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# Influence of Annealing Temperatures on the Properties of Dual-Layer W-$TiO_2$ Thin Films

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**Abstract.** W-$TiO_2$ (W, tungsten) dual-layer thin films are deposited by RF magnetron sputtering onto glass substrates and annealed at 150°C~400°C for 4hrs. The crystal structure, morphology, and trans- mittance of annealed W-$TiO_2$ dual-layer thin films are investigated by X-ray diffraction, FESEM, and UV-Vis spectrometer, respectively. The annealing temperatures have large effect on the properties of W-$TiO_2$ dual-layer thin films. The band gap energy values of W-$TiO_2$ dual-layer thin films are evaluated from $(\alpha h\nu)^{1/2}$ versus energy plots. The energy gap for un-annealed W-$TiO_2$ dual-layer thin film is 3.16 eV. As the annealing temperature increases from 150°C to 400°C, the energy gap decreases from 3.16 eV to 3.10 eV.

## Introduction

Titanium dioxide ($TiO_2$) has been widely used in hydrophilic mirrors because it has excellent photocatalytic properties such as self-cleaning ability [1], super-hydrophilicity [2], and decomposition of organic species [3]. Titanium dioxide ($TiO_2$) is widely studied by researchers in the basic sciences as well as in industrial engineering because its phase transformation has been widely studied for optical and electronic applications. Recently, titanium dioxide has drawn more attention because of its high efficiency for photocatalytic degradation of organic compounds, including a large fraction of environmental toxins [4]. The photocatalytic reactivity of $TiO_2$ thin film has been found to be sensitive to the crystallographic phase and microstructure [5], in addition, crystal orientation might also be an influencing factor. Visible light response is a very important factor in the research into titanium dioxide as a photocatalyst. For the photocatalysis activity, the value of the band gap is a key property. In the past, several techniques such as remodelling of the band structure, combination with different semiconductors, and dye-sensitization had been attempted. Besides keeping the thin films in the rutile pahse, there are many methods are also developed for shifting the band gap to visible light range. One method was added other materials as dopant and the other was fabricated the multi-layer thin films. In the case of $TiO_2$ deposition on glass, the adsorption of $Na^+$-ion from the glass on the stoichiometric $TiO_2$ surface tends to lower the work function to about 2.5 eV [6].

This reduced value of work function lowers the redox power by fast electron-hole recombination, which results in the degradation of hydrophilicity. The tungsten has a wok function of 4.55 eV, it is a suitable dopant material to fabricate W-$TiO_2$ dual-layer thin films. $TiO_2$ thin films can be prepared on the substrate by various techniques such as chemical vapor deposition, chemical spray pyrolysis, electrodeposition, and sol-gel method. The sol-gel method has the advantage of easy control of metallic or inorganic chemical composition of thin films. In this study, W-$TiO_2$ dual-layer thin films with different thickness of tungsten were prepared on glass slides by RF sputtering process. RF magnetron sputtering is a suitable method for preparing titanium dioxide thin films in basic research. The tungsten is hoped to increase the electron transmittance of $TiO_2$ thin films and decrease the energy band of $TiO_2$ thin film. RF magnetron sputter is used to prepare nano-crystal $TiO_2$ thin film and W-$TiO_2$ dual-layer thin films. The influences of depositing time of tungsten thin films on

transmittance and the crystal structure of $TiO_2$ in the W-$TiO_2$ dual- layer thin films are studied. After that, the different annealing temperatures are used to develop the influence of post-heating process on the characteristics of W-$TiO_2$ dual-layer thin films.

