

## CHAPTER 3

### Experimental Processes

In this research, a major role in depositing of titanium dioxide thin films on various substrates: glass slide, p-type silicon wafer and conducting Fluorine doped tin oxide (FTO) glass for different analysis techniques as shown in Table 3.1, however the substrate preparation, film deposition and analysis process are the same. While, the various deposition conditions coated DLC films are deposited on the silicon wafer only.

Table 3.1 Various substrate types for their specific analysis techniques. “Y” is defined that each analysis technique is applied for a substrate, while “N” is defined that each analysis technique is not applied for a substrate.

Substrate type	Analysis technique				
	SEM	EDS	Raman Spectroscopy	AFM	Power Conversion Efficiency Test
Glass	Y	Y	N	N	N
Silicon	N	N	Y	Y	N
FTO glass	N	N	N	N	Y

#### 3.1 Substrate preparation

The p-type silicon wafer is needed to be cut into  $1 \times 1 \text{ cm}^2$  pieces in order to be analyzed in the Raman spectroscopy and AFM, while Sigmaaldrich® #735167 FTO glass is also needed to be cut into  $2 \times 3 \text{ cm}^2$  to do its power conversion efficiency test. Although some of glass slide is needed to be cut into  $1 \times 1 \text{ cm}^2$ , some of them are not needed to be cut because it requires a large deposition surface area for detecting the  $\text{TiO}_2$  film mass.

The whole substrates' surface must be prepared by being boiled in acetone contained in an ultrasonic cleaner with 70°C for 10 minutes. Consequently, they must be dried by nitrogen purging process.

### 3.2 Film deposition

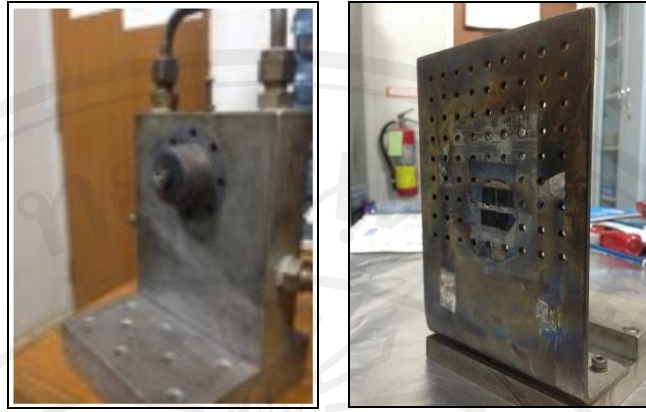
After preparing a set of substrates, they must be attached on a substrate holder by carbon tape and be partly attached their surface by transparent tape for a specific analysis purposes; For glass, an area of 5.0x2.5 cm<sup>2</sup> must be left for calculating the film's surface area, while silicon are half-pasted and the FTO glass must leave 0.5x2.0 cm<sup>2</sup> for deposition.



Figure 3.1 Small pure titanium rod is attached to the end of stainless steel rod.

Pure titanium rod in Figure 3.1 must be painted by graphite before installing into a cathode to reduce its resistance to be lower than 400 k $\Omega$ , consequently installing the cathode into a cathode holder. In addition, in case of installing a graphite rod, it required its resistance to be lower than 200 k $\Omega$ , unless it may not respond to the input voltage and ends up with failure of the deposition.

Install the cathode holder and substrate holder in Figure 3.2, into the chamber as shown in Figure 3.3 with connecting with a several wires as well as a biasing plug into the substrate holder, then start pumping by a rotary pump until a deposition chamber's pressure reaches 10<sup>-2</sup> torr. Then continue pumping by a modified diffusion pump until the pressure reaches 10<sup>-5</sup> torr, defined as the deposition's base pressure.



(a)

(b)

Figure 3.2 FCVAD cathode holder and substrate holder  
(a) a prepared cathode holder and (b) a substrate holder.

