and nano-beam electron diffraction (NBED) were performed using Gatan Software Digital Micrograph software version 3.7.4 (Gatan Inc., Pleasanton, CA, USA).

The thin-film samples' transmission spectra were monitored on a UV–VIS spectrophotometer (UV/Vis, U-3310, Hitachi Ltd., Hitachi, Japan) with a wavelength of 300–800 nm. X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010MX, Japan Electronics Corp, Akishima, Japan) was used to examine the films' quantitative composition on the surface and the internal area. Internal profile experiments were performed by sputter etching at a rate of 28 nm/min in the thin films for 20 s using argon gas. The analyzer was operated at voltage 10 kV and current 5 mA with a Mg K α radiation line. X-ray photoelectron spectra were referenced to the C 1s peak (Eb = 285 eV) that presented on the sample surface.

2.4. Photocatalytic Activity

The photocatalytic performance of the thin-film samples was evaluated by testing the decolorization of a high-purity $C_{16}H_{18}CIN_3S \cdot xH_2O$ (methylene blue (MB)) decomposition solution (Alfa Aesar; Thermo Fisher Scientific, Lancashire, UK) with an initial concentration (C_0) of 10 mg/L. Thin-film samples with 26 mm \times 38 mm dimensions were immersed into a 20 mL aqueous MB solution (1 mg/L) in a beaker. The distance between the reactor and the lamp was kept at 9 cm. The photocatalytic performance of the Ti-TiO₂ bilayer thin film was investigated under 8 watt UV-C lamp irradiation (UV-C T8; $\lambda = 253.7$ nm, Philip, Amsterdam, The Netherlands). The dye solution with the photocatalyst was kept in the dark for 10 min to reach adsorption–desorption equilibrium before irradiation. Briefly, from the end of the dark-storage time ($t = 0 \min, C_t$), the dye solution sample was collected at a regular interval of 30 min for 3 h (t = 30–180 min, C_{30} to C_{180}). The collected sample was analyzed by a UV–VIS spectrophotometer (UV/Vis, U-3310, Hitachi Ltd., Tokyo, Japan) to obtain the absorbance for quantifying the concentration of MB (the maximum absorption wavelength of the dye at 664 nm) [27]. The methylene blue degradation was reported by calculating the percentage of the concentration of the dye that remained (C_t) over the initial dye concentration (C_0), obtained from the absorbance standard curve. The degradation performance was evaluated by considering the following Equation (1):

Methylene blue degradation (%) =
$$[1 - (C_t/C_0)] \times 100$$
 (1)

The kinetics of MB photodegradation on the TiO_2 surface can be described by the first-order reaction kinetics Equation (2):

$$\ln(C_t/C_0) = -kt,$$
(2)

where C_0 is the initial concentration of MB and C_t is the MB dye concentration at a certain time (mg/L). In the pseudo-first-order photodegradation kinetics, the $\ln(C_t/C_0)$ linear fit slope in the function of time (t) plot represents the kinetic constant (*k*) of the photodegradation.

3. Results and Discussion

Figure 2 shows X-ray diffraction patterns of samples that were oxidized in air for 3 h. When the temperature was set at 450 $^{\circ}$ C, we found that only the TiO₂ rutile phase was detected in sample 1. The formation of a single rutile phase at 450 °C is much lower than the formations synthesized using other methods [4,17]. An amorphous phase was found, since XRD peaks showed lower intensities for sample 1, which implied the coexistence of an amorphous structure and crystalline rutile. Three phases coexisted in sample 2: TiO (hexagonal (110)), TiO_{1.04} (110), and rutile. However, hexagonal TiO and TiO_{1.04} phases appeared. This is because the titanium dioxide bottom layer does not provide sufficient oxygen for the pure titanium film upper layer during thermal oxidation. This is attributed to the titanium oxide bottom layer being an as-deposited film (insufficient oxygen). This means that a non-stoichiometry TiO layer exists between the upper and the bottom layer. Further study of the microstructure using FE-TEM will be performed to prove this supposition. However, the coexistence of anatase and rutile phases (JCPDS card: 21-1272 and 21-1276) was clearly observed in sample 3. It has to be pointed out that the anatase phase was formed in this investigation. This may be due to the TiO₂ bottom layer, which can provide sufficient oxygen to the Ti upper layer. Ting et al. reported that the formation of a significant quantity of oxygen vacancies in the oxidized film accelerates the anatase-to-rutile transformation [25]. Therefore, it is believed that the phase evolution effects on the Ti films oxidized using thermal oxidation depend strongly on the bottom layer.