## Experimental Procedure

The raw materials of titanium oxide ($TiO_2$) powder (99.8%) in an average diameter of 110 nm was used as the source powder to prepare ceramic target. The polyvinylalcohol (PVA) was added into the $TiO_2$ powder as binder. The mixing powder was uniaxially pressed into pellets in a steel die with the size of 5 mm in thickness and 56 mm in diameter. After debindering, the sintering of $TiO_2$ ceramic was carried out at 1400°C for 4h. From the X-ray diffraction pattern of $TiO_2$ ceramic the rutile phase was obtained. $TiO_2$ (no W thin films) and W-$TiO_2$ thin films were deposited onto well cleaned glasses slide substrates by RF magnetron sputter. For deposition process, the base pressure was less than $2\times10^{-6}$~ $3\times10^{-6}$ Torr, and the work pressure of argon was followed to be set at $5\times10^{-3}$ ~$5\times10^{-2}$ Torr and Argon was used as sputtering gas. The working distance was 50 mm for $TiO_2$ target and 120 mm for tungsten target. The $TiO_2$ thin film and W-$TiO_2$ dual-layer thin films were deposited at glass substrate temperature of 150°C. The depositing time for $TiO_2$ was 30 min and the depositing time for tungsten thin film was changed from 15 sec to 60 sec. After deposition, the phase ratio of anatase and rutile were estimated from X-ray diffraction patterns with Cu Kα radiation (λ=1.5406 Å) in the scanning angle (2θ) from 20° to 80°. The 60 sec-W-deposited thin film was annealed at 150°C~400°C for 4hrs. The morphology and thicknesses of W-$TiO_2$ dual-layer thin films were observed and measured by field effect scanning electron microscope (FESEM). Transmittances of thin films were measured by using UV-Vis-NIR spectrophotometer.

## Results and Discussion

Fig. 1 shows the XRD patterns of $TiO_2$ thin film (no tungsten) and W-$TiO_2$ dual-layer thin films. As shown in Fig. 1(a), the rutile, anatase, and amorphous phases coexist. As the tungsten is used to deposit as W-$TiO_2$ dual-layer thin films, the rutile, anatase, and amorphous $TiO_2$ phases also coexist in the XRD patterns. According to Miyagi's study, the formation of anatase phase is dominated by the deposition temperatures (>400°C) [7]. In this study, we will show that the formation of anatase phase can be dominated by the thickness of tungsten. Comparing the XRD patterns in Fig.1(a) and 1(b), the main peak, (101), of the anatase $TiO_2$ in the W-$TiO_2$ dual-layer thin films have smaller full width at half maximum (FWHM) values than the main peak in the $TiO_2$ thin film. And this result suggests that $TiO_2$ in the W-$TiO_2$ dual-layer thin films have the better crystal characteristics. When tungsten is deposited on $TiO_2$ layer, as shown in the Fig.1(b)- 1(c), as the tungsten-deposited time increases from 0 to 30 sec, the crystal intensities of anatase and amorphous $TiO_2$ phases apparently decrease and the crystal intensity of rutile phase apparently increases. Further increasing the depositing time of tungsten to 60 sec, the crystal intensity of anatase $TiO_2$ phase increases and the crystal intensity of rutile phase decreases. The phase ratio of $TiO_2$ thin film and W-$TiO_2$ dual-layer thin films could be obtained by the following [7]:

$$A\% = 100/(1+ 1.265I_R/I_A) \quad (1)$$

where A was the ratio of anatase phase (%), $I_R$ was the crystal intensity of rutile phase at 27.5°, and $I_A$ was the crystal intensity of anatase phase at 25.3°. As the depositing time of tungsten, calculated by the Spurr and Myers [8] method, increases from 0 sec to 15 sec, 30 sec, to 60 sec, the phase ratio of rutile changes from 63 % to 87%, 93%, and 73%. Based on the XRD results, it can be suggested that the presence of anatase phase is caused by re-sputtering effect of tungsten. For that, the 60sec-W-deposited thin film is annealed. SEM surface observations of W-$TiO_2$ dual-layer thin films as a function of annealing temperatures are shown in Fig.2. All thin films are found to be uniform and the nano-scaled grains are observed. For the un-annealed W-$TiO_2$ dual-layer thin film, the grain size is in the range of 20–100 nm. Fig.2 shows that the particle size of $TiO_2$ grain decreases and grain boundary becomes unclear as annealing temperatures increase. This may be related to a change in the

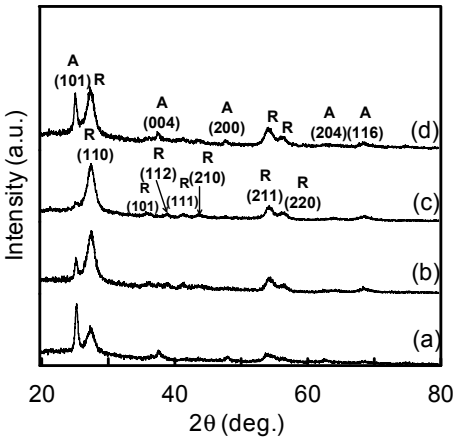


Fig.1 XRD patterns of W-$TiO_2$ films of tungsten deposition duration of (a)0, (b) 15, (c) 30 and (d) 60 sec.

