Synthesis and Characterization of Filtered-cathodic-vacuum-arc-deposited TiO2 Films for Photovoltaic Applications

C Aramwit1, S Intarasiri2,3, D Bootkul3,4, U Tippawan1,3, B Supsermpol4,5, N Seanphinit4,5, W Ruangkul3 and LD Yu1,3,*

1 Plasma and Beam Physics Research Facility, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
2 Science and Technology Research Institute, Chiang Mai University, Chiang Mai 50200, Thailand
3 Thailand Center of Excellence in Physics, Commission on Higher Education, 328 Si Ayutthaya Road, Bangkok 10400, Thailand
4 Departments of General Science, Faculty of Science, Srinakharinwirot University, Bangkok 10110, Thailand
5 Western Digital Thailand Co. Ltd., Ayutthaya 13160, Thailand

* Email: yuld@fnrf.science.cmu.ac.th

Abstract. Titanium dioxide (TiO2) is well-known as a photovoltaic and photocatalytic material. For improvement in the dye-sensitized solar cell (DSSC) performance efficiency, the photocatalyst TiO2 layer would be desired in nanoporous anatase. In this research, TiO2 films were synthesized on glass or p-type silicon substrate using our in-house Filtered Cathodic Vacuum Arc Deposition (FCVAD) system. The deposition was operated at varied oxygen (O2) partial pressures of 10-4, 10-3, 10-2 to 10-1 torr with fixed 0 or 250-V bias and 600-V arc for 10 or 20 minutes. The film transparency increased with increasing of the O2 pressure, indicating increase in the structure required for applications in dye-sensitized solar cells. The films were characterized using the Energy-Dispersive X-ray spectroscopy (EDS) and Raman spectroscopy techniques. The EDS confirmed that the transparent deposited films contained stoichiometric titanium and oxygen under the medium O2 pressure. Raman spectra confirmed that the films were TiO2 containing some rutile but no anatase which needed annealing to form. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used for evaluation of the film’s surface morphology and thickness. The result showed that increasing of the O2 pressure decreased the thickness to a nanoscale but increased the amount of TiO2.

1. Introduction
In the world trend of developing green energy, solar cells are the first choice. Among types of the solar cells, dye-sensitized solar cells (DSSC) [1,2,3] developed in recent two decades are considered to be the third generation solar cells because of their lower cost and higher efficiency compared with other traditional solid-state-semiconductor solar cells [4]. A DSSC basically consists of six components, i.e. normal glass, conducting glass, wide-band semiconductor, dye, electrolyte and a metal counter electrode. The semiconductor material popularly used is titanium dioxide (TiO2) in anatase [2]. Critical factors to increase the performance efficiency of DSSC include the porosity and the electron transportation property of the TiO2. Highly nanostructured TiO2 can greatly increase the material porosity so that the material surface area can be increased to let more electrons be injected. Metal or
nonmetal-doped TiO₂ can further improve the material electron transportation property [5,6,7]. DSSCs are currently very attractive to the market owing to the high ratio between efficiency and cost, good workability under weak sunlight conditions and higher temperatures, and strong mechanical structures.