Figure 2. Thin-film X-ray diffraction patterns with different sputtering process parameters thermally oxidized at 450 °C.

Figure 3 shows the XRD patterns of samples with different sputtering process parameters annealed at 550 °C. A further increase in temperature to 550 °C resulted in increased diffraction intensity with an associated decrease in the XRD patterns' amorphous background, indicating improved Ti film crystallinity. Only a rutile crystallization phase was clearly observed in samples 1 and 3 at 550 °C. This indicates complete anatase transition into the rutile phase at 550 °C for samples 1 and 3. As is well known, anatase is a metastable phase that may be transformed into the rutile phase during heat treatment [18,28]. For Ti film thermal oxidation, Ti atoms absorb oxygen from the air into the films. The Ti and O atoms react to form TiO₂ when the oxidation temperature is 550 °C. However, there was a main rutile phase with a minor TiO phase in sample 2 oxidized at 550 °C. This result indicates that TiO₂ (as-deposited) as the bottom layer does not provide sufficient oxygen to the upper layer during thermal oxidation at 550 °C. Chung et al. reported that the formation of TiO was from the Ti thin film after thermal oxidation at 500–550 °C [29].

In the case of the rutile tetragonal crystal structure ($a = b \neq c$), the lattice constant is calculated using the following formula:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a} + \frac{l^2}{c^2} , \qquad (3)$$

where d_{hkl} is the interplanar separation corresponding to Miller indices *h*, *k*, and *l* and *a* and *c* are the lattice constants. For all samples, the calculated structural parameters corresponding to peaks (110) and (101) are given in Table 1. When compared with standard rutile TiO₂ (a = b = 4.5933 Å and c = 2.9592 Å), a slight increase in the lattice constant *a* and a decrease in the lattice constant *c* for sample 2 when thermally oxidized at 450 °C were observed. This is due to the TiO and TiO_{1.04} crystal peaks that represent an oxygen vacancy in a thin-film sample.

100

Rutile,syn (Tetragonal

TiO (Hexagonal)

Intensity (a.u.)



Sample-1

Manham

 20
 30
 40
 50
 60
 70
 80

 2θ (∘)
 2θ (∘)

Figure 3. Thin-film X-ray diffraction patterns with different sputtering process parameters thermally

Figure 3. Thin-film X-ray diffraction patterns with different sputtering process parameters thermally oxidized at 550 °C.

(211)

Table 1. Optimized lattice parameters of the rutile phase in $Ti-TiO_2$ bilayer thin-film samples as a function of oxidation temperature.

Oxidation Temperature (°C)	Sample	a (Å)	с (Å)	Unit Cell Volume (Å ³)
450	Sample 1	4.5501	2.9685	61.4581
	Sample 2	4.6147	2.9400	62.6086
	Sample 3	4.5990	2.9649	62.7100
550	Sample 1	4.5816	2.9942	62.8510
	Sample 2	4.5829	2.9708	62.3964
	Sample 3	4.6145	2.9734	63.3147

High-resolution TEM (HR-TEM) was used to analyze TiO_2 thin films to determine whether they were crystalline or amorphous. The TEM specimen microstructures (samples 1, 2, 3) thermally oxidized at 450 °C are shown in Figures 4–6, respectively. Figure 4 shows typical bright- and dark-field HR-TEM images of sample 1 thermally oxidized at 450 °C. A film thickness of 120 nm was observed, as shown in Figure 4a. From the dark-field microstructure view, an interface was apparent in the film, separating the crystalline and amorphous zones, as shown in Figure 4b. The oxidation zone in the Ti films was about 57 nm less than the 63 nm amorphous zones. The Ti films thermally oxidized at 450 °C with crystalline structures are exhibited in the upper zone in Figure 4c,d. According to HR-TEM micrograph analysis, the crystalline grains belonged to the rutile crystalline phase (111). Figure 4e clearly shows that the bottom-zone film microstructure is amorphous. However, the film near the surface layer has obviously crystallization. Oxygen diffuses into the internal film zone from the surface by thermal oxidation at 450 °C.



