

Cathodic electrodeposition of amorphous titanium oxide films from an alkaline solution bath

C. D. LOKHANDE, SUN-KI MIN, KWANG-DEOG JUNG, OH-SHIM JOO*

Eco-Nano Research Center, Korea Institute of Science and Technology, P.O. Box 131, CheongRyang, Seoul, Korea
E-mail: joocat@kist.re.kr

TiO₂ has been investigated for diverse applications in the optical and semiconductor industries because of its interesting semiconducting and dielectric properties. TiO₂ has been especially employed in making different electronic devices, including oxygen sensor, varistor, photoelectrode etc. Fujishima and Honda [1] first showed that *n*-TiO₂ could be used as a photoanode for the photoelectrolysis of water in a photoelectrochemical (PEC) cell. The *n*-TiO₂, with bandgap energy of 3.2 eV, absorbs mainly light in UV region and a small amount of light in visible region. However, despite this drawback, the porous and compact TiO₂ layers have found many applications due to its high oxidative power, stability and non-toxicity. The porous TiO₂ film in anatase phase could accomplish the photocatalytic degradation of organic compounds under the radiation of UV. It has many application prospects in the field of environmental protection such as sterilization and sewage disposal. A recent interest is focused on an amphiphilic TiO₂ surface induced by UV irradiation, which is expected to be applicable to windshields and mirrors for vehicles [2]. On the other hand, in the field of alternative energy, a dye-sensitized solar cell is now a hot topic due to its high conversion efficiency produced with a porous TiO₂ electrode which is composed of a few tenths of nanometer-sized particles TiO₂ film with rutile phase [3, 4].

Different types of composite coating films such as TiO₂-CdS, TiO₂-ITO, TiO₂-Al₂O₃, Cd₃P₂-TiO₂, etc. have been studied for photocatalytic work and development of photoelectrochemical devices [5–8]. A compact coating of TiO₂ is useful for arresting photodecomposition of low bandgap semiconductor and as a buffer layer in solid solar cells and dye-sensitive solar cells. The nanostructured TiO₂ possess very high effective surface area and the incident photon-to-current conversion efficiency is found to be in excess of 80%.

Consequently, a low-cost preparation and fixation of the TiO₂ photocatalyst with small sized particle is necessary for practical applications. From the point of view of practical use, some methods to fix the porous and compact TiO₂ layer have been developed. Many deposition methods such as thermal and anodic oxidation of titanium, electron beam evaporation, chemical vapor deposition, plasma enhanced chemical vapor deposition, reactive sputtering, sol-gel, spray pyrolysis, etc.

have been reported to prepare nanometer-sized particle thin films [9].

Among the various methods in use for the production of porous as well as compact titanium oxide thin films, the electrodeposition appears to be a simple and low cost method. The main advantage is the easy control of film thickness, morphology, composition etc. through electrical quantities such as deposition current and applied potential. Relatively few reports are available on the electrodeposition of TiO₂ film. Both the types, cathodic and anodic electrodeposition, have been reported in the literature. Natarajan and Nogami [10] and Zhitomirsky [11–13] have reported on cathodic deposition of TiO₂ film. Kavan *et al.* [14] have reported on deposition of TiO₂ film on F-doped tin oxide glass and metallic (Pt, Au Ti) electrodes by anodic oxidative hydrolysis of acidic TiCl₃ solution. Matsumoto *et al.* [9] have reported the TiO₂ deposition from (NH₄)₂[TiO(C₂O₄)₂] solution onto alumite, followed by pulsed deposition from TiCl₃ solution. Flood *et al.* [7] have prepared transparent nanocrystalline semiconductor sandwich electrodes of configurations CdS-TiO₂ and TiO₂-CdS on F-doped tin oxide glass, where TiO₂ was deposited from TiCl₃ solution at room temperature.

In all the above electrodeposition experiments, the solution of titanium salts is used in the acidic P^H range of 1 to 3 only [9, 11–14]. The titanium ions are not complexed and the deposition baths are unstable due to precipitation of titanium hydroxide. The hydrogen peroxide is used as an oxidizing agent. The TiO₂ thin films obtained are porous and of anatase phase.

