

Characterization of electrophoretically deposited nanocrystalline titanium dioxide films

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Abstract

In the present study, nanocrystalline TiO₂ powders were electrophoretically deposited on the surface of a stainless steel substrate. Post heat treatment at 600 or 800 °C was performed to improve the adhesion strength. The as-prepared and heat-treated samples were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and synchrotron X-ray absorption spectroscopy. Experimental results show that the as-deposited nanocrystalline TiO₂ films exhibited anatase phase. Heat treatment at 600 °C not only retained the original nanocrystalline TiO₂ anatase phase but also increased the adhesion strength of the film. Anatase to rutile transformation was observed when the TiO₂ films were heat-treated at 800 °C. Crack formation due to the phase transformation was also noted and further decreased the adhesive properties of the TiO₂ films.

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1. Introduction

TiO₂ materials possess strong reduction and oxidation capability, excellent chemical stability, harmless to environment, and relative low cost and have attracted many R&D interests. TiO₂ materials, which functioned as a photocatalytic material [1–3], can be used in many applications including bacteria and fungus resistance, air and water purification [4], self-cleaning, and solar cell [5], etc.

Many attempts have been tried to prepare TiO₂ films or coatings, such as physical vapor deposition [6], chemical vapor deposition [7], sol–gel process [8], liquid phase deposition [9], and electrophoretic deposition [10,11], etc. Among these techniques, electrophoretic deposition (EPD) [12], achieved via movement of charged particles and deposited on substrate under an applied electrical field, has widely attracted attention. For instance, functionally

graded materials [13], patterned electrode [14], sensors and functional ceramics [15], and fuel cells [16] have been successfully prepared by electrophoretic deposition. In the present study, the feasibility of preparing nanocrystalline TiO₂ films by electrophoretic deposition was investigated. The influences of pH value of suspension, applied voltage, and post annealing treatment of the nanocrystalline TiO₂ films were evaluated.

2. Experimental procedures

Nanocrystalline anatase phase TiO₂ powders used in the present study were commercially available product (ST-01, Ishihara, Japan) with a mean grain size of ~ 7 nm and a specific surface area of 300 m²/g. Nanocrystalline TiO₂ powders (0.3 g/l) were added into acetone and agitated by ultrasonic vibration for 30 min. The pH value of the suspension was adjusted to a pre-determined value within a range of 2 to 5. The temperature of the suspension during deposition was kept at room temperature. Two stainless steel

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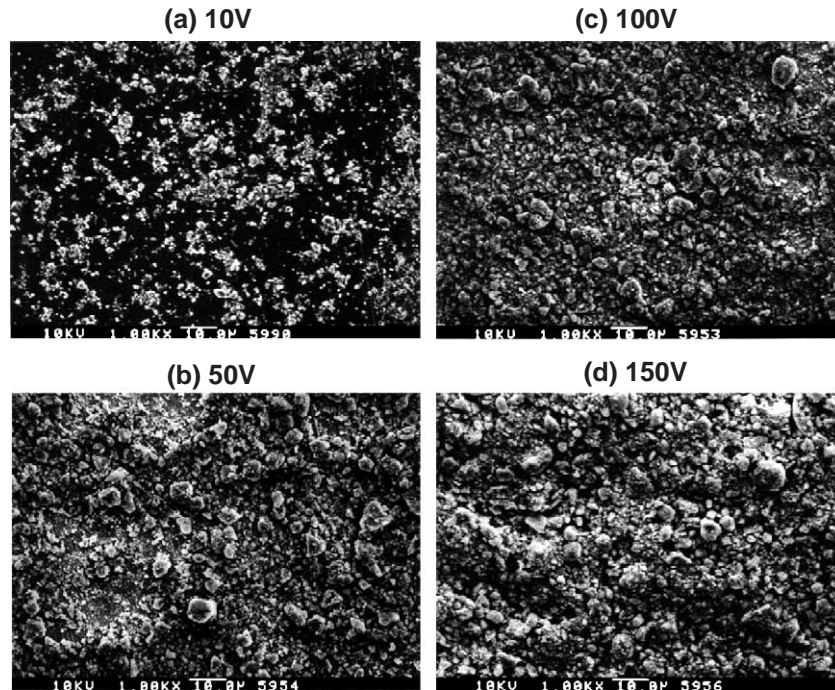


Fig. 1. SEM micrographs of nanocrystalline TiO_2 thick films that were electrophoretically deposited under various applied voltage (deposition time, 5 min; pH value of suspension, 4).

sheets were positioned by fixtures with adjustable distance and acted as substrate and counter-electrode. A standard dc power voltage was applied to the electrodes that were submerged into the EPD tank with prepared suspension. Except for the pH value, the processing parameters including applied voltage (10 to 240 V), current (1 to 6 mA) and deposition time (up to 10 min) were investigated. After deposition, the as-obtained samples were annealed at 600 or 800 °C for 1 h to enhance the adhesion strength of the films.