Figure 4. TEM micrographs of a sample 1 thin film thermally oxidized at 450 °C: (**a**) bright field, (**b**) dark field, (**c**) HR-TEM image showing point A, (**d**) HR-TEM image showing point B, and (**e**) HR-TEM image showing point C.



Figure 5. TEM micrographs of a sample 2 thin-film thermally oxidized at 450 °C: (**a**) plane view of the film, (**b**) HR-TEM image showing point A, (**c**) HR-TEM image showing point B, (**d**) HR-TEM image showing point C, (**e**) NBED showing point B, and (**f**) NBED showing point A.



Figure 6. TEM micrographs of a sample 3 thin-film thermally oxidized at 450 $^{\circ}$ C; (**a**) plane view of the film, (**b**) HR-TEM image showing point A, (**c**) HR-TEM image showing point B, and (**d**) NBED showing point C.

Figure 5 shows sample 2 HR-TEM micrographs and SAED patterns from thermal oxidation at 450 °C for 4 h. The microstructure shows the same interface in the film. It can be divided into two zones. The oxidation thickness in Ti films was about 70 nm at 450 °C for 4 h thermal oxidation, as shown in Figure 5a, which was higher than that for sample 1 (57 nm). According to HR-TEM micrograph analysis, the upper-zone (apart) crystalline grains belong to the rutile crystalline phase (111), as shown in Figure 5b. Two kinds of phase structures coexisted in the interface zone (B part), amorphous and TiO_2 grains, as shown in Figure 5c. It clearly shows that the film microstructure is amorphous on the Ti film bottom zone. The TiO_2 film bottom layer C part was also analyzed, as shown in Figure 5d. The TiO_{1.04} (200) and TiO (110) microcrystalline phases coexisted in bottom-layer films. This is attributed to the TiO_x film bottom layer deposited onto glass without annealing, which does not readily form the TiO₂ crystalline phase stoichiometry. Sekhar et al. reported that TiO₂ films deposited using DC reactive magnetron sputtering are amorphous in a continuous gas flow if no bias voltage or heating is applied to the substrate [30,31]. Electron diffraction pattern analysis was carried out to identify crystalline grains, as shown in Figure 5e,f. The SAED pattern displayed a rutile phase in the upperzone A part (Figure 5f). However, the SAED pattern showed TiO_{1.04} (200) and TiO (300) planes on the interface-zone B part (Figure 5e). This observation is consistent with the XRD results in the above section. TiO existed in the bottom layer, implying a lack of oxygen

content in the film. The oxygen partial pressure influences the crystal formation of Ti films during sputtering [32].

Figure 6 shows HR-TEM micrographs and SAED patterns of sample 3 thermally oxidized at 450 °C. It was mentioned in the above section that sample 3 was TiO₂ films deposited on glass substrates as the bottom layer, and it was annealed at 550 °C for 3 h first, and then pure titanium film was deposited on the bottom layer (TiO₂ films). In the dark-field view, there was no amorphous zone observed in the films, as shown in Figure 6a. This shows that the film has good crystallinity in all zones, as shown in Figure 6b,c. According to SAED pattern analysis, the crystalline grains belong to the rutile and anatase phases in the films, as shown in Figure 6d. The related literature reported that in the reactive sputtering process, the rutile-and-anatase-mixture-phase TiO₂ growth is induced, and the anatase phase increases with the increase in oxygen in the sputter chamber [31,32].

As is well known, anatase phase formation requires sufficient oxygen. Comparing sample 1 to sample 3, the oxygen diffusion from the bottom titanium oxide layer influences the microstructure and phase evolution of Ti films during thermal oxidation. For example, mixture phases (rutile and anatase) with good crystallinity in oxidized Ti films can be obtained when the bottom layer is rutile TiO_2 films. Figure 7 shows the amorphous layer thickness of the Ti films on different bottom layers as a function of the oxidation temperature. The amorphous layer thickness was analyzed using TEM. The results showed that the amorphous layer thickness depends strongly on the bottom layer's oxygen concentration and the oxidation temperature for all samples. The amorphous zone decreased significantly with increasing thermal oxidation temperature. However, a film without an amorphous structure (fully crystalline) was found at 450 °C for sample 3 and at 550 °C for samples 1 and 2. This explains how annealed titanium oxide films as the bottom layer lead to Ti films becoming TiO₂ crystalline phases after 450 °C thermal oxidation.



