Effects of Pressure in Cathodic Deposition of TiO₂ and SnO₂ with Supercritical CO₂ Emulsified Electrolyte

Wei-Hao Lin^{1,2}, Chun-Yi Chen^{1,3,a}, Tso-Fu Mark Chang^{1,3,a,}, Yung-Jung Hsu^{2,*}, and
Masato Sone^{1,3,a}*

¹Precision and Intelligence Laboratory, Tokyo Institute of Technology, 4259-R2-35 Nagatsuta-cho Midori-ku Yokohama 226-8503 Japan.

²Department of Materials Science and Engineering, National Chiao Tung University, 1001 University Road, Hsinchu, 30010 Taiwan.

³CREST, Japan Science and Technology Agency, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

*E-mail: chang.m.aa@m.titech.ac.jp (T.-F.M.C.); yhsu@cc.nctu.edu.tw (Y.-J.H.)

a: ISE member

Abstract

This study reports the effect of the high pressure on properties, especially the crystallinity, of the TiO_2 and SnO_2 films cathodically deposited in supercritical CO_2 emulsified electrolyte. The as-deposited metal oxides are usually amorphous when cathodic deposition is applied. An additional heat treatment process is needed to have crystalline metal oxides. In this study, the TiO_2 and SnO_2 thin films cathodically deposited at elevated pressure showed an improvement in the crystallinity with an increase in the pressure using X-ray diffraction analysis. The high-resolution transmission electron microscopy and selected-area electron diffraction confirmed that the TiO_2 deposited at 35 MPa had the anatase crystal structure. An enhancement in the charge carrier dynamics at the TiO_2 electrode/electrolyte interface with an increase in the pressure was observed from the electrochemical impedance spectroscopy, which is a result of the improved crystallinity. The effect of the pressure on the crystallinity of the SnO_2 was more obvious than that on the TiO_2 . Grain size of the SnO_2 films estimated by the Scherrer equation was increased from 3.5 to 14.8 nm when the pressure was increased from 5 to 25 MPa.

Keywords: cathodic deposition, titanium dioxides, tin dioxides, high pressure, crystallinity

1. Introduction

As an important class of materials with a multitude of potential applications, metal oxide thin films and the methods for their preparation have gathered a lot of attention. The synthetic approaches include hydrothermal methods [1, 2], cathodic deposition [3-9], anodic oxidation [10, 11], sol-gel method [12, 13], and spray pyrolysis [14, 15]. Among them, cathodic deposition offers a low-cost yet effective process for production of metal oxides thin films with controllable morphology and crystal structure [5, 8]. For a typical cathodic deposition, hydroxide ions are generated by polarizing the substrate cathodically, which then causes a concentration gradient of hydroxide ions from the substrate surface to the bulk solution. Since the concentration of hydroxide ions is locally high at the substrate surface, metal ions initially dissociated in the electrolyte would combine with the hydroxide ions and subsequently form metal hydroxides and/or oxides on the surface of the substrate. By employing cathodic deposition, thin films of metal oxides such as TiO_2 and SnO_2 can be directly deposited on conductive substrates with complicated surface geometry. Such a feasibility of obtaining TiO_2 and SnO_2 thin films has significant implications in the aspects of photoelectrochemical applications [16, 17], H_2O_2 sensor [18], and anode material for Li-ion batteries [19].

However, the as-deposited TiO_2 and SnO_2 are usually amorphous when the deposition is conducted in an aqueous solution, such as sol-gel method and cathodic deposition [3-9, 13]. An additional heat treatment process, for example, annealing at 400 °C for 1 hr, is needed to obtain crystalline TiO_2 and SnO_2 . The need of the post-heat treatment limits selection of the substrates in cathodic deposition of the metal oxides, which further hinders the applicability of the products. Therefore, it is practically significant if crystalline metal oxides can be obtained directly from cathodic deposition without the additional heat treatment, or lower the temperature needed in the

1
2
3
4 heat treatment. On the other hand, the effect of pressure on the crystallinity of metal oxides
5
6 deposited from the solution phase is rarely investigated. In a previous study, grain size of the
7
8 TiO_2 cathodically deposited with a supercritical CO_2 (sc- CO_2) emulsified electrolyte (SCEM)
9
10 was found to be increased with an increase in the pressure, which a post-heat treatment at 400 °C
11
12 for 1 hr was still needed to have crystalline TiO_2 [5].
13
14