Filtered cathodic vacuum arc deposition (FCVAD) is a simple and effective plasma technique to make metallic as well as carbon thin films [8,9,10]. Owing to many advantages [11], such as a very high deposition rate, a good control of the deposition parameters, and an excellent quality and good adhesion of the coating, FCVAD has been utilized to TiO₂-film coating for many applications, including optics, photocatalysis, photo energy conversion and biocompatibility. Titanium oxide has three major crystalline phases: rutile, anatase and brookite [12], but only the anatase is good for photo energy conversion [3]. Moreover, nanostructure of TiO₂ greatly affects the photo energy conversion [2]. Formations of TiO₂ (anatase) and its nanostructure by using FCVAD depend on the deposition conditions, including oxygen (O₂) partial working pressure, substrate temperature, substrate bias, deposition time, arc current, and pulse parameters (e.g. the pulse width and frequency), etc. [11,12]. The microstructure of FCVAD-TiO₂ is generally amorphous at the substrate temperature below 330°C under the O₂-pressure lower than about 3 × 10⁻⁴ torr without bias [13,14]. At a higher substrate temperature and using bias, anatase can possibly be formed. However, there are many controversial experimental results to show different phase formation under similar conditions [15-19]. Therefore, using FCVAD to form TiO₂ (anatase) is still a complex issue because of so many conditions or parameters involved. In physics principle, elevated substrate temperature and bias increase the ion energy so as to increase activation of the phase transformation. O₂-pressure controls the TiO₂ phase stability [20] and it cooperates with the arc current and the pulse parameters [21] to control the amounts of two elements deposited and thus the phase formation. Moreover, the microstructure of the deposited film is governed by the famous structural zone model for coating growth [22-24]. According to the model, lower temperature and higher working gas pressure could result in porous structure. This really leads to a challenge that at what appropriate working temperature and gas pressure the deposited TiO₂ film has both porosity and anatase. The present research was aimed a systematic investigation on the effect on microstructure of the TiO₂ films from FCVAD. But, this report presents preliminary results of the study in the effect of the O₂-pressure. The laboratory of the Plasma and Beam Physics Research Facility at Chiang Mai University which has been the unique comprehensive ion beam and plasma research laboratory in the ASEAN region has had a long history of working on ion beam and plasma technology. We have a number of ion beam accelerators with the beam energy ranging from 30 keV to 2 MeV and plasma facilities with the working pressure ranging from low to atmospheric pressures. Our FCVAD system has been in-house developed in the cooperation with the Lawrence Berkeley National Laboratory and applied for various applications [25-27]. To contribute to green energy development we are utilizing the novel FCVAD technique for advanced TiO₂ film coating.

2. Methodology

Before deposition of the films, substrates of glass and p-type silicon in sizes of 1×1 cm² (for analysis) or 2×8 cm² (for measurements of macro-properties) were cleaned by boiling in acetone with applying an ultrasonic frequency of 35 kHz at 60°C for 6 minutes. Then, they were dried by blowing pure nitrogen gas flow. The in-house developed FCVAD system (Figure. 1) was used for film deposition. Ti was the cathodic material which was made into a small rod (about 3 mm in diameter and a few cm in length) to put in the cathode house. Pulsed high-temperature arc that was generated by a-few-kV voltage between the cathode and the anode melted and vaporized the cathodic metal to form Ti-vapor plasma. Ti ions in the plasma were guided through a 90°-solenoid filter to the substrate surface for deposition. The prepared and cleaned substrate was mounted on the target holder which was connected to a bias power supply for deposition. The deposition chamber atmosphere and pressure were controllable during the deposition by controlling the gas inlet. In our experiment, O₂ gas was used for forming metal oxide. The working pressure with O₂ inlet was varied from the base pressure of 5×10⁻⁵ torr to 1×10⁻⁴, 1×10⁻³, 1×10⁻² and 1×10⁻¹ torr, respectively. The arc voltage was 600 V, the bias was 0 or -250 V, and the deposition time was 10 and 20 minutes, respectively.
The FCVAD-synthesized films on glass were characterized for their morphology by scanning electron microscopy (SEM) and the composition by energy dispersive x-ray spectroscopy (EDS) which had been widely used as a characterizing method to identify elements in deposited films. The titanium on the substrate would emit X-rays at energy around 4.5 keV and 0.45 keV, while oxygen would emit X-ray at 0.52 keV [28]. However, the deposited film on the glass substrate was not suitable to using Raman spectroscopy due to the imperfection of glass which could produce a large amount of noises in the spectrum. Therefore, films deposited on Si in the same deposition condition were analyzed using Raman spectroscopy for phase formations. Raman spectroscopy has often been used to investigate thin film’s structure. The vibration of film’s structure has its own frequency. The TiO$_2$ in the rutile structure responds to the wave numbers 143 cm$^{-1}$, 447 cm$^{-1}$, 612 cm$^{-1}$ and 826 cm$^{-1}$, different from the anatase structure which responds to 144 cm$^{-1}$, 197 cm$^{-1}$, 399 cm$^{-1}$, 513 cm$^{-1}$, 519 cm$^{-1}$ and 639 cm$^{-1}$ [29]. The film surface morphology and thickness were measured using atomic force microscopy (AFM). To measure the film thickness, before deposition a tape was used to cover a part of the substrate and after deposition the tape was removed to form a step between the deposited and undeposited areas for AFM to scan.