The as-prepared and annealed samples were examined by atomic force microscope (AFM, NT-MDT Solver P47, Russia), scanning electron microscope (SEM, TOPCON, ABT-150S Thermionic Emission SEM, Japan), X-ray diffraction (XRD, SRA-M18-XHF), and synchrotron X-ray absorption spectroscopy. X-ray absorption spectroscopy measurements were performed at the Wiggler-C beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan.

3. Results and discussion

Since electrophoretic deposition is achieved by moving charged particles towards a substrate electrode under an applied field, the acidity of suspension and the applied power during the process will vary the deposition efficiency [12]. Though not shown here, the pH value of the suspension did influence the deposition of nanocrystalline TiO_2 thick films. When the pH value was higher than 5, the deposition rate was so slow and no observable difference can be noticed after 20 min of processing. When the suspension exhibited a pH value ranging from 3 to 5, successful deposition of nanocrystalline TiO_2 can be noticed. Under a fixed applied voltage, the lower the pH value of the suspension, the higher the deposition rate. When the suspension became more acidic ($\text{pH} < 3$), though the deposition rate increased, corrosion of electrodes occurred and degraded the TiO_2 thick films.

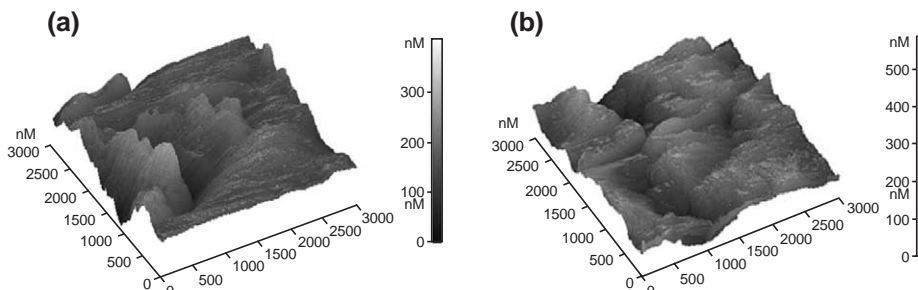


Fig. 2. Atomic force microscope images for nanocrystalline TiO_2 thick films deposited with an applied voltage of 50 V for (a) 15 and (b) 30 s ($\text{pH}=4$).

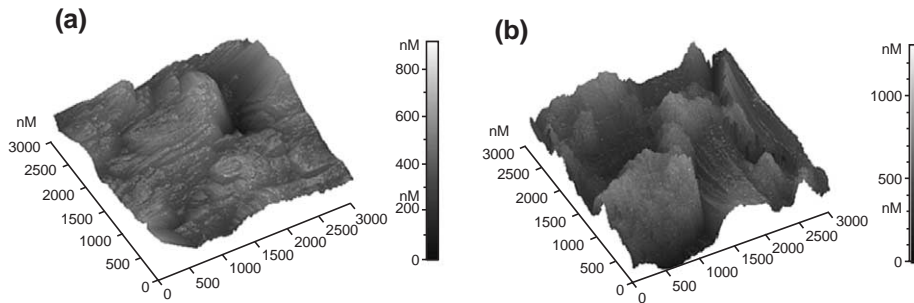


Fig. 3. Atomic force microscope images for nanocrystalline TiO_2 thick films deposited with an applied voltage of 150 V for (a) 15 and (b) 30 s ($\text{pH}=4$).