15
16 In this work, the effect of the pressure on the crystallinity of the as-deposited TiO_2 and SnO_2
17
18 thin films will be evaluated. Two types of the metal oxides would be studied to clarify general
19
20 effect of the high pressure on the crystallinity. TiO_2 and SnO_2 were selected because these two
21
22 metal oxides are usually amorphous when synthesized in the aqueous solution.
23
24
25
26
27
28
29

30 **2. Experimental**

31
32
33

34 **2.1 Chemicals.** All chemicals including CO_2 (Nippon Tansan Gas, 99.99 %), TiCl_3 (Kanto
35
36 Chem. Co., 20 %), NaNO_3 (Kanto Chem. Co., 99.0 %), NaCl (Kanto Chem. Co., 99.5 %),
37
38 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Kanto Chem. Co., 97.0 %), HNO_3 (Kanto Chem. Co., 70 %), and a surfactant
39
40 polyoxyethylene lauryl ether ($\text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{15}\text{OH}$, Toshin Yuka Kogyo, 25%) were used as
41
42 received without further purification.
43
44
45

46 **2.2 Cathodic Deposition with the SCEM.** The cathodic deposition with the SCEM (CD-SCEM)
47
48 was conducted in an apparatus especially design to conduct electrochemical reactions at high-
49
50 pressure as shown in Fig. 1. 20 vol.% of CO_2 , 0.08 vol.% of the surfactant, a Pt foil (1.0×2.0
51
52 cm^2) as the counter electrode, and a Pt wire (0.5 mm in diameter and 2.0 cm in length) as the
53
54 reference electrode were used in all of the cathodic depositions. For the TiO_2 , the working
55
56 electrode was a Ti substrate ($1.0 \times 2.0 \text{ cm}^2$). The electrolyte was composed of 25 mM TiCl_3 , 0.47
57
58
59
60
61
62
63
64
65

M NaCl, and 75 mM NaNO₃. The depositions were conducted at a constant cathodic current density of 2.5 A/dm² for 10 min with a potentiostat (1287A, Solartron Analytical). The pressure was varied from the atmospheric pressure to 35 MPa, and the temperature was either 40 or 70 °C. For the SnO₂, the working electrode was a Cu substrate (1.0 × 2.0 cm²). The electrolyte was composed of 25 mM SnCl₂•2H₂O and 75 mM HNO₃. The depositions were conducted at a constant cathodic current density of 1.0 A/dm² for 20 min with the potentiostat. The pressure was varied from the atmospheric pressure to 25 MPa, and the temperature was varied from 70 to 100 °C. The TiO₂ thin films deposited at *x* MPa and *y* °C were denoted as TI-*x*MPa-*y*C. For example, when 15 MPa and 70 °C were used, the sample would be named TI-15MPa-70C. When the atmospheric pressure was used, the sample would be named TI-ATM-*y*C. As for the SnO₂, the abbreviation of SN would be used.

2.3 Characterizations. The morphology and dimensions of the deposited films were examined with a field-emission scanning electron microscope (FESEM, JEOL, JSM-6500). The crystallographic structure was investigated by X-ray diffraction (XRD, Rigaku, Ultima IV), transmission electron microscopy (TEM, JEOL, JEM-2100), and selected-area electron diffraction (SAED, an accessory of JEM-2100). The Raman spectra were recorded by a microscopy Raman spectroscopy (Horiba Jobin Yvon, HR800). The excitation wavelength was 514.5 nm provided by the Ar laser. The electrochemical impedance spectroscopy (EIS) spectra were recorded at AC frequency from 1000 kHz to 0.1 Hz under open circuit voltage conditions.

3. Results and discussion

Figure 2 displays morphology of all of the TiO₂ thin films prepared in this work. The TiO₂ thin film deposited at atmospheric pressure and 40 °C (TI-ATM-40C) was porous and composed of aggregates of tiny particles. The pores are suggested to be a result of the gases formed during electrogeneration of the hydroxide ions as shown in the following equations:

The sample surface became more compact with an increase in the deposition temperature. At 70 °C, the TiO₂ thin film (TI-ATM-70C) contained a number of microscale islands. When CO₂ was introduced to exert the high pressure, the island-like-surface was cracked and the films consisted of coalesced particles with typical dimensions of several microns. This observation suggested that both deposition temperature and exerted pressure affected the growth of the TiO₂ during the cathodic deposition process.