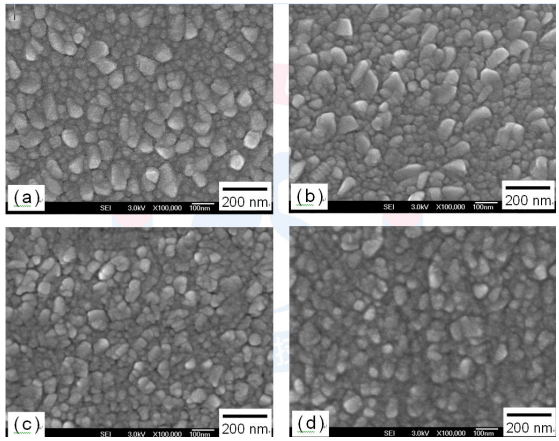


Fig.2 Morphology observations of W-$TiO_2$ thin film, annealing at (a)150°C, (b)200°C, (c)300°C, and (d)400°C for 4hrs.

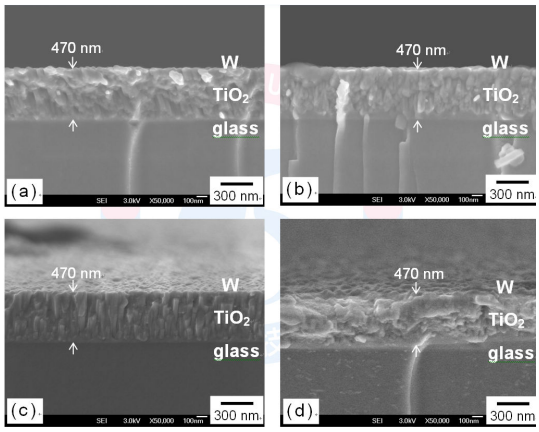


Fig.3 Cross section observations of W-$TiO_2$ films, annealing at (a)150°C, (b)200°C, (c)300°C, and (d) 400°C.

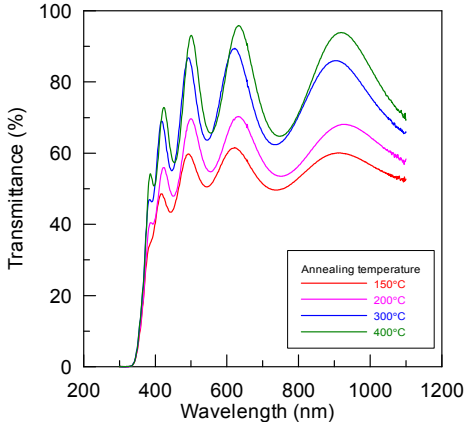


Fig.4 Transmittance of W-$TiO_2$ films, with different annealing temperatures.

surface structure of thin films due to crystal phase transformations.

The thicknesses are measured from the images of the cross sections shown in Fig.3. The thickness of $TiO_2$ in the W-$TiO_2$ dual-layer thin films has no apparent change as the annealing temperatures increase. Fig.4 shows the UV–VIS spectrum of W-$TiO_2$ dual-layer thin films in wavelength range of 300–1100 nm. The W-$TiO_2$ dual-layer thin films prepared have high transparency in the visible range of 400–1100 nm and the transparency apparently increase with the increase of annealing temperatures. The band fluctuation is due to the interference color of the thin films that appears in the wavelength range of 400–1100 nm. However, the amplitude of interference spectra increases with the increase of tungsten depositing time. This result suggests that the tungsten film will decrease in the refractive index of $TiO_2$ thin films.