![Figure 1. The in-house developed FCVAD system at Chiang Mai University.](image)

(a) Photograph of the entire FCVAD system. (b) Schematic diagram of the system inside the chamber. Here it shows only one of three technical configurations, dual-cathode source unit.

### Table 1

A summary of the deposition and characterization of the 10-min deposited TiO$_2$ film samples. Y: yes. N: no. Pressure unit is in torr.

| Sample No. | Substrate | Base pressure | O$_2$ pressure | SEM | EDS | Raman analysis |
|------------|-----------|---------------|----------------|-----|-----|----------------|
| 1          | Glass     | 5x10$^{-5}$   | 0              | Y   | Y   | N              |
| 2          | Glass     | 5x10$^{-5}$   | 1x10$^{-4}$    | Y   | Y   | N              |
| 3          | Glass     | 5x10$^{-5}$   | 1x10$^{-3}$    | Y   | Y   | N              |
| 4          | Glass     | 5x10$^{-5}$   | 1x10$^{-2}$    | Y   | Y   | N              |
| 5          | Glass     | 5x10$^{-5}$   | 1x10$^{-1}$    | Y   | N   | N              |
| 6          | Si        | 5x10$^{-5}$   | 0              | N   | N   | Y              |
| 7          | Si        | 5x10$^{-5}$   | 1x10$^{-4}$    | N   | N   | Y              |
| 8          | Si        | 5x10$^{-5}$   | 1x10$^{-3}$    | N   | N   | Y              |
| 9          | Si        | 5x10$^{-5}$   | 1x10$^{-2}$    | N   | N   | Y              |
| 10         | Si        | 5x10$^{-5}$   | 1x10$^{-1}$    | N   | N   | Y              |
3. Results and Discussion

The deposition and characterization of the TiO$_2$ films are summarized in Table 1 under the conditions of 10-minutes deposition, 600-V arc voltage and -250-V bias. Figure 2 shows the SEM images of the film surface morphology and the film cross section. Compared with the glass control surface (without coating) (Figures 2a and 2b), the pure Ti film (without O$_2$ inlet) (Figures 2c and 2d) is seen obviously to be present with a film thickness of about 3 µm. The Ti film seems poor in adhesion to the substrate and integration to a large-area solid. However, after O$_2$ was introduced, even a small amount (at an O$_2$-partial pressure of $10^{-4}$ torr), the film (Figures 2e, 2f, and 2g) looks more condense and solid compared with the pure Ti film. Because of the densification, the film thickness is less than 3 µm, around 2-3 µm. With increase in the working pressure or O$_2$ inlet, the film surface becomes smoother (Figure 2h). On the other hand, the film transparency increases as increasing of the O$_2$ pressure, as shown in Figure 3. High film transparency is one of the requirements for the DSSC to receive more sunlight.

The film surface morphology observed by AFM scanning in comparison with the substrate surface is shown in Figure 4. The result is in consistence with the SEM-observed result. The film thickness measured by AFM scanning across the boundary between the film and the substrate surfaces is shown in Figure 5. The film thickness decreases as increasing of the pressure and reaches a nanoscale at $10^{-2}$ torr. The film thickness decrease is cooperated with the film transparency increase as increasing of the pressure. The results on the morphology and transparency indicated that a transformation in the film material characteristics occurred when the O$_2$ inlet increased in the deposition.

The oxygen content in the film was measured using EDS (Figure 6) and the result is shown in Figure 7. The O$_2$ content in the Ti-O film due to the O$_2$ inlet was calculated from the measured O$_2$ content in various pressures minus the original O$_2$ content in the glass (mainly silicon oxide) measured from the condition of using the base pressure. It is seen that the O$_2$ content in the film increases as increasing of the partial O$_2$ pressure and the optimized stoichiometric ratio of Ti to O which should be 1:2 for the TiO$_2$ formation is nearly achieved at the working pressure of $1\times10^{-3}$ torr.