Crystal structure of the TiO₂ thin films was then analysed by the XRD and TEM. In the XRD patterns shown in figure 3, the diffraction peak at about 25.2°, which originated from {101} planes of anatase TiO₂, was chosen as the index to determine the crystallinity of the TiO₂ thin films. For TI-ATM-40C, the characteristic peak at 25.2° was unidentifiable, reflecting the amorphous nature of the deposited film at 40 °C. For TI-ATM-70C, the peak at 25.2° emerged as a result of the improved crystallinity caused by the increased temperature. Upon the exertion of high pressure, the deposited samples exhibited sharpened diffraction peaks, suggesting that the high pressure was particularly beneficial for the crystallization of anatase TiO₂. The crystallographic structure of the sample deposited at 35 MPa and 70 °C (TF-35MPa-70C) was

1
2
3
4 further characterized by the HRTEM and SAED pattern. In figure 4, the lattice fringes of 0.35
5
6 nm corresponds to the {101} planes of anatase TiO₂, and the SAED pattern indicates the
7
8 polycrystalline features of the film.
9

10
11 A quantitative analysis on the charge carrier dynamics at the TiO₂ electrode/electrolyte
12 interface was conducted by the EIS measurements to further illustrate the effect of the pressure
13
14 on the crystallinity. Figure 5 shows the EIS spectra recorded on the TiO₂ thin films deposited at
15
16 various pressure and 70 °C. The charge transfer resistance (R_{sc}) at the TiO₂/electrolyte interface
17
18 can be calculated by fitting the semi-arc in the low frequency region. Smaller circular radius
19
20 represents lower charge transfer resistance and thus better charge separation efficiency for the
21
22 sample. The model used to fit the EIS data is depicted in the inset of figure 5 and the fitting data
23
24 are summarized in table 1. As noted in table 1, the R_{sc} of the TiO₂ electrode was significantly
25
26 reduced with an increased in the pressure, indicating that the charge transfer at the
27
28 TiO₂/electrolyte interface was promoted, and the charge recombination was demoted for the
29
30 TiO₂ thin film deposited at higher pressure. A diffusion-recombination model was further
31
32 utilized to compute the carrier lifetime (τ_c) for the tested electrodes [20]. The calculation results
33
34 showed that the TiO₂ had a longer carrier lifetime as the exerted pressure was raised. The
35
36 reduction in the charge transfer resistance and the increase in the carrier lifetime are both
37
38 suggested to be results of the improved crystallinity from the exerted high pressure [21].
39
40
41
42
43
44
45
46
47

48 Morphology of the SnO₂ thin films deposited at pressure ranged from 5 to 25 MPa and
49
50 constant temperature of 100 °C is shown in figure 6. Generally, the effect of pressure on the
51
52 morphology is not obvious. The relatively large circular-shaped pores observed on the film are
53
54 suggested to be caused by the enhanced gas evolution at 100 °C. As shown in figure S1, the
55
56
57
58
59
60
61
62
63
64
65

circular-shaped pores were observed in the SnO₂ thin films deposited at temperature higher than 70 °C.

Effect of the pressure on the crystal structure of the SnO₂ thin films could be observed from the XRD patterns, which are shown in figure S2, 7 and 8. When atmospheric pressure and 70 °C were used, the diffraction peaks of crystalline SnO₂ were not obvious, and the major peaks observed were all from metallic Sn, as shown in figure S2. When the temperature was increased from 70 to 100 °C at 15 MPa, the intensity of the diffraction peaks of metallic Sn gradually decreased, and the diffraction peaks of crystalline SnO₂ were sharpened. At 15 MPa and 100 °C, the diffraction peaks of metallic Sn could not be identified, and sharp crystalline SnO₂ diffraction peaks were observed. As shown in figure 7, similar results were observed when the pressure was increased from 15 to 25 MPa at 90 °C, which the intensity of the diffraction peaks of metallic Sn gradually decreased. For the SnO₂ thin films deposited at pressure ranged from 5 to 15 MPa and 100 °C, the major diffraction peaks were all {110} planes of crystalline SnO₂, shown in figure 8. In order to clarify effect of the pressure on the crystallinity, grain size of the SnO₂ was estimated using full width at half maximum of the (110) peak and the Scherrer equation. The Scherrer equation is shown in the following:

$$\text{Average grain size (nm)} = \frac{\lambda}{\beta \cos \theta} \quad (4)$$

λ : x-ray wavelength, 0.15418 nm

β : Full width at half maximum, in radians

θ : Bragg angle

Grain sizes of the SnO₂ thin films are shown in figure 9. At 15 MPa, the grain size increased from 2.5 to 3.9 with an increase in the temperature from 70 to 100 °C, indicated by the ■ symbol. This result is expected since high temperature is usually beneficial in improving the crystallinity.

