Journal of Ceramic Processing Research. Vol. 17, No. 12, pp. 1283~1286 (2016)

J O U R N A L O F
Ceramic
Processing Research

Structure and optical properties of anatase thin films produced by filtered cathodic vacuum arc method

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Titanium dioxide (TiO_2) thin films were deposited on glass substrates by filtered cathodic vacuum arc system (lab-made) for various number of pulse modes at -50 VDC, and followed by 450 ^{o}C annealing in air for 1 hr. The deposition pulses were 500 -2,000 pulses and the anatase film thickness was 13.0-37.5 nm. In this research, the roughness was increased with the increasing in the number of deposition pulses and film thickness. The transmission at 600 nm wavelength was 65-85%, decreasing with the film thickness, and the optical energy gap was in the range of 3.55-3.65 eV.

Key words: Anatase thin films, Filtered cathodic vacuum arc, Electron microscopy, Spectroscopy.

Introduction

Titanium dioxide (TiO_2) is a wide band gap semiconductor [1] with different applications controlled its optical properties [2] and electronic structure. TiO_2 thin film has attractive properties due to its applications: photocatalysis [3-6], optical coatings [7-10], optoelectronic devices [11, 12] and photoelectrodes of dye-sensitized solar cells [13-15]. There are many techniques used to fabricate TiO_2 thin films such as magnetron sputtering [5, 15-17], spray pyrolysis [18], chemical vapor deposition (CVD) [19, 20] and sol-gel method [13, 21].

Filtered cathodic vacuum arc (FCVA) method is used for metal thin film deposition [22-24]. The metal ion was produced by FCVA with the metallic source as a cathode. Metal plasma would diffuse through a 90 ^{o} electromagnetic duct to deposit on the substrate [25-27]. The ion energy can be controlled by applying a negative bias voltage to the substrate to attract the ions [25]. The film thickness is controlled by number of deposition pulses [29, 30]. In this work, FCVA system was used to produce titanium thin film on glass slide. These deposited metal films would be annealed for titanium dioxide thin film formation. There are three different forms of titanium dioxide: rutile, anatase and brookite [17]. The most intense photocatalytic activity is anatase. Different deposition techniques play the role in film structure and optical properties. Upon annealing the metallic films,E their structure, surface morphology, optical properties and energy gap were intensively investigated [31].

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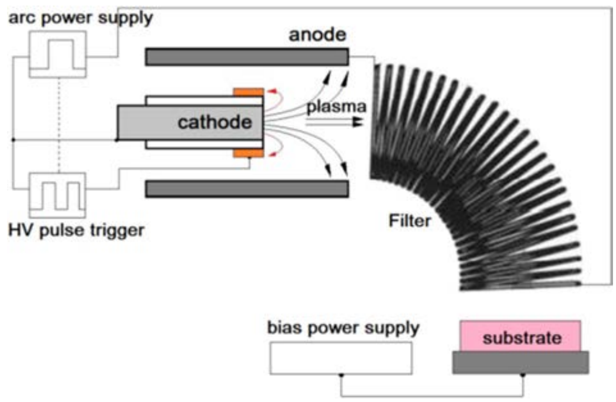

Fig. 1. Schematic diagram of FCVA system.

Experimental Details

Titanium dioxide thin films were fabricated on $1 \times 10 \times 10$ mm^3 soda-lime glass by FCVA system (Fig. 1). The experimental apparatus included a cathodic arc plasma source with 90 ^{o} electromagnetic duct filter, placed between the plasma source and substrate to remove macro-particles in a vacuum chamber. The cathode used in this experiment was a 99.9% pure Ti rod with 5.8 mm in diameter. The arc was ignited with 1 ms pulse width at the repetition rate of 1 pps. The arc current was 195 A. The Ti cathodic plasma arc was guided to the clean substrate by an applied electromagnetic filed induced by an arc current. A market pen was used to draw a line on surface of the attached sample. It will be removed after film deposition to be a trace without film cover for film thickness surface profile measurement. Each substrate was placed 5 cm apart from the magnetic exit duct. The chamber was tightly closed. A rotary and cryogenic vacuum pump was evacuated to

6.0×10^{-5} mbar. There are four deposition conditions: 500, 1000, 1500 and 2000 pulses, and the substrates were biased by −50 VDC.

Upon deposition the titanium thin films, they were annealed at 450 ºC in air for 1 hr to oxidize Ti to TiO_2. The TiO_2 films were analyzed by Raman spectrophotometry (T64000 Horiba JobinYvon). The film thickness and roughness was measured by atomic force microscopy (AFM, NanoScope IIIa, MMAFML N, Veeco). The surface morphology was investigated by scanning electron microscopy (SEM, Jeol JSM-6335F). The optical properties were evaluated by UV-VIS spectroscopy (Lambda 25 Perkin Elmer).

