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Effects of tungsten thickness and annealing temperature on the electrical properties of W–TiO_2 thin films

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Abstract

TiO_2 thin films were prepared by RF magnetron sputtering onto glass substrates and tungsten was deposited onto these thin films (deposition time 15–60 s) to form W–TiO_2 bi-layer thin films. The crystal structure, morphology, and transmittance of these TiO_2 and W–TiO_2 bi-layer thin films were investigated. Amorphous, rutile, and anatase TiO_2 phases were observed in the TiO_2 and W–TiO_2 bi-layer thin films. Tungsten thickness and annealing temperature had large effects on the transmittance of the W–TiO_2 thin films. The W–TiO_2 bi-layer thin films with a tungsten deposition time of 60 s were annealed at 200 °C–400 °C. The band gap energies of the TiO_2 and the non-annealed and annealed W–TiO_2 bi-layer thin films were evaluated using $(\alpha h\nu)^{1/2}$ versus energy plots, showing that tungsten thickness and annealing temperature had major effects on the transmittance and band gap energy of W–TiO_2 bi-layer thin films.

Keywords: A. Films; C. Electrical properties; C. Ferroelectric properties; D. TiO_2

1. Introduction

Titanium dioxide (TiO_2) is widely studied because of its ability to photo-oxidize harmful chemicals to CO_2 in both air and water in the presence of UV light. TiO_2 also shows promise for energy applications such as water splitting [1] and photochemical solar cells [2]. Despite the many potential applications of TiO_2, wider practical use requires that its photo-response be farther extended into the visible light region and its photo-efficiency be increased by reducing charge recombination. It is therefore interesting to explore the structure, phase, and orientation of TiO_2 thin films. Visible light response is a very important factor when examining TiO_2 as a photocatalyst, and the band gap energy value is a key property for photocatalytic activity.

In the past, many methods were developed to shift the band gap energy of rutile phase TiO_2 to a visible light range. Thin film coating of photocatalytic TiO_2 via various processes is a key technology for the practical use of this material. One method is adding other materials as dopants; another method is fabricating TiO_2-based multi-layer thin films. For example, many studies have incorporated different dopants, such as Fe [3,4], Mo, Ru, Os, Re, V, Rh, Co, and Al [4], SiO_2 [5], as well as Cr and Mo [6], into TiO_2 substrates by various mixing and coating techniques to increase the photocatalytic sensitivity in UV and visible light environments. Many metals, such as Ag [7], Ni, Cu, V, and Fe [8], can also be deposited onto TiO_2 thin films to form a bi-layer structure, thereby shifting the band gap energy of the rutile phase of TiO_2. In this study, tungsten (W) was deposited on TiO_2 thin films to form W–TiO_2 bi-layer thin films. The effects of tungsten deposition time (thickness) on transmittance and on the crystal structure of TiO_2 thin films in the bi-layer structure were studied. For comparison, W–TiO_2 thin films (tungsten deposition time:

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60 s) were also annealed in air at different temperatures. The effect of annealing temperature on the characteristics of W–TiO_2 thin films was also investigated.

2. Experimental procedure

Polyvinylalcohol (PVA) was added into the TiO_2 powder as a binder and the mixture was uniaxially pressed into pellets in a steel die. After debindering, sintering of the TiO_2 ceramic was carried out at 1400 °C for 4 h. An X-ray diffraction pattern of TiO_2 ceramic in the rutile phase was obtained. TiO_2 single-layer and W–TiO_2 bi-layer thin films were deposited onto well-cleaned glass substrates by RF magnetron sputtering at a pure argon work pressure of between 5×10^{-3} and 5×10^{-2} Torr. The working distance was 50 mm for the TiO_2 target and 120 mm for the tungsten target. First, the W–TiO_2 thin films were deposited at a glass substrate temperature of 150 °C. The deposition time for TiO_2 was 30 min and the time for the tungsten thin film was changed from 15 s to 60 s. The morphologies and thicknesses of the TiO_2 and W–TiO_2 bi-layer thin films were observed and measured by field effect scanning electron microscopy (FESEM) and the transmittance was measured by UV–vis–NIR spectrophotometry (HP-8453E). For comparison, the W–TiO_2 bi-layer thin films with a tungsten deposition time of 60 s were also annealed at 200–400 °C for 4 h.