On the other hand, the grain size increased from 3.1 to 14.4 nm with an increase in the pressure from 15 to 25 MPa at 90 °C, indicated by the ▲ symbol, and from 3.5 to 14.8 nm with an increased in the pressure from 5 to 25 MPa at 100 °C, indicated by the ● symbol. The effect of the pressure on the crystallinity of the SnO₂ was more obvious than that on the TiO₂. Here, “hydrobaric effect” is termed to describe the phenomenon observed from the effect of the high pressure (baric) on the properties of the metal oxides since the cathodic deposition mainly takes place in aqueous solutions (hydro), analogous to the derivative origin of “hydrothermal”. The hydrobaric effect includes the effect of the high pressure on the morphology and the crystal structure of the materials deposited in an aqueous solution.

The improved crystallinity endowed by the exertion of high pressure is suggested to be related to the electrogeneration of the hydroxide ions, shown in reaction 1 to 3. The crystallinity of cathodically deposited TiO₂ is reported to be affected by the electrogeneration of the hydroxide ions [22, 23]. As the hydroxide ion electrogeneration is promoted, the crystallinity of the deposited TiO₂ is improved. Reactions involved in cathodic deposition of TiO₂ and SnO₂ are similar, therefore, crystallinity of the SnO₂ is also expected to be affected by the hydroxide ion electrogeneration.

The pressure dependence of the rate constant (k) for condensed-phase reactions can be described by the expression [43]:

$$-RT \left(\frac{\partial \ln k}{\partial P} \right)_T = \Delta V^\ddagger \quad (5)$$

According to this expression, the reaction rate increases with pressure as a negative activation volume ($\Delta V^\ddagger$) is obtained. The value of $\Delta V^\ddagger$ for a specific reaction can be further estimated from the equation:

$$\Delta V^\ddagger = \sum pV_P - \sum rV_R \quad (6)$$

p and r are the order of the product and reactant in the chemical reaction, respectively, and V_P and V_R are the corresponding molar volumes. By calculating the $\Delta V^\ddagger$ values of the reaction 1 to 3 at different pressure, we can estimate the reaction rate of the reaction 1 to 3 at different pressure. The molar volumes of H_2O , H_2 , N_2 , and NH_3 at 70 °C under different pressure were acquired from the NIST Reference Fluid Thermodynamic and Transport Properties Database [24], shown in table S1. As to OH^- and NO_3^- , we can merely obtain the values at 70 °C under saturation vapor pressure [25, 26]. Considering that the molar volume of the solvent H_2O barely varied with pressure, we assumed that the value of OH^- and NO_3^- at increasing pressure remained unchanged. By substituent the molar volume data into equation (6), the value of $\Delta V^\ddagger$ for the reaction 1 to 3 can be further computed, as summarized in table 2.

As shown in table 2, for the three reactions involved in the electrogeneration of the hydroxide ions, the $\Delta V^\ddagger$ values decreased with an increase in the pressure. This result suggested that the electrogeneration of the hydroxide ion would be significantly promoted at the high exerted pressure, which then leads to the improved crystallinity. However, more studies are still needed to confirm the mechanism proposed. On the other hand, the results reported in this study clearly demonstrate the hydrobaric effect, which is the effect of the high pressure on the morphology and the crystallinity of the metal oxides fabricated by cathodic deposition.