Results and Discussion

Deposition rate

Film thickness measured by AFM step profile drag pass across the edge of thin film and trace. The film thickness (Fig. 2) appears to increase slightly from 13.0 nm at 500 deposition pulses to 37.5 nm at 2000 deposition pulses. Deposition rate of TiO_2 films was approximately 1.6×10^{-2} nm per pulse or about 1 nm.min^{-1}. The deposition rate rather low because electromagnetic filter removed most of the titanium plasma, and only a small content of the plasma reached the substrate.

Raman spectroscopy

The Raman spectra (Fig. 3) of the TiO_2 films deposited at −50 VDC and annealed at 450 ºC for 1 hr show no significant change in the peak position when the film thickness increased, although the intensities of the peaks were increased. Due to the report for bulk TiO_2 [32], the rutile phase exhibits major peaks at 610, 446 and 242 cm^{-1}, and anatase exhibits at 635, 514, 396, 197 and 144 cm^{-1}. For the present analysis, broad peaks similar to the anatase were detected, and the anatase was attributed to form as the majority.

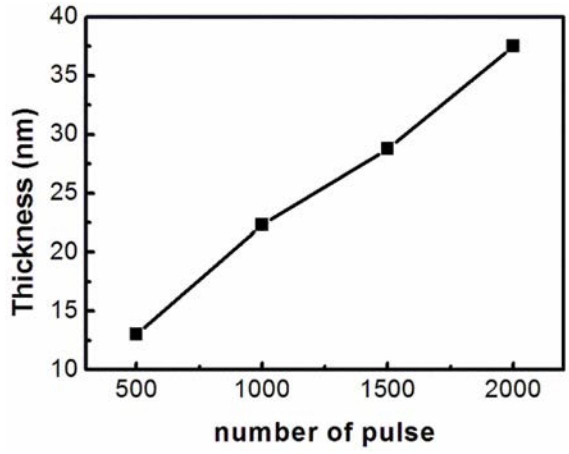

Fig. 2. TiO_2 film thickness at different deposition pulses.

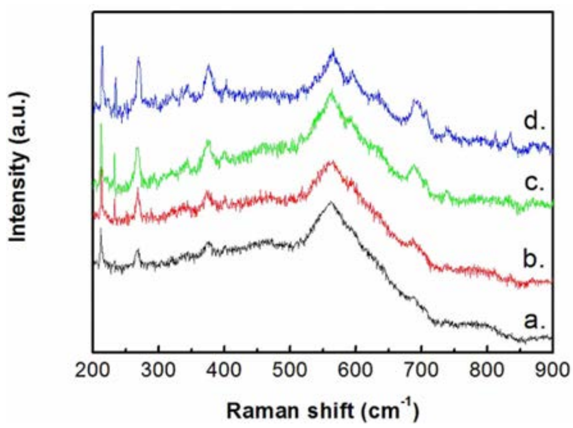

Fig. 3. Raman spectra of the TiO_2 thin films deposited on glass substrates at the deposition of (a-d) 500, 1000, 1500 and 2000 pulses, respectively.

Surface morphology

Surface morphology and roughness of the films were characterized by AFM. The AFM images of the

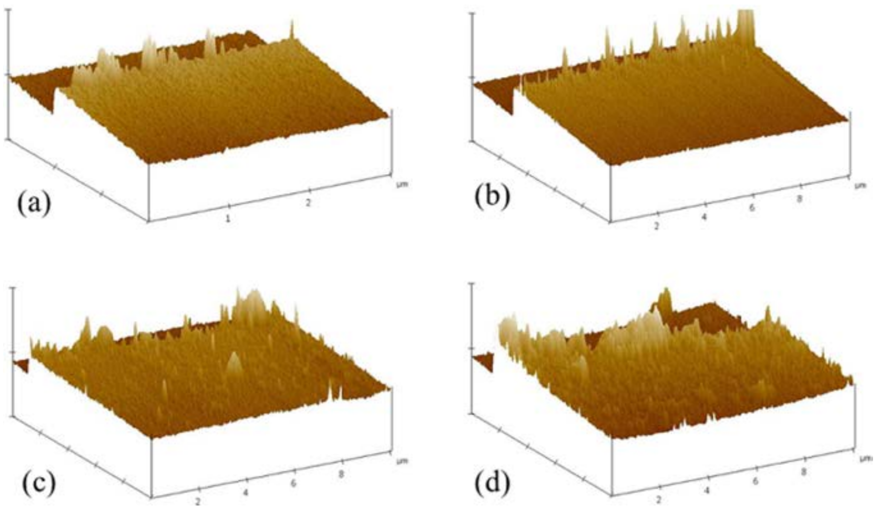

Fig. 4. AFM images of TiO_2 thin films prepared by FCVA at the deposition pulses of (a-d) 500, 1000, 1500 and 2000 pulses, respectively.

