



Short communication

Cathodic deposition of TiO₂ thin films with supercritical CO₂ emulsified electrolyte

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ARTICLE INFO

Article history:

Received 3 April 2013

Received in revised form 24 April 2013

Accepted 24 April 2013

Available online 2 May 2013

Keywords:

TiO₂
Cathodic deposition
Supercritical CO₂
Morphology
Grain size

ABSTRACT

TiO₂ thin films were fabricated by cathodic deposition with a supercritical CO₂ (sc-CO₂) emulsified TiCl₃ + NaNO₃ electrolyte. Morphology and average grain size were evaluated by SEM, TEM and XRD. SEM micrographs showed that the TiO₂ films fabricated by TiCl₃ + NaNO₃ electrolyte were porous, and the films were composed of particles and aggregates of the particles. Also, size of the particles increased when the sc-CO₂ emulsified electrolyte was used. Average grain size of the TiO₂ films was calculated using Scherrer equation. The average grain size was found to increase when the sc-CO₂ emulsified electrolyte was used. In addition, both particle sizes observed from SEM and average grain size calculated using Scherrer equation were found to increase when pressure was increased from atmospheric pressure to 20 MPa.

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1. Introduction

TiO₂ has been extensively investigated for applications in various fields of technology, such as solar cell [1], photocatalysis [2], hydrogen generation [3], and gas sensing [4]. TiO₂ thin films can be fabricated by chemical vapor deposition [5], sol-gel method [6], spray pyrolysis [7], and hydrothermal reaction [8]. These techniques usually involve prolonged reaction time which causes poor morphological control of the films. Among the different synthetic routes, cathodic deposition offers a low-cost yet effective process for fabrication of TiO₂ thin films [9–11].

Supercritical CO₂ (sc-CO₂) is one of the solutions to overcome problems encountered when applying electrochemistry in miniaturization of electronic devices [12]. However, CO₂ is non-polar. Metal salt solubility and electrical conductivity are both extremely low in CO₂, which limit application of sc-CO₂ in electrochemical reactions. Therefore, a surfactant is used to form an emulsified electrolyte composed of the aqueous electrolyte and sc-CO₂ in order to conduct electrochemical reactions [13]. Surface roughness and grain size of the electroplated Ni [14] and Cu [15] films are both found to decrease with application of sc-CO₂ emulsified electrolyte. On the other hand, Cu filled into a confined space such as nano-via by electroplating with sc-CO₂ emulsified electrolyte was reported to be single crystal [16].

This study would be the first report on application of sc-CO₂ emulsified electrolyte in cathodic deposition of oxide films, such as TiO₂. Applications of TiO₂ thin films are highly dependent on morphology

and crystal structure of the films [17]. The sc-CO₂ emulsified electrolyte is expected to affect the morphology and crystal structure of the TiO₂ films deposited significantly. Therefore, this study is focused on studying effects of sc-CO₂ emulsified electrolyte on morphology and crystal structure of the TiO₂ films deposited.

2. Experimental

Details of the high-pressure experimental apparatus used can be found in a previous study [13]. CO₂ with a minimum purity of 99.9% was used. The TiO₂ electrolyte was composed of 0.47 M NaCl, 25 mM TiCl₃, and 75 mM NaNO₃. A non-ionic surfactant, polyoxyethylene lauryl ether (C₁₂H₂₅(OCH₂CH₂)₁₅OH) was used to form the emulsion. Ni plates with dimensions of 1.0 × 2.0 cm² were used as the working electrode at cathode. Pt plates with dimensions of 1.0 × 2.0 cm² were used as the counter electrode at anode.

The deposition with only the TiO₂ electrolyte is denoted as conventional deposition (CONV). TiO₂ films were also prepared by CONV with 0.08 vol.% (CONV-8) and 0.16 vol.% (CONV-16) of the surfactant with respect to total volume of the reaction chamber to clarify the effects of the surfactant. The deposition with the sc-CO₂ emulsified electrolyte is denoted as DSCE. For DSCE, 20 vol.% of CO₂ and 0.08 vol.% of the surfactant with respect to total volume of the reaction chamber were used. The pressures used for DSCE were 10 MPa (DSCE-10) and 20 MPa (DSCE-20). Cathodic current density of 25 mA/cm², temperature of 40 °C, and deposition time of 10 min were used for all the deposition processes.

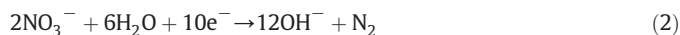
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Morphology of the TiO₂ films was examined by a scanning electron microscope (FESEM, S-4300SE, Hitachi). Crystal structural analysis was conducted by transmission electron microscopy (TEM, JEM-2100, JEOL, operated at 200 keV) and X-ray diffraction (XRD, Ultima IV, Rigaku) at a glancing angle of 1.0°. The samples were annealed in air at 400 °C for 1 h before the SEM, TEM, and XRD analysis. Average grain size was calculated using Scherrer equation. At least three samples were prepared with each condition for calculation of the average grain size.