4. Conclusions

In conclusion, a high pressure cathodic deposition method with a sc- CO_2 emulsified electrolyte has been developed to prepare crystalline TiO_2 and SnO_2 thin films at a relatively low temperature, which was 70 and 100 °C for the TiO_2 and SnO_2 , respectively. The success was

1
2
3
4 achieved by exerting high pressure during the deposition process, which is proposed to promote
5
6 the hydroxide ion generation to improve the crystallinity of the deposited TiO_2 and SnO_2 . When
7
8 compared to the TiO_2 obtained at ambient atmosphere, the charge transfer resistance at the
9
10 TiO_2 /electrolyte interface was significantly lowered with an increased in the pressure, which is a
11
12 result of the improved crystallinity. The enhancement of the crystallinity was more obvious for
13
14 the SnO_2 for which the grain size increased from 3.5 to 14.8 nm when the pressure was increased
15
16 from 5 to 25 MPa at 100 °C. This current study demonstrated the hydrobaric effect and its
17
18 significant implications in the solution-phase synthesis of metal oxides such as TiO_2 and SnO_2 .
19
20
21
22
23
24
25
26

27 **Acknowledgements**

28
29 This work was supported by CREST Project operated by the Japan Science and Technology
30
31 Agency (JST). Y.J. Hsu acknowledges the financial support from the Ministry of Science and
32
33 Technology of Taiwan under grant NSC-102-2113-M-009-005-MY2.
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

References

- [1] Y.C. Pu, G.M. Wang, K.D. Chang, Y.C. Ling, Y.K. Lin, B.C. Fitzmorris, C.M. Liu, X.H. Lu, Y.X. Tong, J.Z. Zhang, Y.J. Hsu, Y. Li, Au nanostructure-decorated TiO₂ nanowires exhibiting photoactivity across entire UV-visible region for photoelectrochemical water splitting. *Nano Lett.* 13 (2013) 3817-3823.
- [2] H.C. Chiu, C.S. Yeh, Hydrothermal synthesis of SnO₂ nanoparticles and their gas-sensing of alcohol. *J. Phys. Chem. C* 111 (2007) 7256-7259.
- [3] C.C. Huang, H.C. Hsu, C.C. Hu, K.H. Chang, Y.F. Lee, Morphology control of cathodically deposited TiO₂ Films. *Electrochim. Acta* 55 (2010) 7028-7035.
- [4] C.C. Hu, C.C. Huang, K.H. Chang, A novel solution for cathodic deposition of porous TiO₂ films. *Electrochem. Commun.* 11 (2009) 434-437.
- [5] T.F.M. Chang, W.H. Lin, Y.J. Hsu, T. Sato, M. Sone, Cathodic deposition of TiO₂ thin films with supercritical CO₂ emulsified electrolyte. *Electrochem. Commun.* 33 (2013) 68-71.
- [6] T.F.M. Chang, W.H. Lin, Y.J. Hsu, T. Sato, M. Sone, Effects of fluorinated surfactant in cathodic deposition of TiO₂ films with supercritical CO₂ emulsified electrolyte. *ECS Electrochem. Lett.* 3 (2014) D1-D2.
- [7] T.F.M. Chang, T. Sato, M. Sone, Fabrication of TiO₂ micro-structures by cathodic deposition. *Microelectron. Eng.* 121 (2014) 80-82.
- [8] S.T. Chang, I.C. Leu, M.H. Hon, Novel methods for preparing nanocrystalline SnO₂ and Sn/SnO₂ composite by electrodeposition. *J. Alloys Compd.* 403 (2005) 335-340.
- [9] M. Lai, J.H. Lim, S. Mubeen, Y. Rheem, A. Mulchandani, M.A. Deshusses, N.V. Myung, Size-controlled electrochemical synthesis and properties of SnO₂ nanotubes. *Nanotechnology* 20 (2009) 185602.
- [10] Z. Liu, W. Hou, P. Pavaskar, M. Aykol, S. B. Cronin, Plasmon resonant enhancement of photocatalytic water splitting under visible illumination. *Nano Lett.*, 11 (2011) 1111-1116.
- [11] H.C. Shin, J. Dong, M. Liu, Porous tin oxides prepared using an anodic oxidation process. *Adv. Mater.* 16 (2004) 237-240.
- [12] D.P. Macwan, P.N. Dave, A review on nano-TiO₂ Sol-Gel type syntheses and its applications. *J. Mater. Sci.* 46 (2011) 3669-3686.
- [13] F. Gu, S.F. Wang, M.K. Lü, G.J. Zhou, D. Xu, D.R. Yuan, Photoluminescence properties of SnO₂ nanoparticles synthesized by sol-gel method. *J. Phys. Chem. B*, 108 (2004) 8119-8123.