![Figure 2](image_url)

**Figure 2.** SEM images of the films. (a) (top view) and (b) (cross section): glass without film. (c) (top view) and (d) (cross section): Ti film deposited at the base pressure. (e), (f) (top views) and (g) (cross section): pressure $1\times10^{-4}$ torr. (e) shows a border section between the coated (right) and uncoated (left) areas. (h) (top view): pressure $1\times10^{-1}$ torr.
Figure 3. The film transparency at pressure (a) $1 \times 10^{-4}$, (b) $1 \times 10^{-3}$, (c) $1 \times 10^{-2}$, (d) $1 \times 10^{-1}$ torr.

Figure 4. AFM-measured film surface morphology across the boundary between the film and the substrate as a function of the working pressure. (a) Base pressure $5 \times 10^{-5}$ torr. (b) $1 \times 10^{-4}$ torr. (c) $1 \times 10^{-3}$ torr. (d) $1 \times 10^{-2}$ torr. (e) $1 \times 10^{-1}$ torr.

Figure 5. The film thickness as a function of the working pressure. The curve is only a guideline.
Figure 6. An example of the EDS spectrum from the film deposited at $1 \times 10^{-4}$ torr. The vertical axis is the X-ray intensity and the horizontal axis is the X-ray energy in keV. The dispersed energy peak intensities can be converted to the percentages of elements in samples such as those of Ti and O as shown in Figure 7.

Figure 7. The Ti and O contents in the Ti-O film calculated from the EDS spectra as a function of the working pressure.

| Relative Atomic% of varying O2 pressure |
|------------------|----------------|
|                  | Non-doping(5x10^-5) | 10^-4 torr | 10^-3 torr | 10^-2 torr | 10^-1 torr |
| OK               | 0                  | 0          | 3.77       | 4.28       | 7.71       |
| TiK              | 9.22               | 5.29       | 2.28       | 1.28       | 0.02       |

Figure 8. Preliminary Raman spectra of the deposit TiO$_2$ films. Note: Raman spectroscopy analysis is still ongoing to confirm the results since some confusions exist in the spectra.
The FCVAD-formed film microstructure was analyzed using the Raman spectroscopy as shown in Figure 8. Three rutile characteristic peaks at 447, 612 and 826 cm$^{-1}$ can be identified from the spectra, but no anatase characteristic peaks (e.g. 399 and 639 cm$^{-1}$) are seen. These rutile peaks increase their intensities as the O$_2$ pressure decreases to $1 \times 10^{-3}$ torr. This result tells that with the deposition conditions used, the film microstructure contains the rutile phase of TiO$_2$ but no anatase phase. This is not completely in agreement with previously reported results, which showed that in similar conditions the Ti-O film was amorphous and definitely no anatase which must be formed with annealing at a temperature higher than 330°C [13,14]. Our result showed that although there was no anatase, rutile was present besides amorphous structure.

4. Conclusion
The report presents preliminary results from our study on using the FCVAD technique to deposit TiO$_2$ films for green energy applications. Among a number of technical parameters of FCVAD, only a limited number of conditions were tested, such as varied O$_2$ pressure and deposition time with and without bias at room temperature. From the investigation we mainly concluded that at the O$_2$ pressure of about $1 \times 10^{-3}$ torr hundred-nanometer-thick TiO$_2$ films with the optimized stoichiometric ratio containing the rutile structure could be synthesized. The film was transparent and solid enough. Since the film did not contain anatase which was the desired phase, elevated temperature or annealing was needed. This still remained challenged as higher temperature treatment might be harmful to create porous structure which was also desired. Therefore, further investigations on the film characteristics and structure with more varied parameters such as varied bias and substrate temperature and using more advanced analysis techniques such as Rutherford backscattering spectrometry (RBS) and positron annihilation spectroscopy (PAS) of ion beam analysis techniques are being carried out.

5. Acknowledgements
The study was supported by the Development and Promotion of Science and Technology Talented Project (DPST) scholarship, Thailand, the Thailand Center of Excellence in Physics (ThEP), and the International Atomic Energy Agency (IAEA).