3. Results and discussion

Morphology of the TiO₂ film deposited by CONV (no surfactant used) was porous as shown in Fig. 1(a) and (b). The film was composed of nano-scale pores and mostly micro-scale aggregates. The aggregates were composed of nano-scale particles. The results are similar to the results reported by Hu et al., where nano-scale pores were observed when the temperature was higher than 30 °C [9–11]. When the surfactant was added, increase in size of the pores was observed. Size of the aggregates and the particles did not change much as shown in Fig. 1(c), where 0.08 vol.% of the surfactant was used. The pores were suggested to be mainly caused by evolution of gases as shown in reactions 1 to 3 [10]:



Adsorption of gas bubbles on the surface of cathode was expected to be more significant after addition of the surfactant, which were reported in electroplating of Ni and Cu with sc-CO₂ emulsified electrolyte [13,15]. This should be the main cause for increase of the pore size observed after addition of the surfactant.

When sc-CO₂ emulsified electrolyte was used, particles with size in several hundreds of nm were observed as shown in Fig. 1(d), where the pressure was 10 MPa. Nano-scale particles could still be found surrounding the micro-scale particles for DSCE-10. For the size of the pores, distribution of the pore size became more uniform when comparing between Fig. 1(c) and (d). The more uniform distribution of the pore size should be caused by more uniform adsorption and desorption of the H₂·N₂, and NH₃ from the surface of cathode after emulsifying the electrolyte with sc-CO₂. The dispersed phases in the sc-CO₂ emulsified electrolyte are like micelles in oil-in-water emulsion [13]. The dispersed phases would constantly have contact with the cathode to lead to more uniform adsorption and desorption of the H₂·N₂, and NH₃. Morphology of the TiO₂ film fabricated by DSCE-20 was similar to the case of DSCE-10 as shown in Fig. 1(e), where particles with size in several hundreds of nm were observed.

From XRD patterns shown in Fig. 2, the particles forming the aggregates and the films observed in Fig. 1 were confirmed to be