In the present work, for the first time, thin film of titanium oxide has been deposited on ITO substrate by cathodic galvanostatic deposition from an aqueous alkaline solution containing complexed titanium with ethylene-diamine-tetra acetic acid (EDTA). The process is conducted at room temperature and results into an amorphous, compact, non-porous and uniform titanium oxide film on ITO substrate. The deposition and characterization of these TiO₂ films are reported.

A room temperature (300 K) cathodic galvanostatic deposition of titanium oxide film on ITO substrate has been carried out using the following procedure. In brief, 0.05 M TiCl₃ solution was made by mixing TiCl₃ in concentrated. HCl in 1:2 ratio. The 0.05 M TiCl₃ solution was taken in a beaker and 0.1 M EDTA was mixed into 1:1 ratio, under constant stirring. The P^H

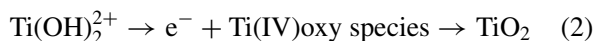
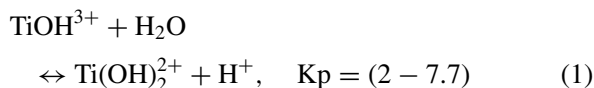
*Author to whom all correspondence should be addressed.

of this solution was -1.10 and the solution color was violet-black. To this, a solution of ammonium hydroxide (28%) was added with constant stirring. The solution color changed from violet-black to dark black, as P^H changed from -1.1 to 5.0 . Above P^H equal to 5.0 , the black precipitate was formed in the solution, which was re-dissolved after stirring. At P^H equal to 10.0 , a whitish-gray precipitate was formed in the solution. In the present case, a P^H equal to 12.20 was obtained by further addition of ammonia solution. In a few minutes, the whitish-gray precipitate settled down in the solution, leaving clear, transparent, solution above it.

A platinum sheet with $1.5 \times 1.5 \text{ cm}^2$ area was used as the counter electrode. A scanning galvanostat/potentiostat (E G and G model-273A) was used in galvanostatic mode. A constant current of $0.5\text{--}25 \text{ mA/cm}^2$ was passed between ITO cathode and platinum anode. The deposition was carried out for a time period of 30 min. After deposition, the film was cleaned with triple-distilled water and dried under argon flow. The film thickness of TiO_2 film was estimated to be $0.1\text{--}2.5$ micron.

A thin film of titanium oxide was characterized using the following techniques. The XRD pattern was obtained by using X-ray diffractometer (RINT/PMAX 2500, Rigaku, Japan). Microstructural study was carried out with scanning electron micrographs, obtained from FE-SEM, (SM-6340F, Jeol, Japan). The optical absorption study was carried out with UV-VIS spectrometer (Varian Cary 100, Australia). The photoactivity of TiO_2 thin film in 1 M NaOH electrolyte was studied using a conventional three-electrode system using platinum counter electrode and Ag/AgCl reference electrode. A Xe lamp (450 W, Thermo Oriel Co., USA), with illumination intensity of 100 mW/cm^2 at 300 nm wavelength was used as a light source.

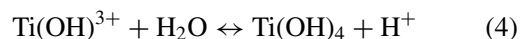
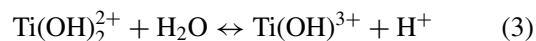
The reaction mechanism for electrodeposition of TiO_2 from acidic TiCl_3 solution under anodic bias, has been reported in the literature [14–16]. Under anodic bias and in acidic solution, the deposition mechanism of TiO_2 has been proposed as



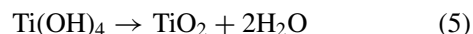
Ti(OH)_2^{2+} will be produced by the hydrolysis of Ti^{3+} on the dilution and p^H adjusting process of TiCl_3 solution. Ti(OH)_2^{2+} will then be oxidized to Ti(IV)oxy species. According to Kavan *et al.* [14], the Ti(IV)oxy species is an intermediate between TiO^{2+} and TiO_2 , consisting of partly dehydrated polymeric Ti(IV) hydroxide, which will be finally converted into TiO_2 by dehydration during electrolysis.