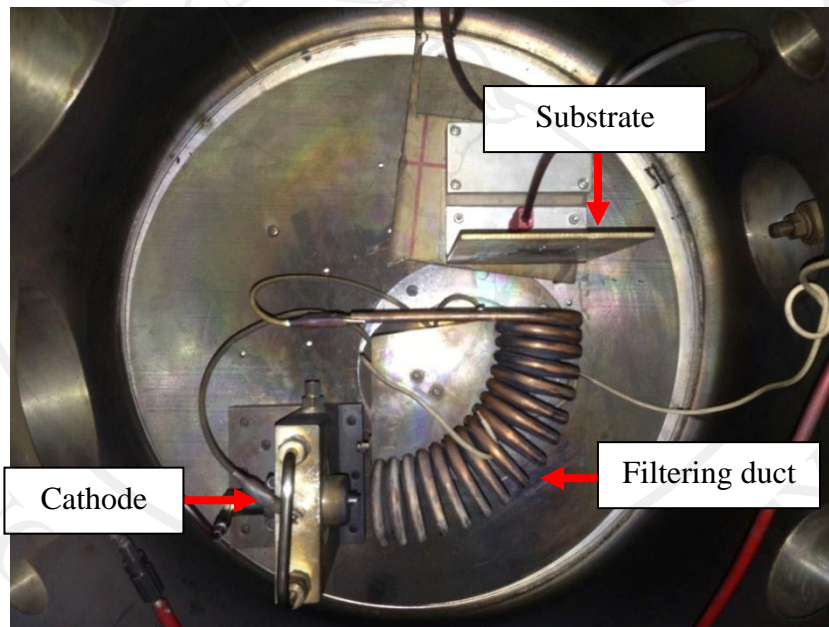


Figure 3.3 The installed instrument in a deposition chamber.

Open a reactive gas flowing system, which can fill the chamber with Oxygen gas for a reactive gas until reaching a preferred pressure. In Figure 3.4 shows the  $10^{-4}$  torr doping of  $O_2$ .



Figure 3.4 Active gauge controller is being used to measure the deposition chamber's pressure lower than  $2 \times 10^{-2}$  torr.

Turn on a trigger generator and set a power supply to 600 V for arc voltage as shown in Figure 3.5, then start deposition by an arc controller program. In 20 minutes later, stop arcing and flow gas until the chamber's pressure reaches atmospheric pressure.



Figure 3.5 The power supply is set to provide a fixed arc voltage at 0.600 kV without fixing arc current.

After start arc triggering, the plasma beam is emitted from cathode through a filtering duct and deposited on a substrate as shown in Figure 3.6. Moreover, the average arc current can be estimated from the varied-overtime detected pulsed arc current, the collected pulses' maximum voltage are varying between 3.13 to 6.10 Volt as shown in Figure 3.7. As a result, the average pulse current is 4.22 V from collecting data for 5 minutes with the full width half maximum of the peak is 0.36 ms. Finally, the partly deposited substrate is ready to be annealed or analyzed by several techniques shown in Figure 3.8.

