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ORIGINAL PAPER

Microstructure and Optical Properties of Tantalum Modified TiO_2 Thin Films Prepared by the Sol–Gel Process

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Abstract Tantalum doped TiO_2 thin films $((TiO_2)_{1-x}(Ta_2O_5)_x, x = 0, 0.1\%, 0.3\%, 0.5\%, 0.8\%)$ were prepared on ITO-coated substrates by means of the sol–gel method and spin coating technology followed by rapid thermal annealing treatment (RTA). The effects of various processing parameters, including Ta content ($x = 0$–0.8%) and annealing temperature, on the growth and properties of thin films were investigated. Structural characteristics by X-ray diffraction analysis indicated that the doping of Ta_2O_5 in the TiO_2 without change the anatase structure of TiO_2 thin films. The optical transmittance of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films decrease from 50% down to 20% with increasing the Ta_2O_5 concentrations from $x = 0.00$ to $x = 0.8\%$. The absorption coefficient shows energy gap were decreased with increasing Ta_2O_5 content from 2.932 eV for $x = 0.00$ to 2.717 eV for $x = 0.8\%$. Doping TiO_2 with Ta_2O_5 can lower its band gap and shift its optical response to the visible region.

Keywords TiO_2 · Microstructure · Optical properties · Band gap

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1 Introduction

Titanium oxide (TiO_2) is well known as a metal oxide semiconductor, has been extensively studied in many applications. For example, it is used for photo-electrodes, photocatalysts, and dye-sensitized solar cells (DSSC) applications with high performance due to its fine physical, chemical, and optical properties [1–4]. In the application of photocatalysts, ultraviolet (UV) light is only a small part of the solar spectrum. Therefore, the improvement of photocatalysts that can yield efficient reaction under solar irradiation will be very valuable. Many studies have been proposed to the red shift of absorption edge in the band gap of TiO_2. One main approach is to dope TiO_2 with transition metals [5, 6].

Many researches have fabricated TiO_2-based thin films by various methods, including sputtering, laser ablation, metallorganic chemical vapor deposition, sol–gel methods, and metallorganic decomposition [7–10]. Chemical-solution methods, such as sol–gel technology, offer flexible and precise control over stoichiometry, for achieving TiO_2-based thin films with a precise stoichiometric ratio and a homogeneous composition distribution.

In this paper, we focus on the deposition of $(TiO_2)_{1-x}(Ta_2O_5)_x$ films with various tantalum contents on ITO-coated glass substrates, and the evolution of optical properties of the films are investigated. The microstructures and optical properties of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films are examined using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-vis spectrometer.

2 Experimental

Titanium diisoprop-oxide bis (2,4-pentanedionate) (TIAA), $Ti(OC_3H_7)_2$ $(CH_3COCHCOCH_3)_2$ (Alfa, 99.9%+ purity),

and tantalum isopropoxide, $Ta[OCH(CH_3)_2]_5$ (Alfa, 99.9%+ purity), were used as precursors and 2-methoxyethanol, $C_3H_8O_2$ (Fluka, 99.9%+ purity) was used as a solvent. The gravimetrically assayed $Ti(OC_3H_7)_2(CH_3COCHCOCH_3)_2$ and $Ta[OCH(CH_3)_2]_5$ reagents were dissolved in a mixture of 2-methoxyethanol solution at room temperature. The mixture was refluxed at 120 °C for 4 h under ambient atmosphere and then cooled to 80 °C for 2 h to promote its homogeneity. A stock solution of ∼1 M concentration with a golden color was obtained by this procedure.

The stock solutions were spin-coated on ITO-coated glass substrates at a spin rate of 3,000 rpm for 30 s using a commercial photoresist spinner. After each coating step, the gel films were pyrolyzed on the hot plate at 300 °C for 2 min before final annealing. The average thickness of a single-coated as-fired layer, measured by an α-step surface profiler, was found to be about 0.1 μm. After multi-coating, $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films ($x = 0$–0.8%) were annealed at 400–700 °C for 2 min by the rapid thermal annealing (RTA) in an oxygen atmosphere. The desired $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films thickness of 1.0 μm were achieved by repeating the spin-coating and annealing cycles.