The effect of changing p^H of the TiCl_3 solution from acidic to alkaline medium on titanium species is seen from the following reaction mechanism. When the p^H is less than 2.45 , the solution contains the Ti(OH)_2^{2+} species in TiCl_3 solution. However, if the

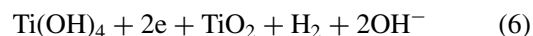
p^H is greater than 2.45 , the Ti(OH)_4 species are present in the solution as per the following reactions [15, 16].



The Ti(OH)_4 species are soluble in an aqueous solution and remain soluble in a bath in the alkaline p^H region ($p^H > 7.0$). From this solution, chemical precipitation of TiO_2 occurs as



Under normal deposition conditions, when concentration of Ti species is greater than 10^{-5} M , the TiO_2 forms a stable insoluble phase which is in equilibrium with soluble Ti(OH)_4 phase [15, 16]. From such a bath containing Ti(OH)_4 and TiO_2 phases in equilibrium, the cathodic deposition of TiO_2 on substrate is possible as per the reaction



The cathodic deposition condition depends upon bath temperature, nature of substrate, metal ion concentration, complexing agent and its concentration, etc. The addition of EDTA as a complexing agent was found to be advantageous as it stabilized the deposition bath for days without forming any precipitation. The thick TiO_2 film (2.5 micron) was deposited from an EDTA complexed bath. The deposition current density was varied in the range of 0.5 to 25 mA/cm^2 to control film thickness. The p^H range ($7\text{--}12$) allowed the control of film morphology and thickness.

The crystallinity of TiO_2 film was analysed using X-ray diffraction patterns. Fig. 1 shows a typical XRD pattern of TiO_2 film on ITO substrate. Practically, no difference was observed between XRD patterns corresponding to ITO coated glass and corresponding to the as-deposited TiO_2 film on ITO coated glass substrate, which indicates the amorphous character of TiO_2 film. Deposition of amorphous TiO_2 film from acidic baths containing H_2O_2 as an oxidizing agent