In order to evaluate the effect of applied voltage during EPD process, the pH value of suspension was fixed at 4 and deposition proceeded for a same during 5 min. Fig. 1 shows the SEM micrographs of the nanocrystalline TiO_2 thick films deposited under different applied voltages. As shown in Fig. 1a, when the applied voltage was 10 V, only limited nanocrystalline TiO_2 powders were successfully

electrochemically deposited on the substrate. As the applied voltage rose slightly to 20 V, more nanocrystalline powders (a few of them were larger than those under 10 V, Fig. 1a) can be deposited. However, some substrate surface can still be revealed. When the applied voltage increased to 50 V as shown in Fig. 1b, the substrate was fully covered with nanocrystalline TiO_2 powders. Some

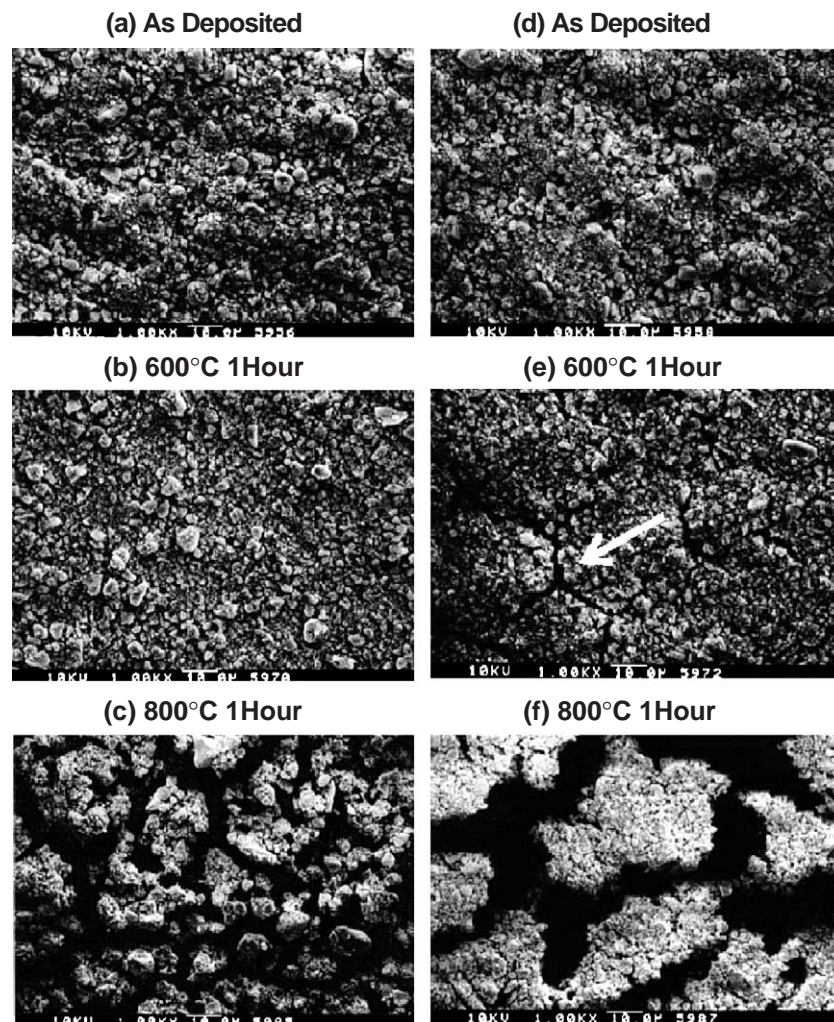


Fig. 4. SEM micrographs of as-deposited and annealed nanocrystalline TiO_2 thick films. Samples for (a) to (c) and (d) to (f) were prepared with an applied voltage of 150 and 220 V, respectively ($\text{pH}=4$, 5 min).

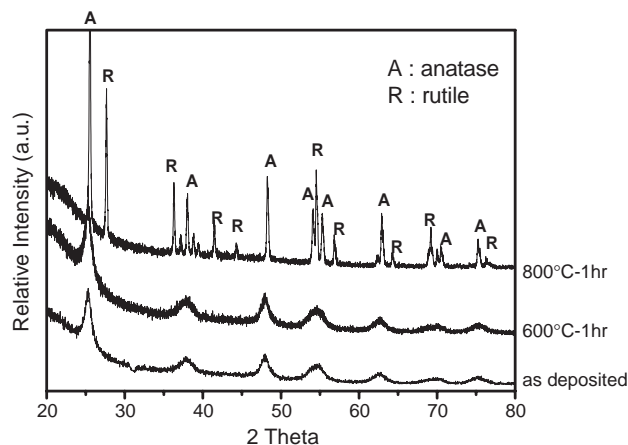


Fig. 5. X-ray diffraction patterns of as-deposited and annealed nanocrystalline TiO_2 thick films (150 V, 5 min, pH=4).

particles obviously larger in size as compared to those in Fig. 1a can be observed. Larger particles can be noticed when the applied voltage was further increased to 150 or 220 V.