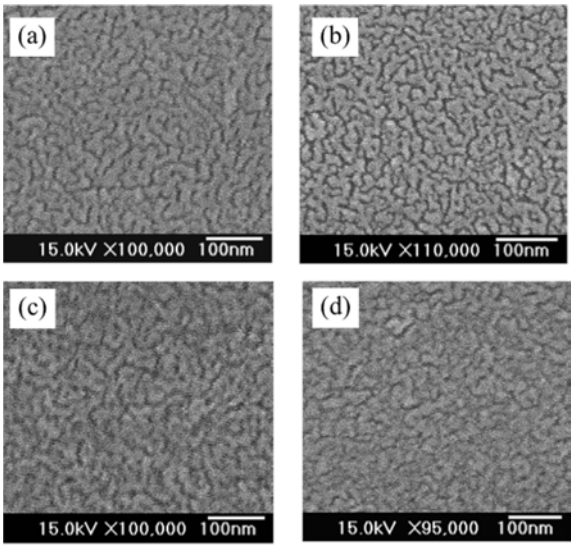

Fig. 5. SEM images of TiO2 thin films prepared by FCVA at the deposition pulses of (a-d) 500, 1000, 1500 and 2000 pulses, respectively.

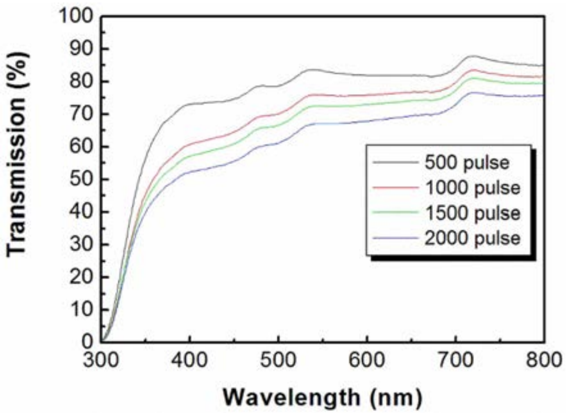

Fig. 6. Variation of transmittance with the wavelength at different deposition pulses.

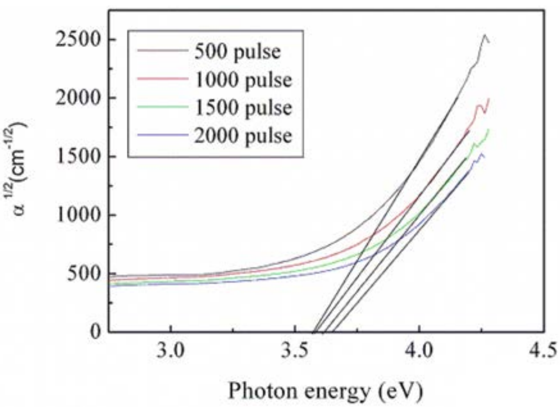

Fig. 7. Absorption coefficient and optical band gaps at various deposition pulses.

samples prepared by different number of deposition pulses are shown in Fig. 4. The lower part is the substrate and the upper one is the deposited film. Their surface roughness was increased with the increasing in the number of deposition pulses. SEM images of the TiO_2 thin films (Fig. 5) show tiny humps which were related to surface roughness.

Optical properties

Fig. 6 shows the optical transmittance of the coating films deposited at different deposition pulses annealed in air for 1 hr. In this research, the transmittance of the films decreased when the deposition pulse (including film thickness) was increased. For 600 nm wavelength, the film transmission was controlled by the film thickness, in the range of 65 to 85%.

Since TiO_{2fif} is a semiconductor with a large energy gap, the optical energy gap can be determined by the formula [18]

$$\alpha = -\frac{1}{d}\ln(T) \cong A^{*}(h\nu - E_g)^2 \qquad (1)$$

, where α, d, T, A*, h, ν and E_g are absorption coefficient, film thickness, transmission, constant (independent of hν), Planck's constant, frequency and indirect energy gap (eV), respectively.

From Fig. 7, the intercept of the tangent to the absorption edge can be used to evaluate the indirect band gap energy [33, 34], ranging from 3.55 eV to 3.65 eV for anatase [2], in accordance with those of 3.20-3.56 eV (anatase), larger than those of 3.00-3.34 eV (rutile) [35-39].

Conclusions

TiO_2 thin films were successfully prepared by FCVA and followed by 450 °C annealing in air for 1 hr. The deposition rate was approximately 1 nm.min^{-1} operating at 1 pps with 90 ° electromagnetic duct filter. Raman analysis confirmed the formation of anatase in the films. The surface roughness was increased with the increase of the deposition pulses and film thickness. For 600 nm wavelength, the film transmission was in the range of 65 to 85%. The band gap energies of the films were 3.55-3.65 eV.

Acknowledgments

We wish to thank Thailand's Office of the Higher Education Commission, Thailand Research Fund, and Chiang Mai University for financial support through the MRG program no. MRG5580137, and Thailand's Office of the Higher Education Commission for financial support through the National Research University (NRU) Project for Chiang Mai University.

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