3. Results and discussion

The surface morphology and microstructure of TiO_2 thin films depend closely on the final tungsten thickness (Fig. 1). The nano-crystalline TiO_2 grains grew significantly with increasing tungsten deposition time. The thicknesses of TiO_2 and tungsten were measured from the cross-section images of TiO_2 and W–TiO_2 thin films shown in Fig. 2. The thickness of TiO_2 in the lower layer showed no apparent change, while the thicknesses of the W–TiO_2 thin films increased with increasing tungsten deposition time. For deposition times of 15, 30, and 60 s, the tungsten thickness was 14 nm, 26 nm, and 44 nm, respectively.

The XRD patterns of the W–TiO_2 thin films were investigated for different tungsten deposition times. As shown in Fig. 3, in the single-layer TiO_2 thin films, the rutile, anatase, and amorphous phases coexisted. After the tungsten was deposited to form the W–TiO_2 bi-layer thin films, those same TiO_2 phases also coexisted in the XRD patterns. Fig. 4(a) shows the UV–vis spectrum of the TiO_2 and W–TiO_2 bi-layer thin films in the wavelength range of 300–1100 nm. The prepared thin films had a high transparency ratio in the visible range of 400–700 nm, and the transparency apparently decreased with increasing tungsten thickness. As tungsten was deposited on the TiO_2 thin films to form W–TiO_2, the absorption edge of the TiO_2 thin films was red-shifted. This result is ascribed to the tungsten, which caused a difference in the ratio of crystal phase transformation (Fig. 3), leading to a difference in the band gap energy of the TiO_2 thin films [9]. In the past, determination of the band gap energy (E_g) was often necessary to develop the electronic band structure of a thin film material. In the high absorption region ($>10^4$ cm^{-1}), the absorption coefficient α is related to the energy $h\nu$ of incident photons as follows [10]:

$$\alpha = \left[\frac{B(h\nu - E_g)^p}{h\nu}\right] \quad (1)$$

$$\alpha = \left[\frac{1}{d}\ln\left(\frac{1}{T}\right)\right] \quad (2)$$

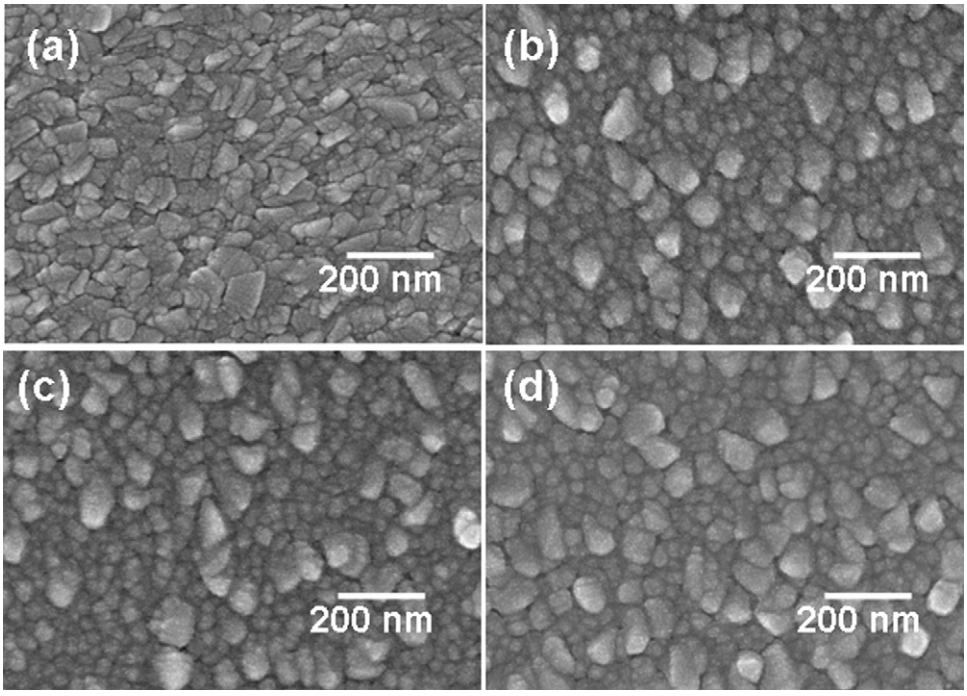

Fig. 1. Morphology of W/TiO_2 thin films for different tungsten deposition time. (a) 0, (b) 15, (c) 30 and (d) 60 s.

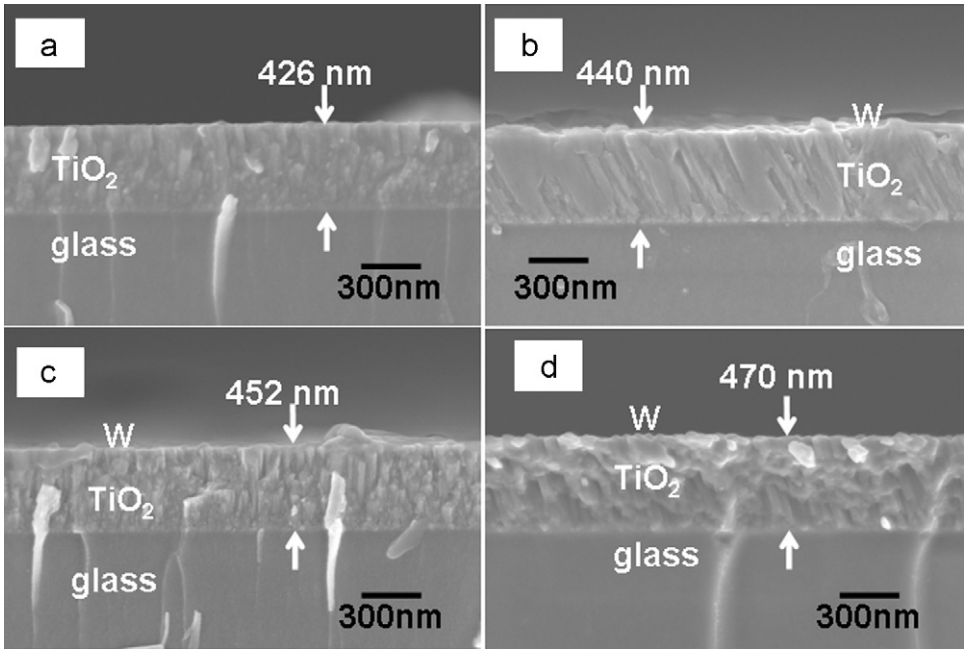

Fig. 2. Cross section observations of W–TiO_2 thin films for different tungsten deposition time. (a) 0 s, (b) 15 s, (c) 30 s, and (d) 60 s.

where B is a constant, p is an index that characterizes the optical absorption process, d is the thickness, and T is the transmittance ratio. At the shorter wavelengths close to the optical band gap, the fundamental absorption has a greater influence on α.

In the high absorption region, α is calculated with Eq. (2) using normal incident transmission data for the single-coated TiO_2 thin films. Fig. 4(b) illustrates the plots of $(\alpha h\nu)^{1/2}$ against $h\nu$ (energy) in accordance with Eq. (1); E_g can be found at $(\alpha h\nu)^{1/2} = 0$. Fig. 5 shows the calculated band gap energies of the TiO_2 and W–TiO_2 thin films. The band gap energy of the crystallite TiO_2 was about 3.21 eV, and the band gap energy of the W–TiO_2 bi-layer thin films decreased from 3.210 to 3.158 eV with increasing tungsten deposition time. From the