Figure 7. Amorphous thickness of Ti films measured as a function of oxidation temperature.

XPS analysis was performed to observe the phase evolution between different sample conditions of Ti-TiO₂ bilayer thin films and the oxidation states of the constituent elements present in the samples. Figure 8 displays the spectra of Ti-TiO₂ bilayer thin films on glass with different oxidation temperatures. Figure 8a shows the high-resolution XPS spectrum of the Ti 2p peak for samples with different bottom layers at 450 °C. The binding energy curves of Ti 2p with two firm peaks were observed at ~457 and ~462 eV, corresponding to core levels of Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, which is in good agreement with the recent



Figure 8. XPS curve of the internal area of the Ti-TiO₂ bilayer thin film at different oxidation temperatures: binding energy curves of Ti 2p, employing a Shirley-type background oxidized at (**a**) 450 °C and (**b**) 550 °C.

It was observed from the XPS spectra in Figure 8b that increasing the oxidation temperature up to 550 °C shows the binding energy peaks of Ti 2p at single-layer films shifting toward a higher binding energy by ~0.7 eV for both bilayer thin films (samples 2 and 3). Fakhouri et al. [36] proposed that increasing the thin-film layer results in the Ti 2p peak shifting toward lower or high binding energy. This phenomenon may be due to a partial reduction in the titanium cations related to the formation of oxygen vacancies in the lattice or a change in stacked electronic affinity at Ti-TiO₂ thin films [36]. According to the literature [37], the chemical states for all thin-film samples (thermally oxidized at 450 and 550 °C) correspond to Ti³⁺ due to the formation of Ti–O bonds at the binding energy of Ti $2p_{3/2 \text{ of}}$ around ~457 eV, characteristic of rutile titanium dioxide that is similar to TiO₂. However, the small Ti²⁺ peaks (456.1 eV) in sample 2 indicated the presence of TiO. The presence of TiO is consistent with the HR-TEM result in Figure 5.

The compositions of Ti-TiO₂ bilayer thin films at different thermal oxidation temperatures were identified using XPS. The relative concentrations of titanium and oxygen were analyzed in the Ti-TiO₂ bilayer thin films. To understand the difference in oxygen concentration between the surface and the internal zone of the upper Ti oxidized films, the film compositions were analyzed at different positions. The average values of each element are listed in Table 2. The oxygen concentration in the internal zone was lower than that on the surface. For bilayer samples oxidized at 450 °C, the internal and surface zone's oxygen content was <59% and >69%, respectively. According to XPS analysis results, it is believed that the upper Ti films' internal zone is not fully oxidized. This means that many oxygen vacancies exist in the films. When the oxidation temperature was enhanced from 450 to 550 °C, the internal zone's oxygen content increased up to ~60%. The results indicate that the oxygen content in the upper Ti films increases by increasing the oxidation temperature.

Oxidation Temperature (°C)	Element _	Atomic Concentration (%)						
		Sample 1		Sample 2		Sample 3		
		a	b	а	b	а	b	
450	Ti	28.34	39.10	30.47	41.22	30.70	42.60	
	0	71.66	60.90	69.53	58.78	69.30	57.40	
550	Ti	15.46	35.56	29.91	40.01	23.46	39.96	
	0	84.54	64.44	70.09	59.99	76.54	60.04	

Table 2. Chemical composition of the Ti-TiO₂ bilayer thin-film surface and internal area with different samples oxidized for 3 h.

a Surface area; b internal area.

UV–VIS spectroscopy was conducted to measure the optical transmission of the Ti-TiO₂ bilayer thin films with different samples thermally oxidized at 450 and 550 °C, as shown in Figure 9. The Ti-TiO₂ bilayer thin-film transmittance spectra curves indicated that the transmittance spectra gradually shift to a short wavelength as the amorphous thickness in the film increases.



Figure 9. UV–VIS transmittance spectra of a thin film with different samples oxidized at (a) 450 °C and (b) 550 °C.