The structure and phase purity of the thin films were measured by X-ray diffraction with Cu-Kα radiation, which were recorded in the 2θ ranges from 20° to 60°. The transmittance optical measurements were performed using ultraviolet-visible spectrometer (Jasco, V-670) at room temperature to investigate the optical properties of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin film.

3 Results and Discussion

Figure 1 shows the XRD patterns of the $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin film with different Ta concentrations ($x = 0$–0.8%) annealed at 700 °C grown on ITO-coated glass substrates. The

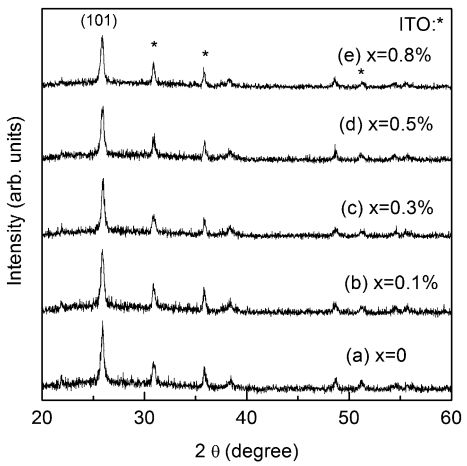

Fig. 1 X-ray diffraction patterns for $(TiO_2)_{1-x}(Ta_2O_5)_x$ films with $x = 0$–0.8% annealed at 700 °C

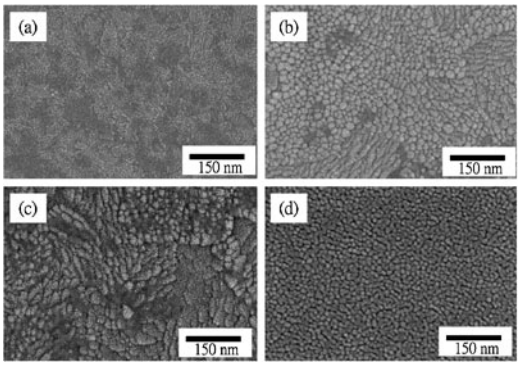

Fig. 2 Surface microstructures of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films with $x = 0.8\%$ annealed at various temperatures; (**a**) 400 °C, (**b**) 500 °C, (**c**) 600 °C, and (**d**) 700 °C. (bar = 150 nm)

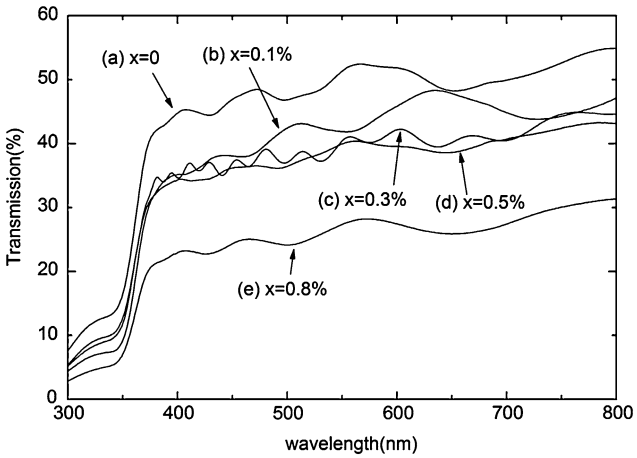

Fig. 3 The optical transmittance spectra for $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films with $x = 0$–0.8% annealed at 700 °C

$(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films show a anatase structure with preferred (101) orientation. As the Ta contents were increased, the peaks of the (101)-plane for samples decreased and the full-width at half-maximum (FWHM) increased indicating a decrease in grain size with increasing Ta contents. The (101) peaks obtained for all samples demonstrate that the doping of Ta ions will not change the anatase structure of TiO_2.