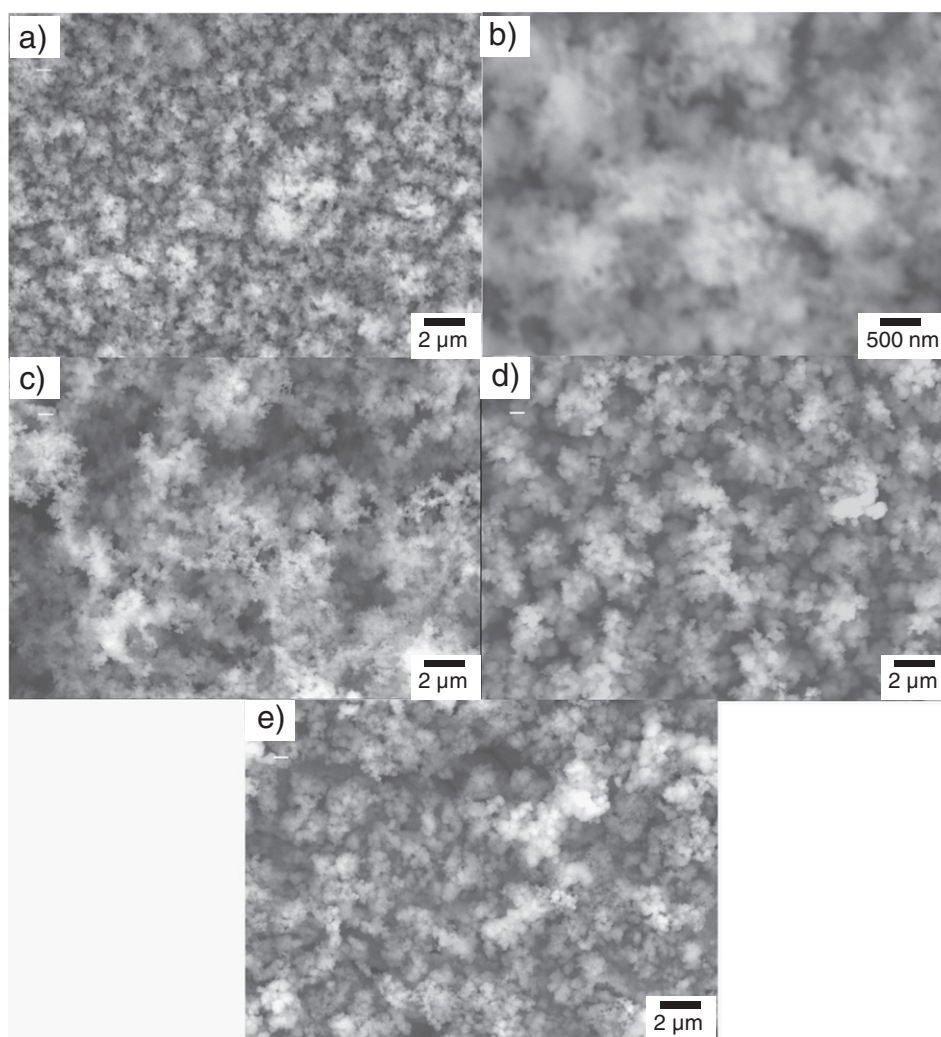


Fig. 1. SEM micrographs of the TiO₂ films fabricated by (a) conventional deposition (CONV), (b) higher magnification of CONV, (c) conventional deposition with 0.08 vol.% of the surfactant (CONV-8), (d) deposition with sc-CO₂ emulsified electrolyte at 10 MPa (DSCE-10), and (e) deposition with sc-CO₂ emulsified electrolyte at 20 MPa (DSCE-20).

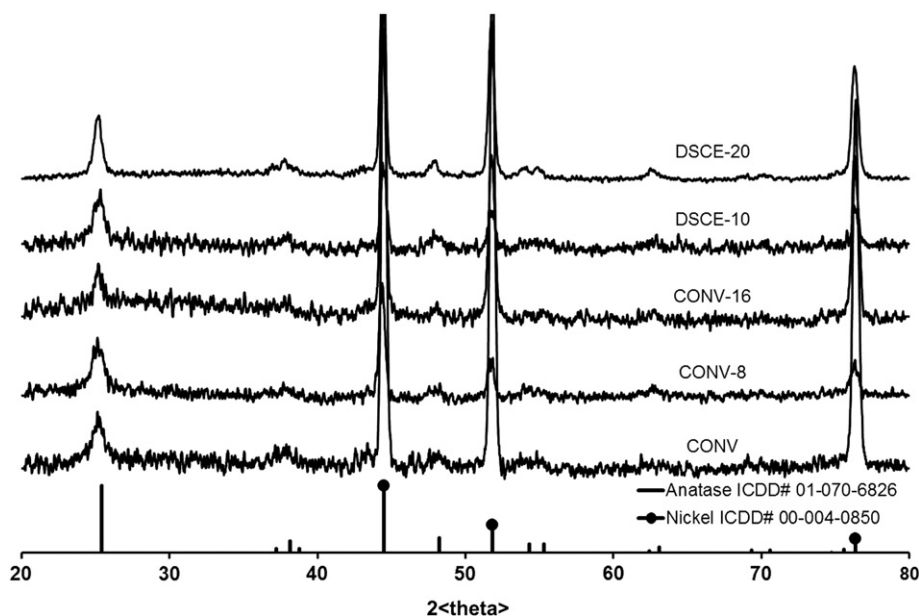


Fig. 2. XRD patterns of the TiO₂ films deposited under different conditions, anatase with ICDD# 01-070-6826, and Ni with ICDD# 00-004-0850.

anatase structure TiO₂. Full width at half maximum of the strongest diffraction peak corresponding to the facet (101) of anatase was used in Scherrer equation to calculate average grain size of the TiO₂ films. For CONV, increase in grain size of the films was observed after addition of the surfactant, where the grain size increased from 8.84 ± 0.45 to 11.27 ± 0.55 nm for surfactant volume fraction from 0 to 0.16 vol.% as shown in Fig. 3. Grain size of the TiO₂ films obtained in this study was in the same range as reported in Hu et al.'s study [11]. Although the experimental conditions used in Hu et al.'s study are not exactly the same as the conditions used in this study, however, composition of the base electrolyte is the same between the two studies.

When sc-CO₂ was introduced to the electrolyte containing 0.08 vol.% of the surfactant, the grain size increased from 9.63 ± 0.33 nm for CONV-8 to 11.46 ± 0.77 nm for DSCE-10. The grain size further

increased to 14.84 ± 0.25 nm when DSCE-20 was used. Grain size of the film fabricated by DSCE-20 was confirmed to be roughly 10 nm from TEM micrograph shown in Fig. 3. The trend of increase in grain size observed here matched the increase in size of the particles observed in the SEM micrographs.