The optical transmission spectra of sample 3 oxidized at 450 °C were exceptionally clear and more than 86% in the visible region. In contrast, sample 1 thermally oxidized at 450 °C had lower transmittance (~41%), while sample 2 had almost no light transmission (0%), as seen in Figure 9a. According to the sample 1 microstructure analysis (Figure 4), oxygen diffusion into the inner film zone slowly occurred at 450 °C, clearly showing that the bottom-zone film microstructure is amorphous. Films with a larger amorphous zone can cause more reflections and light interference, resulting in weak light transmission [38].

The poorest transmittance, especially in the visible region, occurred in sample 2 when oxidized at 450 °C, which is attributed to high absorption in the metallic layer [28], suggesting a sufficient amount of oxygen vacancies that significantly absorbed the incident light [29]. This finding seems consistent with the XRD patterns (Figure 2) and HR-TEM image in Figure 5e, indicating that sample 2 has $TiO_{1.04}$ (200) and TiO (110) microcrystalline phases that coexist in bottom-layer films. TiO existed in the bottom layer, implying the lack of oxygen content in the film. These phenomena resulted in poor light transmission in sample 2, although it had a lower amorphous thickness than sample 1.

Optical transmittance can be significantly improved while increasing the oxidation temperature up to 550 °C. Due to this phenomenon, titanium metal changes to titanium dioxide after thermal oxidization and increases the oxidation layer of the bilayer thin film. Figure 9b displays bilayer thin films on samples 2 and 3, which showed a significant increase in transmission to ~78% and ~88%, respectively. The transmittance result from sample 3 was higher than the Ti single-layer film thermally oxidized at 600 °C reported by some authors [20,39]. The increasing oxidation temperature has been documented to provide adequate energy to diffuse into the film, improving the TiO₂ crystalline strength [40]. However, the transmittance of sample 2 was lower than other samples. It corresponded to TiO (110) instead of the rutile crystallization, as shown in the XRD pattern in Figure 3. As mentioned before, TiO exhibited higher reflective properties due to inadequate oxygen in films. Thin-film transparency improved by increasing the thermal oxidation temperature, which probably removed the residual stress, quantum confinement, and structure order improvement [25], and decreasing the amorphous thickness in the Ti-TiO₂ films.

The Ti-TiO₂ bilayer thin films' photocatalytic activity was determined by the degradation of 10 mg/L of MB solution under UV-C light irradiation, as shown in Figure 10. It can be observed that all thin-film samples that were thermally oxidized at 450 and 550 °C exhibited quick adsorption in the dark. This could be attributed to the high specific surface area and small particle size [41]. Figure 10a shows MB degradation (%) of a thin film with different samples oxidized at 450 °C. It was found that all samples provided high photocatalytic degradation performance with a range of 43–63% compared to the substrate. However, increasing the thermal oxidation temperature to 550 °C decreased the photocatalytic activity of samples 2 and 3 (Figure 10b).



Figure 10. Photocatalytic activity of thin-film samples as the function of the irradiation time in MB solution. Inset: first-order reaction rate of thin-film samples with MB. MB degradation of thin-film samples thermally oxidized at (**a**) 450 °C and (**b**) 550 °C.

According to first-order reaction kinetics, in Figure 10 (inset), the time-dependent $\ln(C_t/C_0)$ terms are illustrated for all thin-film samples. The calculated reaction rate constants (*k*) of the thin films thermally oxidized at 450 °C with different sample preparations (samples 1, 2, and 3) were 2.52×10^{-3} , 4.29×10^{-3} , and 5.07×10^{-3} min⁻¹, respectively (Figure 10a inset), showing a higher rate of degradation for sample 3. The reaction constants (*k*) gradually increased with a decrease in the amorphous thickness. The amorphous area depended strongly on the bottom-layer annealing temperature and oxygen concentration for all samples. However, after increasing the oxidation temperature to 550 °C, the rate

constants (*k*) of all thin-film samples were stable around 3×10^{-3} min⁻¹ (Figure 10b inset). This is attributed to the crystalline phase changing from mixture phases (rutile and anatase) to a single phase (rutile) at 550 °C, as seen in Figures 2 and 3. It is well known that the combination of TiO₂ rutile and anatase phases exhibits higher photocatalytic activity in MB solution decomposition than the pure TiO₂ phase due to the electrons' movement from rutile to anatase TiO₂ during photoexcitation. This prevents anatase charge recombination, leading to more efficient photogenerated electron–hole pair separation and high photocatalytic activity is obtained in thin films with an optimum ratio of anatase and rutile phases. However, higher rutile content lessens their photocatalytic activity due to the photogenerated holes and the electrons' higher recombination rate in the rutile phase.