- [14] E.L. Unger, E. Ripaud, P. Leriche, A. Cravino, J. Roncali, E.M.J. Johansson, A. Hagfeldt, G. Boschloo, Bilayer hybrid solar cells based on triphenylamine-thienylenevinylene dye and TiO_2 . *J. Phys. Chem. C* 114 (2010) 11659-11664.
- [15] F. Paraguay-Delgado, W. Antúnez-Flores, M. Miki-Yoshida, A. Aguilar-Elguezabal, P. Santiago, R. Diaz, J.A. Ascencio, Structural analysis and growing mechanisms for long SnO_2 nanorods synthesized by spray pyrolysis. *Nanotechnology* 16 (2005) 688-694.
- [16] S.U.M. Khan, M. Al-Shahry, W.B. Ingler Jr., Efficient photochemical water splitting by a chemically modified n- TiO_2 . *Science* 289 (2002) 2243-2245.
- [17] J.J.M. Vequizo, J. Wang, M. Ichimura, Electrodeposition of SnO_2 Thin Films from Aqueous Tin Sulfate Solutions. *Jpn. J. Appl. Phys.* 49 (2010) 125502.
- [18] L.C. Jiang, W.D. Zhang, Electrodeposition of TiO_2 nanoparticles on multiwalled carbon nanotube arrays for hydrogen peroxide sensing. *Electroanal.* 21 (2009) 988-993.
- [19] C. Li, W. Wei, H. Wang, S. Wu, S. Fang, R. Chen, Electrodeposition route to synthesize SnO_2 microparticles as an anode material for Li-ion batteries. *J. Phys. Conf. Ser.* 152 (2009) 012035.
- [20] J.S. Yang, W.P. Liao, J.J. Wu, Morphology and interfacial energetics controls for hierarchical anatase/rutile TiO_2 nanostructured array for efficient photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces* 5 (2013) 7425-7431.
- [21] S.H. Kang, S.H. Choi, M.S. Kang, J.Y. Kim, H.S. Kim, T. Hyeon, Y.E. Sung, Nanorod-based dye-sensitized solar cells with improved charge collection efficiency. *Adv. Mater.* 20 (2008) 54-58.
- [22] I.N. Kholmanov, E. Barborini, S. Vinati, P. Piseri, A. Podestà, C. Ducati, C. Lenardi, P. Milani, The Influence of the precursor clusters on the structural and morphological evolution of nanostructured TiO_2 under thermal annealing. *Nanotechnol.* 14 (2003) 1168-1173.
- [23] C.C. Hu, H.C. Hsu, K.H. Chang, Cathodic deposition of TiO_2 : effects of H_2O_2 and deposition modes. *J. Electrochem. Soc.* 159 (2012) D418-D424.
- [24] NIST Reference Fluid Thermodynamic and Transport Properties Database.
- [25] Y. Marcus, Volumes of aqueous hydrogen and hydroxide ions at 0 to 200 °C. *J. Chem. Phys.* 137 (2012) 154501.
- [26] Y. Marcus, The standard partial molar volumes of ions in solution. part 5. ionic volumes in water at 125–200 °C. *J. Phys. Chem. B* 116 (2012) 7232-7239.

List of Figures

Figure 1 High pressure apparatus (a) CO₂ gas tank, (b) CO₂ liquidization unit, (c) liquidization pump, (d) high-pressure pump, (e) thermal bath, (f) reaction cell, with PEEK coating on the inner wall, (g) substrates, (h) stirrer, (i) programmable power supply, (j) back pressure regulator, (k) trap, (l) thermometer.

Figure 2 SEM images of the TiO₂ films. (a) TI-ATM-40C, (b) TI-ATM-70C, (c) TI-5MPa-70C, (d) TI-15MPa-70C, (e) TI-25MPa-70C and (f) TI-35MPa-70C.

Figure 3 XRD patterns of the TiO₂ films deposited under different conditoinis. The inverse triangle mark (▼) represents the peak of TiO₂ anatase (JCPDS #70-6826). The square marks (■) represent the peaks of the Ti substrate (JCPDS #44-1294).

Figure 4 (a) HRTEM image and (b) SAED pattern of the TI-35MPa-70C.

Figure 5 EIS spectra of the TiO₂ films deposited at different pressure and 70°C.

Figure 6 SEM images of the SnO₂ films. (a) SN-5MPa-100C (b) SN-10MPa-100C, (c) SN-15MPa-100C, (d) SN-20MPa-100C, and (e) SN-25MPa-100C.