It is well known that the charged particles moved under an applied field. The larger the applied field (or voltage), the higher the force that can move the particle [17]. In the present study, the starting powders are nanocrystalline and tend to agglomerate together. Thus secondary particle size may exhibit a particle size distribution different from that of its original particles. It is interesting to note that large secondary particles, apparently not separated by the ultrasonic vibration, deposited onto the substrate when large applied voltage was used. In order to better understand the deposition phenomenon, atomic force microscope was used to examine the as-deposited films at the beginning of processing (15 and 30 s) and the results were shown in Figs. 2 and 3 where the applied voltage was 50 and 150 V, respectively. The examination area for the sample deposited under an applied voltage of 50 V and 150 V was the same size of $3 \times 3 \mu\text{m}^2$. It can be noted that the surface roughness increased with the increasing depositing time. For as-deposited samples prepared by an applied voltage of 50 V, the maximum difference in height was ~ 400 nm (Fig. 2a) and 600 nm (Fig. 2b) after deposition for 15 and 30 s, respectively. Those values increased to ~ 900 and 1300 nm when the applied voltage was 150 V (Fig. 3). The difference in height increased as the applied voltage increased. Surface roughness will gradually reach a stable value. It can also be noticed that the deposition rate, at least at the beginning of EPD process, increased with the increasing applied voltage [18].

EPD films (or coatings) usually suffer from weak bonding between the substrate and films. As the thickness increases, cracking during drying or post annealing may occur. Fig. 4 shows the SEM micrographs for two sets of EPD nanocrystalline TiO_2 films prepared by an applied voltage of 150 V and 220 V, respectively (pH=4, 5 min). No significant difference can be noticed from Fig. 4a and

d. As discussed in Fig. 1, the thickness of EPD samples increased with increasing applied voltage. Thus, the thickness for the sample prepared by 150 V (Fig. 4a) will be less than that of Fig. 4d. After post annealing at 600°C , as shown in Fig. 4b, no observable difference can be noticed for films prepared under 150 V (corresponding to Fig. 4a). The 220 V deposited films with a larger thickness than that prepared by 150 V, however, exhibited microcracks on the surface (Fig. 4e). After annealing at 800°C , cracks on the surfaces for both samples can be observed. The microcracks as revealed by Fig. 4f (220 V) were clearer and wider than those in Fig. 4c (150 V).

Not only the thickness of the films but phase transformation during post annealing may induce cracking. Fig. 5 shows the corresponding X-ray diffraction patterns for those shown in Fig. 4a–c, i.e., as-deposited, 600 and 800°C annealed samples prepared under 150 V (pH=4, 5 min). It can be noticed that the as-deposited and 600°C annealed samples exhibited similar XRD patterns (anatase phase). Anatase to rutile transformation, however, can be noticed after annealing at a temperature of 800°C for 1 h. The phase transformation may be attributed to the microcracks of the samples (Fig. 4c and f). The thermal stress arose

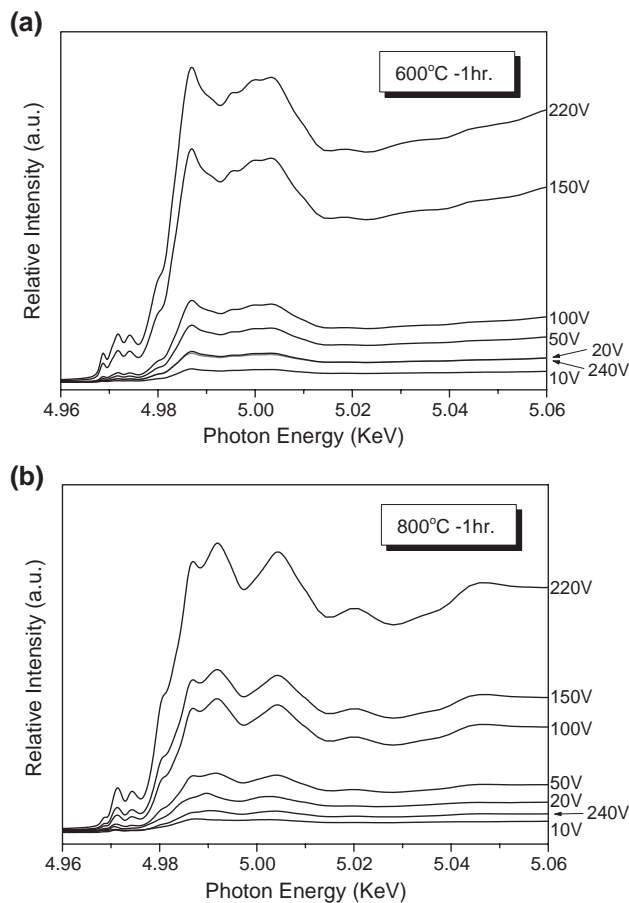


Fig. 6. X-ray absorption near edge spectra for nanocrystalline TiO_2 thick films prepared with different applied voltages and annealed at a temperature of (a) 600°C and (b) 800°C (pH=4, 5 min).