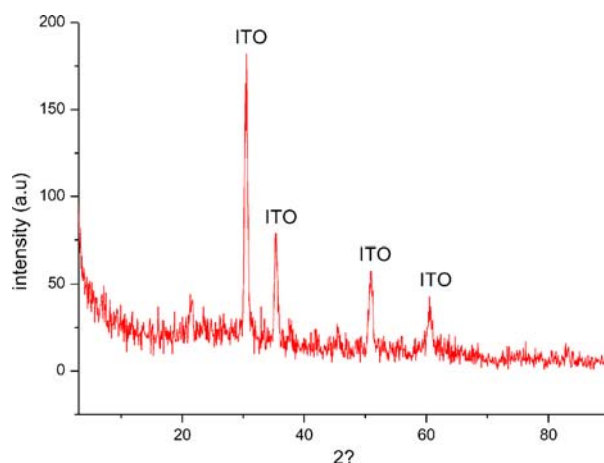
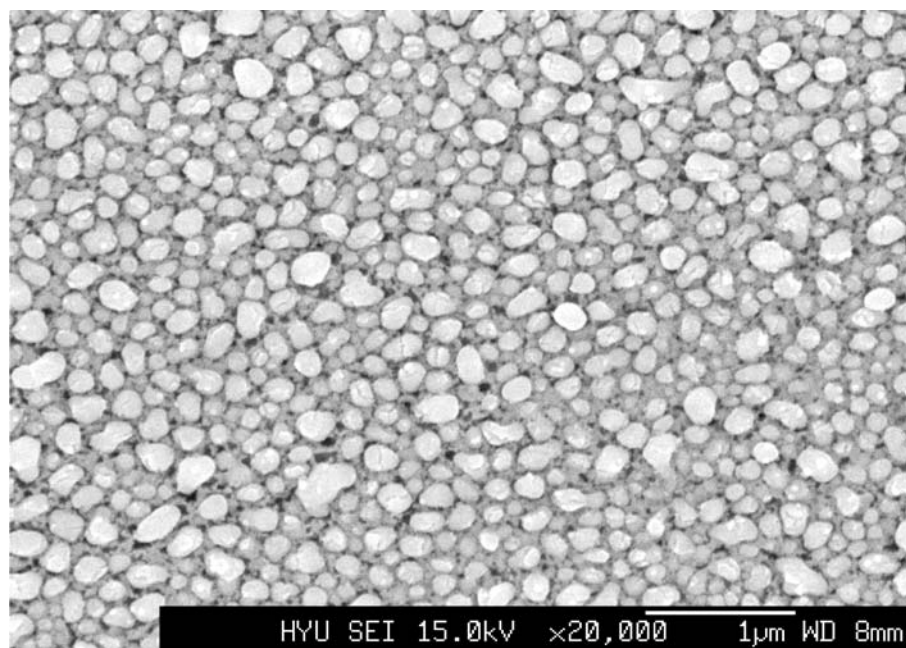
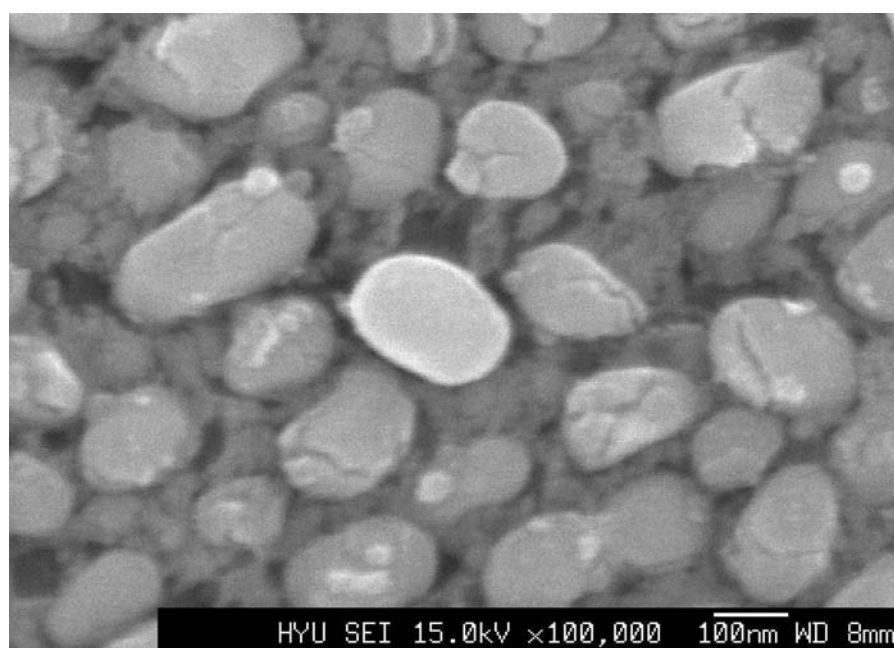


Figure 1 The X-ray diffraction pattern of titanium oxide film deposited on indium doped tin oxide (ITO) coated glass.



(a)



(b)

Figure 2 The scanning electron microscopic (SEM) pictures at magnifications of 20000 \times and 100000 \times of titanium oxide thin film deposited on indium doped tin oxide (ITO) coated glass substrate.

has been reported by Zhitomirsky [11–13] and Karuppuchamy *et al.* [17]. These films showed crystalline anatase phase after annealing above 723 K. However, in the present case, the TiO₂ film remained amorphous and compact after annealing at 723 K in air for 24 hrs.

Scanning electron micrographs of TiO₂ film on ITO coated glass substrate (Fig. 2) at two magnifications (20000 \times and 100000 \times) were observed. A well covering, compact and non-porous TiO₂ coating surface was observed at the magnification of 20000 \times . At high magnification, elongated grains of 100–200 nm sizes are well seen. However, careful observation of the SEM picture finds each grain is made up with an aggregate of amorphous particles. Such morphology remained unchanged even after annealing above 723 K.