The absorption edges of W-$TiO_2$ dual-layer thin films are red-shifted, which is ascribed to the tungsten will cause the difference in the ratio of crystal phase transformation (Fig.1) and then will cause the difference in band gap energy of the $TiO_2$ thin films [9]. In the past, determination of band gap energy ($E_g$) is often necessary to develop the electronic band structure of a thin film material. In the high absorption region (>$10^4$ $cm^{-1}$), absorption coefficient $\alpha$ is related to the energy $hv$ of incident photons by the relation [10]:

$$\alpha = \left[ \frac{B(hv - E_g)^p}{hv} \right] \qquad (2)$$

$$\alpha = \left[\frac{1}{d}\ln\left(\frac{1}{T}\right)\right] \quad (3)$$

where $B$ is a constant, $p$ is an index that characterizes the optical absorption process, and $\alpha$ is the absorption coefficient. At shorter wavelengths close to the optical band gap, the influence of fundamental absorption on $\alpha$ is more prominent than scattering losses and $\alpha$ may be obtained by Eq(3). Where $d$ is the thickness of the film and $T$ the transmittance. In the high absorption region, $\alpha$ are calculated by Eq. (3) from normal incident transmission data of single side coated $TiO_2$ films. Fig. 5(a) illustrate plots of $(\alpha hv)^{1/2}$ against $hv$ (Energy) in accordance with Eq. (2), the $Eg$ can be found at $(\alpha hv)^{1/2}$ =0. Fig. 5(b) shows the calculated energy gaps of W-$TiO_2$ dual-layer thin films. The band gap of rutile $TiO_2$ is 3.0 eV and that of anatase $TiO_2$ is 3.2 eV [11]. Therefore, rutile has better visible light response and anatase has better photocatalysis activity. The $Eg$ obviously decreases in the W-$TiO_2$ dual-layer thin films as shown in Fig. 5(b). The $Eg$ of W-$TiO_2$ dual-layer thin films decrease from the 3.16 eV to 3.10 eV as the annealing temperatures increase from 150°C to 400°C.

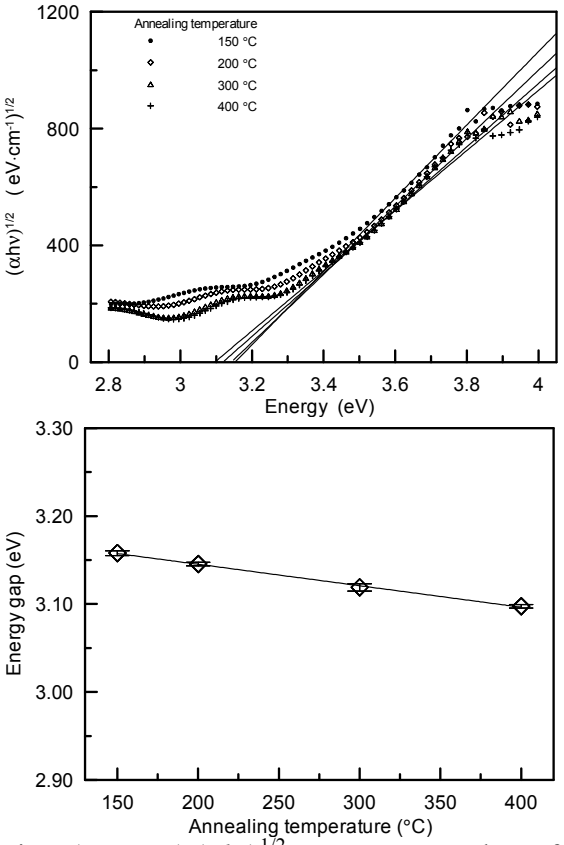


Fig.5 (a, upper) $(\alpha hv)^{1/2}$ versus energy plots of W/$TiO_2$ films as a function of annealing temperature. (b, bottom) Dependence of energy gap of W/$TiO_2$ film on annealing temperature.

## Conclusions

In this work, the deposited $TiO_2$ thin film has the energy gap of 3.21 eV. The addition of tungsten on $TiO_2$ thin film to form the W-$TiO_2$ dual-layer thin films is an important method to decrease the energy gap of $TiO_2$ thin film. For the W-$TiO_2$ dual-layer thin films, the energy gap will shift from 3.18 to 3.16 eV as the deposition time of tungsten increases from 15 sec (the tungsten thickness is about 18 nm) to 60 min (the tungsten thickness is about 44 nm), which is in the range of visible light. When the annealing temperatures of W-$TiO_2$ dual-layer thin films increase from 150°C to 400°C, the energy gap will shift from 3.16 to 3.10 eV.

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