For cathodic deposition of TiO₂, formation of the intermediate products, TiO²⁺ and oxy-hydroxyl-Ti species, is required, as shown in reactions 4 and 5:

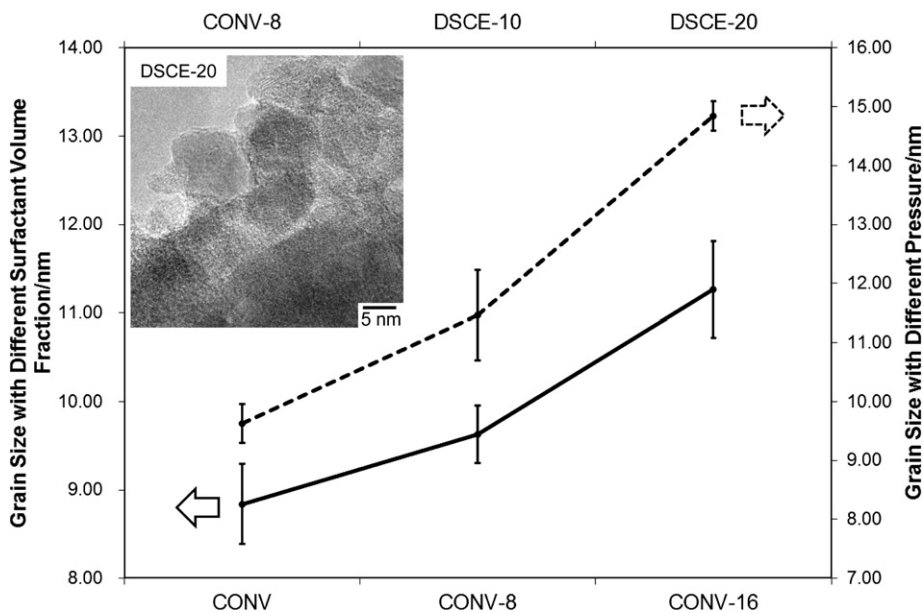
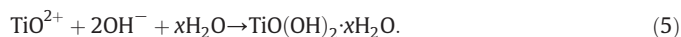


Fig. 3. Effects of the surfactant volume fraction and pressure on average grain size of the TiO₂ films. Left and lower axes correspond to the effects of the surfactant. Right and upper axes correspond to the effects of pressure. The embedded image is high resolution TEM of DSCE-20.

After formation of the oxy-hydroxyl-Ti species, TiO₂ could be formed after annealing as shown in reaction 6:



Source of OH[−] is believed to be the most important step in cathodic deposition of TiO₂, shown in reaction 5 [9–11,17]. Kholmanov et al. reported that larger oxy-hydroxyl-Ti particles led to the formation of larger TiO₂ particles and grains [18], and Hu et al. reported higher generation rate of the OH[−] would lead to formation of larger TiO₂ grains [11]. In DSCE, supply of reactants to the reaction site, such as NO₃[−] to the surface of cathode, and removal of products from the reaction site, such as H₂, N₂ and NH₃ from the surface of cathode, would be enhanced because the dispersed phases could improve transfer of materials into and out of the diffusion layer [15,19,20]. In addition, N₂ and NH₃ produced in reactions 2 and 3 would be in supercritical and liquid state, respectively, where pressure higher than 10 MPa and temperature of 40 °C were used. Critical point of N₂ is −147 °C and 3.3 MPa [21]. Phase transition pressure of NH₃ at 40 °C is about 1.6 MPa [22]. On the other hand, N₂ and NH₃ produced under atmospheric pressure and 40 °C would be both in gas state. Therefore, we believe the reaction rates of reactions 2 and 3 would be enhanced in sc-CO₂ emulsified electrolyte to give a higher generation rate of OH[−] and lead to the grain coarsening effect.

Results obtained in this study showed that morphology of the TiO₂ films could be affected by the surfactant used in this study and the sc-CO₂ emulsified electrolyte. Furthermore, the surfactant and the sc-CO₂ were found to have synergetic effect on the grain coarsening effect. Effects including the interaction between the surfactant and the surface of cathode, and the enhancement in transfer of materials to and away from the reaction site after emulsifying the electrolyte with sc-CO₂, N₂ in supercritical state and NH₃ in liquid state at high pressure are all believed to contribute to the phenomena observed in this study. However, further study is still needed to clarify the main factor causing the phenomena.

4. Conclusions

This study is the first study to report application of sc-CO₂ emulsified electrolyte in cathodic deposition of TiO₂ thin films. Pore size of the TiO₂ film fabricated by CONV was found to increase after addition of the surfactant. Size distribution of the pores became more uniform and size of the particles observed from SEM increased from several to several hundreds of nm when DSCE was applied. In addition, grain size of the TiO₂ films increased after addition of the surfactant and further

increased after emulsifying the electrolyte with sc-CO₂. The results obtained in this study showed that DSCE is a promising process to control morphology, particle size, and grain size of the TiO₂ thin films deposited cathodically.

Acknowledgment

Funding Program for Next Generation World-leading Researchers (NEXT Program) GN037, Cabinet Office (CAO), Japan is acknowledged. W.H. Lin and Y.J. Hsu acknowledge the financial support from the National Science Council of Taiwan (NSC-101-2213-M-009-018).

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