Figure 11 illustrates the photocatalytic performance of Ti-TiO_2 thin films thermally oxidized at different temperatures. It can be clearly seen that both bilayer thin films (samples 2 and 3) had higher photocatalytic performance than the single-layer film (sample 1) due to the lower amorphous thickness in bilayer thin films, as shown in Figure 7. This finding is in agreement with previous research [45].



Figure 11. Photocatalytic activity of TiO₂ thin-film samples at different oxidation temperatures irradiated at 180 min.

It was found that the oxidation temperature affects the sample photocatalytic activity. As the thermal oxidation temperature rose from 400 to 450 °C, both bilayer thin films' degradation rate increased, as seen in samples 2 (57%) and 3 (63%). However, after increasing the thermal oxidation temperature to 550 °C, the bilayer thin-film degradation rate steeply dropped. In addition, sample 2 thermally oxidized at 450 °C showed good photocatalytic activity to degrade MB solution instead of lower optical transmittance. The existence of TiO_{1.04} (200), TiO (110), and rutile phases in sample 2 contributed to poor transmittance results, while good photocatalytic activity (Figure 7) was due to a higher number of oxygen vacancy defects in the films, contributing to increasing photocatalytic activity. As is well known, oxygen vacancies play a vital role in semiconductor photocatalysis. Therefore, inducing large effects on the electronic, photonic, and photocatalytic properties of TiO₂, oxygen deficiencies are critical features [46–48].

Elahifard et al. [49] developed TiO_2 nano-materials with controllable VO contents (0–2.18%) using an in situ solid-state chemical reduction strategy. The work showed that

the bandgap of the resultant rutile TiO_2 reduced from 3.0 to 2.56 eV, indicating enhanced visible light absorption. Furthermore, semiconducting photocatalysts are mainly dependent upon the separation of photogenerated electron–hole pairs and transfer of electrons from the photocatalyst into the organic pollutants through the oxygen vacancy defects on the photocatalyst surface [50,51]. Stojadinović et al. [52] reported different photocatalytic activities of Tb^{3+} -doped TiO₂ coatings, in which a thicker TiO₂ coating oxidation layer has a higher number of oxygen vacancy defects, with the oxide contributing to the increasing photocatalytic activity.

These results indicated that oxygen vacancies are crucial parameters for obtaining high photocatalytic performance. The annealed bottom layer can provide high oxygen diffusion to upper Ti thin films and create a higher number of oxygen vacancy defects in the films, contributing to the increasing photocatalytic activity. Furthermore, an optimum oxidation temperature (450 °C) from TiO₂ rutile and anatase phases exhibits higher photocatalytic activity in MB solution degradation than the pure rutile TiO₂ phase. Thus, the study demonstrates that this bilayer modification strategy promotes the oxygen-induced TiO₂ bilayer thin-film bottom layer that can increase thin films' transmittance and photocatalytic activity. Furthermore, bilayer thin films could have the potential as photocatalytic coating material, including self-cleaning, self-sterilizing (antimicrobial), and water purification.

4. Conclusions

The bottom-layer oxygen dependency of thin-film samples was investigated in detail by using three types of samples (a single layer of Ti, a bilayer of Ti-TiO₂ as-deposited, and a bilayer of Ti-TiO₂ annealed thin films). It was found that the film's phase structure evolution after thermal oxidation was significantly affected by oxygen diffusion from the bottom to the upper layer. Upon further increasing the thermal oxidation temperature, all samples were observed to have a single rutile phase and a notable decline in the amorphous zone in bilayer thin films. The oxygen vacancy is a crucial parameter for obtaining high photocatalytic performance. The annealed bottom layer can provide high oxygen diffusion to upper Ti thin films and create a higher number of oxygen vacancy defects in the films, contributing to increasing photocatalytic activity. This study demonstrates that the bilayer modification strategy promotes the oxygen-induced bottom layer of TiO₂ bilayer thin films.

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