Karuppuchamy *et al.* [17] have reported open porous structure morphology for cathodically deposited TiO₂ film from an acidic bath. The difference in deposition bath conditions might be responsible for this structural difference.

For the purpose of optical absorption study, TiO₂ film of small thickness was deposited. Fig. 3 shows variation of optical absorption with wavelength for TiO₂ film. The optical absorption spectrum of TiO₂ film on ITO coated glass showed a sharp increase in absorption below 350-nanometer wavelength. The high optical absorption coefficient (10^4 cm^{-1}) indicates direct band-gap transition. A tailing absorbance in visible region of 400 to 500 nm was observed. A similar absorbance has been observed for the TiO₂ produced by

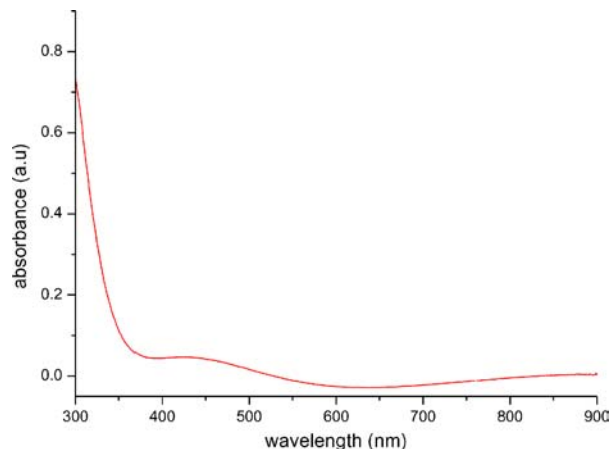


Figure 3 The optical absorption spectrum of titanium oxide film deposited on indium doped tin oxide (ITO) coated glass substrate.

hydrolysis of TiCl_4 [18]. Serpone suggested that the visible absorption is attributed to the charge-transfer transition from Cl^- to Ti(IV) [19]. The same phenomena will occur in the present case, as TiO_2 film is prepared from TiCl_3 solution.

Photoelectrochemical properties of TiO_2 film prepared with various techniques have been studied in different electrolytes such as NaOH , KCl , Na_2SO_4 - NaI , H_2SO_4 , K_3FeCN_6 , etc. [10]. In the present investigation, in order to demonstrate the potential use of deposited TiO_2 coating in photoelectrochemical devices, we have studied I-V characteristic of TiO_2 thin film in 1 M NaOH electrolyte. Fig. 4 shows I-V characteristic for TiO_2 film. The film exhibits photo activity in NaOH electrolyte with *n*-type behavior. The dark current is nearly equal to zero. The photocurrent obtained was of the order of $\mu\text{A}/\text{cm}^2$. The low magnitude of photocurrent may be due to high band gap (>3.2 eV) and amorphous structure (as evidenced by XRD studies) of TiO_2 film and series resistance offered by ITO substrate.

A distinct advantage of this method in using the alkaline solution bath complexed with EDTA is to obtain amorphous, compact, pinhole free and adherent titanium oxide film. Because the bath contains soluble Ti(OH)_4 and insoluble TiO_2 phases in equilibrium,

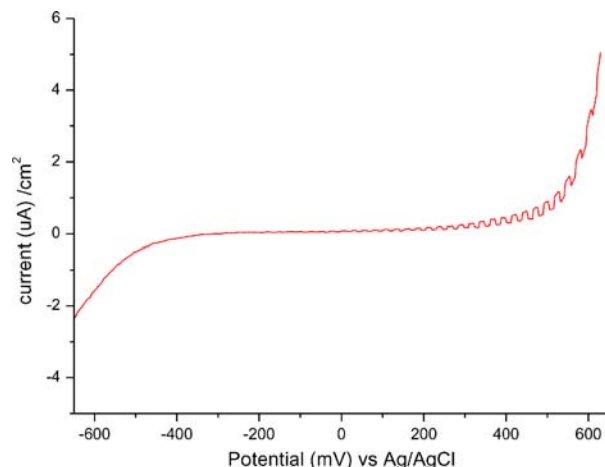


Figure 4 The photocurrent-photovoltage characteristics of titanium oxide film deposited on indium doped tin oxide (ITO) coated glass substrate.