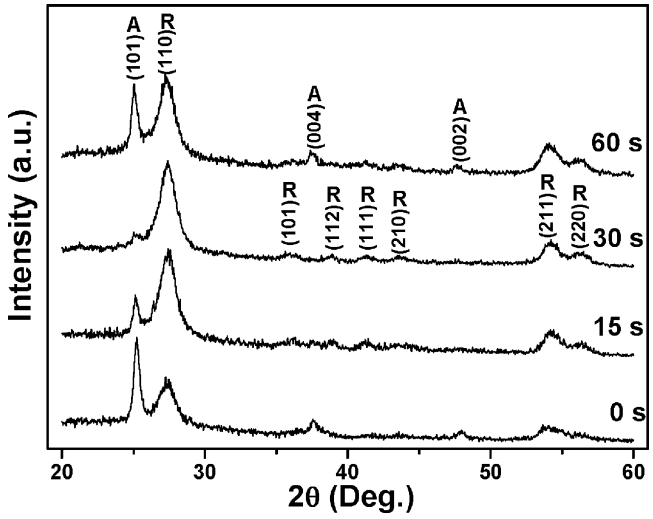

Fig. 3. X-ray diffraction patterns of W–TiO_2 thin films for different tungsten deposition time.

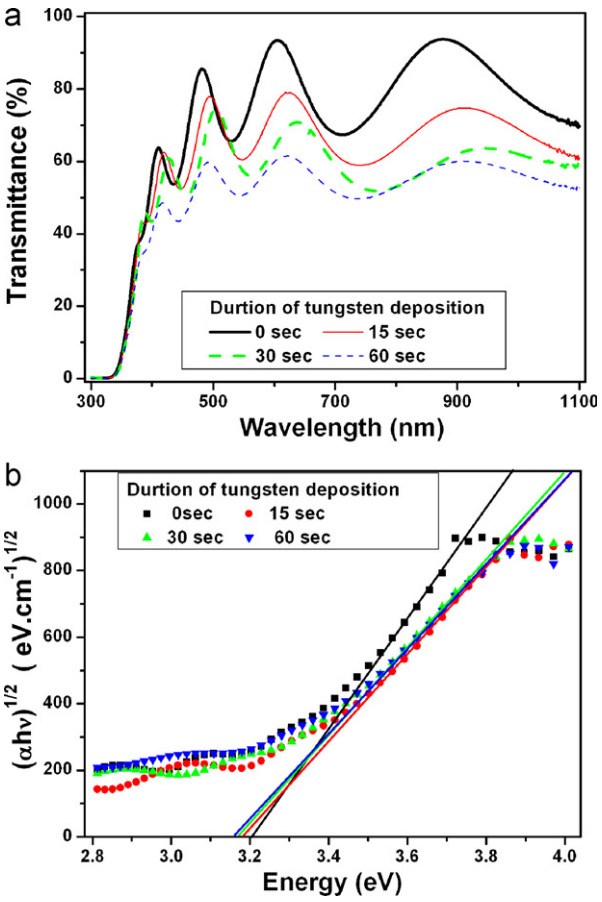

Fig. 4. (a) Transmittance and (b) $(\alpha h\nu)^{1/2}$ plot of W–TiO_2 thin films for different tungsten deposition time.

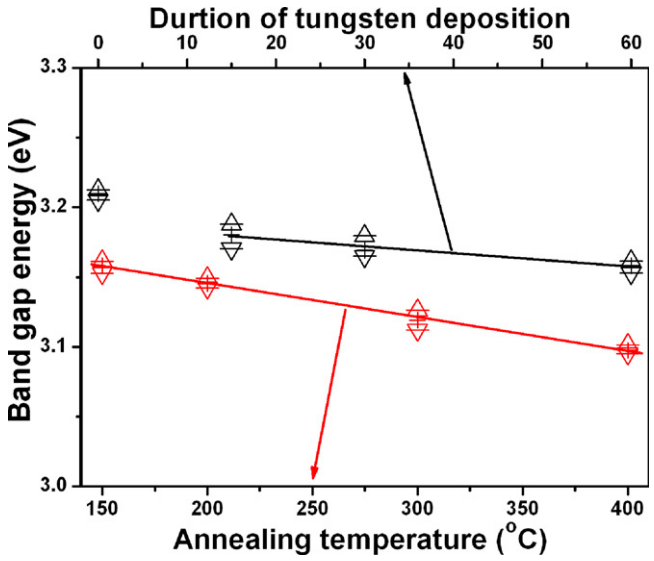

Fig. 5. Band gap energy of W–TiO_2 thin films for different tungsten deposition duration and annealing temperature.