The evolution of surface microstructure of the $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films with $x = 0.8\%$ at annealing temperatures from 400 to 700 °C are shown in Fig. 2. As the annealing temperature was increased to 600 °C, grains measuring <30 nm were identified. At an annealing temperature of 700 °C, a homogeneous microstructure, consisting of uniform grain sizes of ∼20 nm, was obtained. In addition, the surface morphology of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films with $x = 0.8\%$ exhibits nanocrystalline and nanoporous structure which is composed of interconnected nanoparticles.

Figure 3 shows the transmittance spectra of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films annealed at 700 °C. The transmittance spectra of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films were measured as

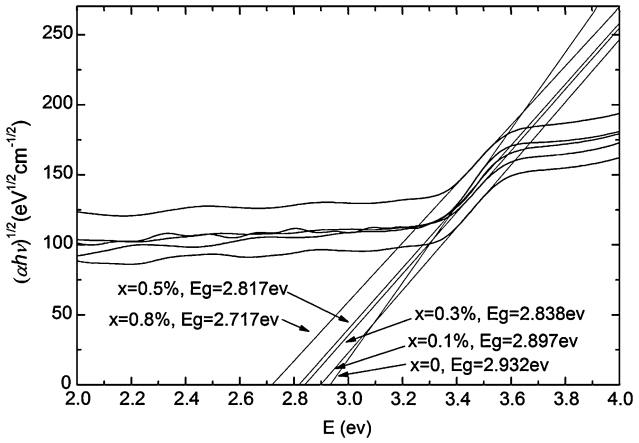

Fig. 4 The $(\alpha hv)^2$ vs. band gap curves for $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films

a function of wave length in the 300–800 nm. The thin films show an average transmittance above 50% and a sharp absorption edge around 340 nm. However, the transparency of $(TiO_2)_{1-x}(Ta_2O_5)_x$ fades away when the Ta contents increase. The absorption edges were increased from 334 nm for pure TiO_2 to 345 nm for $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films with $x = 0.8\%$, which are red shifted with increasing Ta content. The band gaps of these films were determined by means of a graphical method from the absorption coefficient derived from the transmittance results. We can determine absorption coefficient α from the transmittance T using the equation $\alpha = -(1/D)\ln T$, where D is film thickness. The absorption coefficient over the threshold of fundamental absorption obey a relationship $\alpha hv = A(hv - E_g)^n$, where A is a function of refractive index and hole/electron effective masses, h is the Planck's constant, v is the photon frequency, E_g is the band gap and $n = 1/2$ for direct band gap semiconductor. The band gap of all samples were evaluated by extrapolating the straight line part of the curve $(\alpha hv)^2 = 0$ as shown in Fig. 4. The calculated value of the corresponding band gap energy for pure TiO_2 was 2.932 eV and decreased slightly to 0.215 eV from $x = 0$ to $x = 0.8\%$ of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films (2.897 eV for $x = 0.1\%$, 2.838 eV for $x = 0.3\%$, 2.817 eV for $x = 0.5\%$ and 2.717 eV for $x = 0.8\%$). These results show that the doped TiO_2 thin films with Ta_2O_5 can decrease its band gap and shift its optical response to the visible region. It should be effective as a visible-light-driven photocatalyst.

4 Conclusion

In this study, (101)-plane oriented $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films ($x = 0$–0.8%) were deposed on ITO-coated glass substrates fabricated by a sol–gel method. We have investigated the structural and optical characteristics of the $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films. The X-ray diffraction patterns indicated that the anatase structure of the $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin film will not be affected by the substitution of Ta^{3+} for the Ti^{4+} ions. From the UV-vis transmittance spectrum, the red shifted properties of $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films can be observed that the band gap and optical transmittance of thin films decreased with the Ta content increased from $x = 0$ to $x = 0.8\%$. Therefore, the $(TiO_2)_{1-x}(Ta_2O_5)_x$ thin films with a lower band gap and optical transmittance are expected with better photocatalytic properties.

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