the concentration of Ti(OH)_4 remains the same during deposition. This allows us to get reproducible results. Also, as there is no reaction in the electrolyte due to EDTA complex, when current is not passing through the solution, the electrolyte solution can be used many times and for many days. A compact coating of TiO_2 is useful for arresting photodecomposition of low bandgap semiconductor and as a buffer layer in solid-state and dye-sensitive solar cells.

Acknowledgments

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D program, funded by the Ministry of Science and Technology of Korea. One of the authors, (CDL), wishes to thank the Korean Federation of Science and Technology Societies (KOFST), Korea, for the award of Brain Pool Fellowship (2003–04). He is grateful to Prof. M. G. Takawale, Vice Chancellor and Prof. V. M. Chavan, Pro. Vice Chancellor of Shivaji University, Kolhapur, India, for their constant encouragement and sanction of leave.

References

1. A. FUJISHIMA and K. HONDA, *Nature* **238** (1972) 37.
2. T. N. RAO, D. A. TRYK and A. FUJISHIMA, in "Encyclopedia of Electrochemistry," edited by S. Licht (Wiley-VCH, Weinheim, 2002) Vol. 6, p. 536.
3. A. FUJISHIMA and D. A. TRYK, in "Encyclopedia of Electrochemistry," edited by S. Licht (Wiley-VCH, Weinheim, 2002) Vol. 6, p. 497.
4. A. J. McEVROY and M. GRATZEL, in "Encyclopedia of Electrochemistry," edited by S. Licht (Wiley-VCH, Weinheim, 2002) Vol. 6, p. 397.
5. X. QIAN, D. QIN, Q. SING, Y. BAI, T. LI, X. TANG, E. WANG and S. DONG, *Thin Solid Films* **385** (2001) 152.
6. Y. ISHIKAWA and Y. MATSUMOTO, *Electrochim Acta* **46** (2001) 2819.
7. R. FLOOD, B. ENRIGHT, M. ALLEN, S. BARRY, A. DALTON, H. DOYLE, D. TYNAN and D. FITZMAURICE, *Solar Energy Mater. Sol. Cells* **39** (1995) 83.
8. L. SPANHEL, H. WELLER and A. HENGLLEIN, *Ber. Bunsenges Phys. Chem.* **91** (1987) 1359.
9. Y. MATSUMOTO, Y. ISHIKAWA, M. NISHIDA and S. II, *J. Phys. Chem. B* **104** (2000) 4204.
10. C. NATARAJAN and G. NOGAMI, *J. Electrochem. Soc.* **143** (1996) 1547.
11. I. ZHITOMIRSKY, *Mater. Lett.* **33** (1998) 310.
12. *Idem.*, *J. Mater. Sci.* **34** (1999) 2441.
13. *Idem.*, *JOM-e* **52** (2000) 1.
14. L. KAVAN, B. O'REGAN, A. KAY and M. GRATZEL, *J. Electroanal. Chem.* **346** (1993) 297.
15. M. M. LENCKA and R. E. RIMAN, *Chem. Mater.* **5** (1993) 61.
16. F. P. ROTZINGER and M. GRATZEL, *Inorg. Chem.* **26** (1987) 3704.
17. S. KARUPPCHAMY, K. NONOMURA, T. YOSHIDA, T. SUGIURA and H. MINOURA, *Solid State Ion.* **151** (2002) 19.
18. M. KATO, T. OGIHARA, M. IKEDA and N. MITZUTANI, *J. Amer. Ceram. Soc.* **72** (1989) 1598.
19. N. SERPONE, D. LAWLESS and R. KHAIRUTDINOV, *J. Phys. Chem.* **99** (1995) 16646.

Received 5 April
and accepted 18 May 2004