Figure 7 XRD patterns of the SnO₂ films deposited under different conditions. The inverse triangle marks (▼) represent the peak of SnO₂ (JCPDS #88-0287). The circle marks (●) represent the peak of Sn (JCPDS #04-0673). The square marks (■) represent the peaks of the Cu substrate (JCPDS #04-0836).

Figure 8 XRD patterns of the SnO₂ films deposited under different conditions. The inverse triangle marks (▼) represent the peak of SnO₂ (JCPDS #88-0287). The square marks (■) represent the peaks of the Cu substrate (JCPDS #04-0836).

Figure 9 Grain sizes of the SnO₂ thin films.

1
2
3
4
5
6
7
8 **List of Tables**
9

10 **Table 1** Equivalent Circuit-Fitting Results of the TiO₂ films deposited at 70 °C under different
11
12 exerted pressures.
13
14

15
16
17
18
19 **Table 2** Estimated activation volumes ($\Delta V^\ddagger$, mol/L) of the three OH[−] generation reactions at 70
20
21 °C and 1 atm to 35 MPa.
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure 1

Figure 1 High pressure apparatus (a) CO₂ gas tank, (b) CO₂ liquidization unit, (c) liquidization pump, (d) high-pressure pump, (e) thermal bath, (f) reaction cell, with PEEK coating on the inner wall, (g) substrates, (h) stirrer, (i) programmable power supply, (j) back pressure regulator, (k) trap, (l) thermometer.

Figure 2

Figure 2 SEM images of the TiO₂ films. (a) TI-ATM-40C, (b) TI-ATM-70C, (c) TI-5MPa-70C, (d) TI-15MPa-70C, (e) TI-25MPa-70C and (f) TI-35MPa-70C.

Figure 3

Figure 3 XRD patterns of the TiO₂ films deposited under different conditoins. The inverse triangle mark (▼) represents the peak of TiO₂ anatase (JCPDS #70-6826). The square marks (■) represent the peaks of the Ti substrate (JCPDS #44-1294).

Figure 4

Figure 4 (a) HRTEM image and (b) SAED pattern of the TI-35MPa-70C .

Figure 5

Figure 5 EIS spectra of the TiO_2 films deposited at different pressure and 70°C .

Figure 6

Figure 6 SEM images of the SnO₂ films. (a) SN-5MPa-100C (b) SN-10MPa-100C, (c) SN-15MPa-100C, (d) SN-20MPa-100C, and (e) SN-25MPa-100C.

Figure 7

Figure 7 XRD patterns of the SnO₂ films deposited under different conditions. The inverse triangle marks (▼) represent the peak of SnO₂ (JCPDS #88-0287). The circle marks (●) represent the peak of Sn (JCPDS #04-0673). The square marks (■) represent the peaks of the Cu substrate (JCPDS #04-0836).

Figure 8

Figure 8 XRD patterns of the SnO₂ films deposited under different conditions. The inverse triangle marks (▼) represent the peak of SnO₂ (JCPDS #88-0287). The square marks (■) represent the peaks of the Cu substrate (JCPDS #04-0836).

Figure 9

Figure 9 Grain sizes of the SnO₂ thin films.

Table 1

Table 1 Equivalent Circuit-Fitting results of the TiO₂ films deposited different pressure and 70°C.

	R_s (Ω)	R_{sc} (Ω)	C_{sc} (μF)	R_{ce} (Ω)	C_{ce} (μF)	τ_c (ms)
Atmospheric	5.3	11300	57.3	14.2	270	1,545
5 MPa	8.4	9538	52.6	17.5	185	1,994
15 MPa	3.4	1342	92.3	17.1	242	8,077
25 MPa	5.9	837	122.0	15.5	95	9,793
35 MPa	6.1	473	131.0	16.6	140	16,123

Table 2

Table 2 Estimated activation volumes ($\Delta V^\ddagger$, mol/L) of the three OH⁻ generation reactions at 70 °C and 1 atm to 35 MPa.

	Reaction #1	Reaction #2	Reaction #3
1 atm	2.814E+01	2.800E+01	2.786E+01
5 MPa	5.533E-01	4.156E-01	-9.685E-02
15 MPa	1.732E-01	4.008E-02	-9.735E-02
25 MPa	9.749E-02	-3.165E-02	-9.762E-02
35 MPa	6.517E-02	-6.068E-02	-9.776E-02

Effects of High Pressure

Morphology of the TiO_2 films deposited at various pressure