6. References
[1] O'Regan B, Grätzel M 1991 A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films Nature 353 737–740
[2] Grätzel M 2003 J Photochem and Photobio C: Photochemistry Reviews 4 145–153
[3] Grätzel M 2005 Inorg Chem 44 6841-6851
[4] Lewis NS and Crabtree G 2005 Basic Research Needs for Solar Energy Utilization: Report of the Basic Energy Sciences Workshop on Solar Energy Utilization, April 18-21, 2005, (Office of Basic Energy Science, US Department of Energy, Washington DC)
[5] Cheng X, Zeng P, Hu S, Kuang T, Xie G, Gao F 2006 Rare Metals 25 190–194
[6] Guo W, Wu L, Chen Z, Boschloo G, Hagfeldt A, Ma T 2011 J Photochem and Photobio A: Chemistry 219 180-187
[7] Chou TP, Zhang Q, Russo B, Cao G 2008 J of Nanophot 2 023511
[8] Wright AW 1877 Am. J. Sci. Arts 13 49
[9] Edison TA US Patents 526,147 (1884) and 484,582 (1892)
[10] Martin PJ, Bendavid A 2001 Thin Solid Films 394 1–14
[11] Zhirkov IS, Paternoster C, Delplancke-Ogletree MP 2011 Titanium oxide thin film deposition by pulsed arc vacuum plasma J of Phys: Conf. Series 275 012019
[12] Tay BK, Zhao ZW, Chua DHC 2006 Review of metal oxide films deposited by filtered cathodic vacuum arc technique Materials Science and Engineering R 52 1–48
[13] Takikawa H, Matsui T, Sakakibara T, Bendavid A, Martin PJ 1999 Thin Solid Films 348 145
[14] Zhao ZW, Tay BK, Yu GQ 2004 Appl Opt 43 1281
[15] Zhang F, Liu X 1998 Thin Solid Films 326 171
[16] Zhang F, Wang X, Li C, Wang H, Chen L, Liu X 1998 Surf Coat Technol 110 136
[17] Bendavid A, Martin PJ, Jamting A, Takikawa H 1999 Thin Solid Films 355 6
[18] Bendavid A, Martin PJ, Takikawa H 2000 Thin Solid Films 360 241
[19] Zhao ZW, Tay BK, Lau SP, Yu GQ 2004 J Cryst Growth 268 543
[20] Shen YM, Yu H, Yao JK, Shao SY, Fan ZX, He HB, Shao JD 2008 Investigation on properties of TiO₂ thin films deposited at different oxygen pressures Optics & Laser Technology 40 550–554
[21] Bendavid A, Martin PJ, Preston EW 2008 The effect of pulsed direct current substrate bias on the properties of titanium dioxide thin films deposited by filtered cathodic vacuum arc deposition Thin Solid Films 517 494-499
[22] Movchan BA, Demchishin AV 1969 Phys Met Metallogr 28 83-90
[23] Thornton JA 1974 J Vac Sci Techno 11 666-70
[24] Thornton JA 1977 Ann Rev Mater Sci 7 239-60
[25] Anders A, Pasaja N, Sansongsiri S 2007 Filtered cathodic arc deposition with ion-species-selective bias Review of Scientific Instruments 78 063901-5
[26] Pasaja N, Sansongsiri S, Intarasiri S, Vilaithong T, Anders A 2007 Mo-containing tetrahedral amorphous carbon deposited by dual filtered cathodic vacuum arc with selective pulsed bias voltage Nucl Instru Meth B 259 867-870
[27] Medhisuwakul M, Pasaja N, Sansongsiri S, Kuhakan J, Intarasiri S, Yu LD 2012 Surf Coat Technol in press
[28] X-Ray Data Booklet: Photon energies, in electron volts, of principal K-, L-, and M-shell emission lines, http://xdb.lbl.gov/Section1/Table_1-2.pdf, accessed 1 June, 2012.
[29] Kalantar-zadeh K et al 2009 Nanoporous titanium oxide synthesized from anodized filtered cathodic vacuum arc Ti thin films Thin Solid Films 518 1180-1184