XRD patterns shown in Fig. 3 it is evident that the rutile phase ratio for the W–TiO_2 bi-layer thin films changed as the tungsten deposition time increased. Because the band gap energy of the rutile phase is 3.0 eV, the existence of rutile

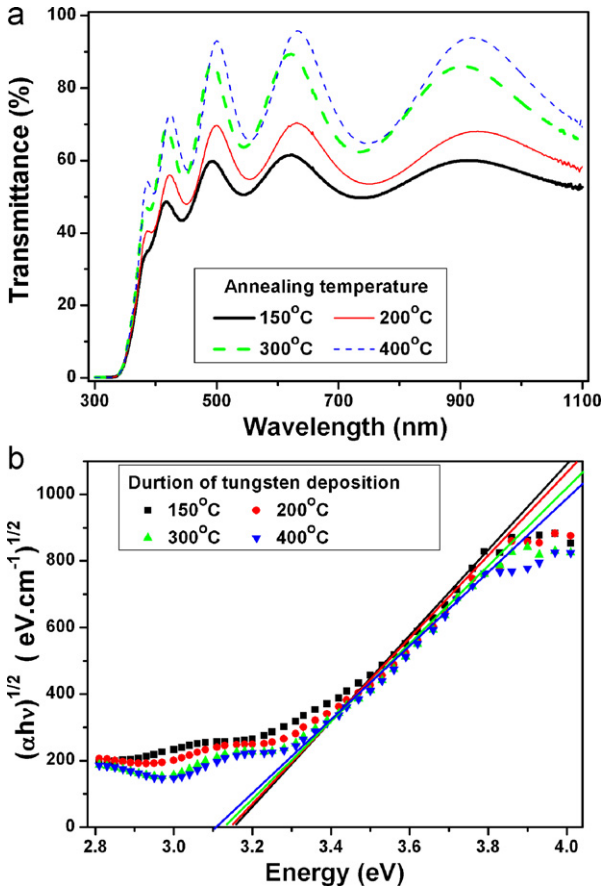

Fig. 6. (a) Transmittance and (b) $(\alpha h\nu)^{1/2}$ plot of W–TiO_2 thin films for different annealing temperature.

TiO_2 is not the only reason for the decrease in the E_g of the W–TiO_2 thin films; the addition of tungsten as the upper layer is another reason.

When the W–TiO_2 bi-layer thin films with a tungsten deposition time of 60 s were annealed at 200–400 °C, the surface morphologies underwent no apparent change. The UV–vis spectra of the W–TiO_2 bi-layer thin films are shown in Fig. 6 as a function of annealing temperature. As Fig. 6 shows, the transparency of the W–TiO_2 bi-layer thin films increased as the annealing temperatures rose. This result may be due to the tungsten diffusing into the TiO_2 layers, decreasing the thickness of the tungsten layer and increasing the transmittance ratio. Fig. 5 also shows that the calculated band gap energy of the annealed W–TiO_2 thin films decreased from 3.158 to 3.098 eV with rising annealing temperature. As this result suggests, annealing W–TiO_2 thin films is another method to decrease the band gap energy of TiO_2-based thin films.

4. Conclusions

The calculated results show that as the tungsten thickness and annealing temperature increased, the band gap energy values decreased. The band gap energy of deposited TiO_2 thin film was 3.21 eV. For the W–TiO_2 bi-layer thin films, as the tungsten deposition time was increased from 15 s to 60 s, the band gap energy shifted from 3.210 to 3.158 eV, which is in the range of visible light. When the annealing temperature of the W–TiO_2 bi-layer thin films was increased from 200 to 400 °C, the band gap energy shifted from 3.158 to 3.098 eV. Annealing was thus demonstrated to be another important method to decrease the band gap energy of TiO_2-based thin films.

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