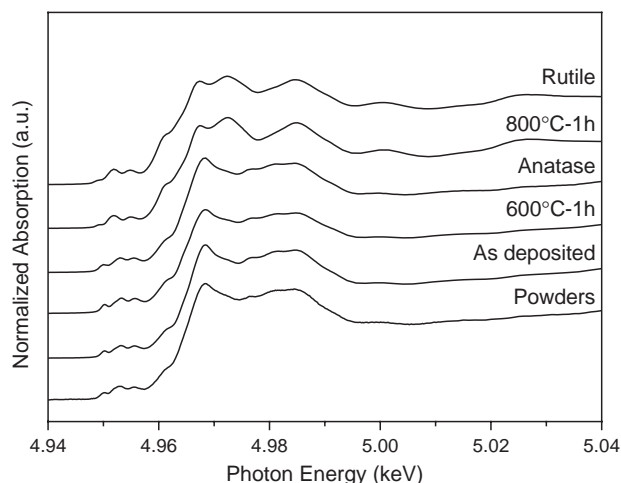


Fig. 7. Normalized X-ray absorption spectra for various TiO₂ samples.

from the difference of thermal expansion coefficient between steel substrate and TiO₂, which may also cause the cracking.

Synchrotron X-ray absorption spectroscopy techniques were also used to characterize the as-deposited and annealed samples. The major advantages of using synchrotron X-ray are the tunable X-ray energy, high brightness and intensity [19]. Fig. 6 shows the X-ray absorption near edge structure (XANES) spectra of annealed samples. The as-deposited samples showed similar spectra as those of 600 °C annealed samples. XANES spectra signify the electronic transition from an inner shell to the outer unoccupied shells induced by X-ray absorption. The local electronic structure and environment around the detected atom can be revealed [20]. Both XANES spectra of anatase and rutile exhibited three weak preedge peaks around 4.97 keV (Fig. 6). They differed in the post edge region due to the resonance patterns of the absorption coefficient [21]. As shown in Fig. 6, the phase transformation of anatase to rutile phase was confirmed. Meanwhile, it is also noted that the relative intensity (indicating relative amount of TiO₂) increased with increasing applied voltage (except that of 240 V). The XANES spectra for samples prepared by 240 V decreased significantly and did not follow the trend, i.e., thickness increased with increasing applied voltage. The differences came from the EPD process. As mentioned earlier, the applied voltage and the pH value will influence the EPD process. When the applied voltage exceeded 220 V, corrosion of substrate can be noticed and the TiO₂ thick films delaminated (SEM image not shown here). Though this information cannot determine quantitatively the amount of deposited nanocrystalline TiO₂ powders, it did imply that the TiO₂ amount increased with increasing applied voltage. This confirmed the results from Fig. 1 (SEM images for samples prepared under different voltages) and Fig. 2 (AFM images for samples at prepared at 50 and 150 V for 15 and 30 s).

In order to better examine the XANES spectra, normalizations of the corresponding spectra were performed and some of them were shown in Fig. 7. It can be noted that the starting powders, as-deposited, and 600 °C annealed samples exhibited similar spectra as that of standard anatase phase TiO₂. The 800 °C annealed films showed a clear difference in post edge (4.97 to 4.99 keV) due to the anatase to rutile transformation. The spectrum of 800 °C annealed films was similar to that of standard rutile phase TiO₂.

4. Conclusions

Nanocrystalline TiO₂ thick films were successfully prepared by electrophoretic deposition process. The pH value of the suspension can influence the EPD process. Nanocrystalline TiO₂ can be deposited when the suspension exhibited a pH value ranging from 3 to 5. Under a fixed pH value and same deposition duration, the film thickness increased with increasing applied voltage. Post heat treatment at a temperature of 600 or 800 °C was performed to improve the adhesion strength. The 600 °C annealed samples exhibited anatase phase, while anatase to rutile transformation occurred when samples were heat-treated at 800 °C for 1 h. Crack formation due to the phase transformation and thermal stress was noted and degraded the adhesive properties of the TiO₂ films.

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