Abstract #936, 223rd ECS Meeting, © 2013 The Electrochemical Society

Preparation of Uniform TiO_2 Thin Films by Supercritical Carbon Dioxide

Wei-Hao Lin,[1] Tso-Fu Mark Chang,[2] Masato Sone,[2]* Tatsuo Sato[2] and Yung-Jung Hsu[1]*

*E-mail: yhsu@cc.nctu.edu.tw
[1]Department of Materials Science and Engineering, National Chiao Tung University
1001 University Road, Hsinchu, Taiwan 30010, Republic of China

[2]Precision and Intelligence Laboratory
Tokyo Institute of Technology
Midori-ku, Yokohama-shi, Kanagawa 226-8503, Japan

As one of the most important semiconductors, TiO_2 has been extensively investigated to foster their applications in various technologically important fields including solar cell [1], photocatalysis [2], hydrogen generation [3] and gas sensing [4]. There have been many synthetic approaches proposed to fabricate TiO_2 thin films, such as CVD [5], sol-gel method [6], spray pyrolysis [7], hydrothermal reaction [8] and so on. These techniques usually involve prolonged reaction time which causes poor morphological control of the products. Among the different synthetic routes, electrochemical deposition affords a low-cost yet effective process for production of uniform TiO_2 thin films. Nevertheless, the evolution of H_2 on the electrode is an inevitable problem to be solved because H_2 bubbles would induce structural defects and damages on the film surface. By introducing supercritical carbon dioxide (denoted as Sc-CO_2) which shows high solubility of H2 in the electrochemical deposition system [9], the typical H2 evolution problem may be effectively solved to attain better crystalline property for the products.

In this work, a Sc-CO_2-assisted galvanostatic cathodic deposition process is developed (Figure 1(a)) for fabrication of TiO_2 thin films with controllable thickness. This is the first demonstration for electrochemical deposition of TiO_2 in supercritical fluid condition. The product is deposited cathodically on Cu substrate in a two-compartment cell under a fixed current density, in which platinum foil is employed as the counter electrode. The electrolyte comprises a mixture of water and Sc-CO_2 and the precursor used is $TiCl_3$. The deposition bath also contains $C_{12}H_{25}(OCH_2CH_2)_{15}OH$, a nonionic surfactant which promotes the solubility of Sc-Co2 in water through the formation of microemulsion. Note that the direct deposition of TiO_2 thin films on Cu substrate may facilitate relevant electrochemical property measurements since Cu substrate can act as the current collector. We systematically investigated the influence of Sc-CO_2 and surfactant additions on the microstructures of the resultant TiO_2. The dependence of electrochemical performance on the film thickness of TiO_2 is also interpreted. Figure 1(b) shows the photograph of Cu substrate upon the Sc-CO_2-assisted electrochemical deposition operation. The white-light color implies the successful deposition of TiO_2 on substrate surface. As displayed in Figure 1(c) and (d), the deposited TiO_2 was considerable uniform, composed of nanoparticles with the typical size of 130~140 nm. The present synthetic approach could be further extended to obtain other metal oxide thin films such as ZnO, CuO, NiO and so on.

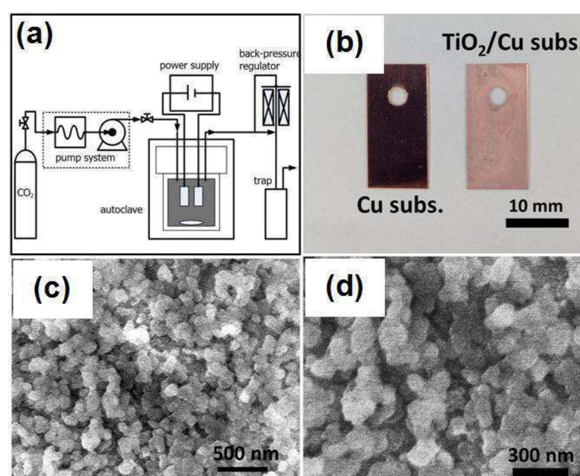

Figure.1. (a) Scheme of Sc-CO_2-assisted electrochemical deposition system. (b) Photographs of TiO_2 thin films on Cu substrate. (c) Low-magnification and (d) high-magnification SEM images of the deposited films.

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