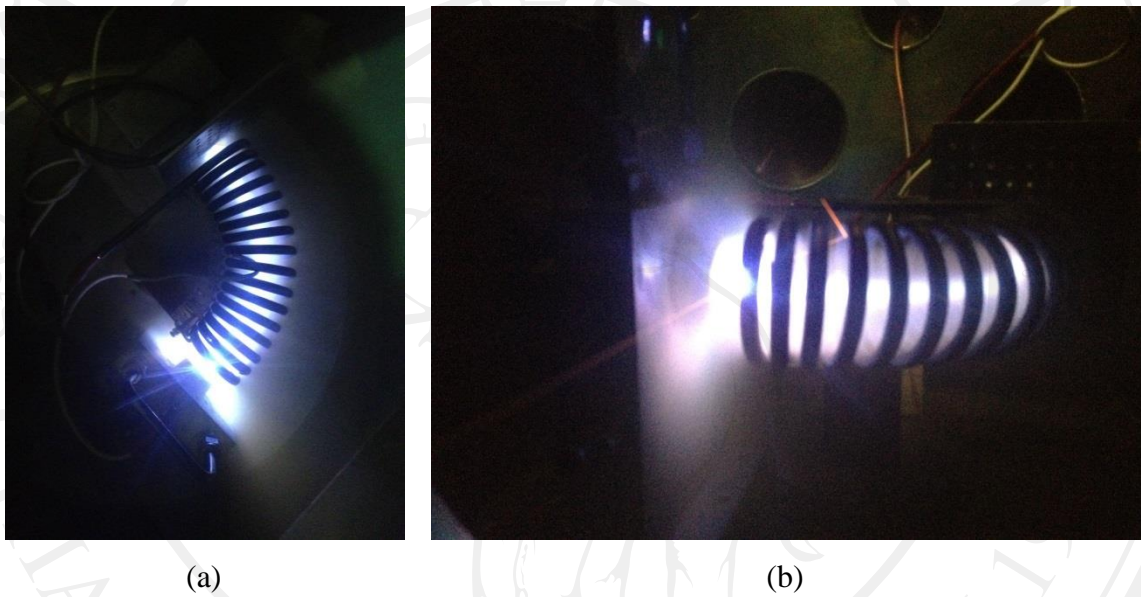


Figure 3.6 The pulsed plasma of Ti with O<sub>2</sub> doped (a) top view (b) side view.

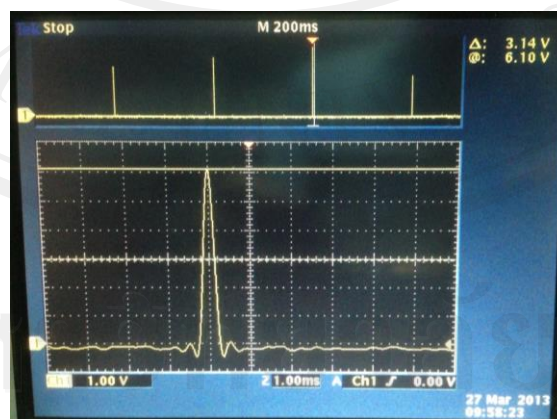


Figure 3.7 The peak of 6.10 Volts is measured.



Figure 3.8 The  $\text{TiO}_2$  post-deposited substrates (a) partly transparent tape pasted, (b) after removing of the tape, it is ready to be analyzed its thickness by AFM (c).

Put the deposited p-type silicon wafer samples into the annealing furnace in Figure 3.9. Increasing the annealing temperature at  $5^\circ\text{C}$  per minute from the room temperature until it reaches the  $400^\circ\text{C}$ , annealing the film at the constant  $400^\circ\text{C}$  for 2 hours. Then stop annealing and waiting for the sample's cooling down until it reaches the room temperature, which is approximately 18 hours. If the annealing chamber is opened while the samples' temperature is high compared to the room temperature, the film will form a drastically high amount of oxide on its surface. It can be concluded that there are various deposition conditions are prepared for the experiment as shown in Table 3.2.



Figure 3.9 The LTD® annealing furnace is being used for annealing  $\text{TiO}_2$  film.

Table 3.2 The TiO<sub>2</sub> film deposited with various deposition conditions, while keeping 3 cm distance between filter and substrate, arc voltage 600 V with arcing frequency at 90 times per minute. The different colour highlighted conditions stated for different experiments; Green for “Oxygen partial pressure”, Blue for “Bias voltage”, Red for “Annealing and Deposition time” and Purple for “Application on solar cell”.

No.	Substrate	Distance Filter vs Substrate (cm)	Arc Voltage (V)	Bias Voltage (V)	Time (min)	Base (torr)	O <sub>2</sub> Doped (torr)	400°C 2 hrs. Annealing
1g	Glass	3	600	-250	20	5x10 <sup>-5</sup>	0	N
2g	Glass	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-4</sup>	N
3g	Glass	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
4g	Glass	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-2</sup>	N
5g	Glass	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-1</sup>	N
1s	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	0	N
2s	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-4</sup>	N
3s	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
4s	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-2</sup>	N
5s	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-1</sup>	N
BA1	Silicon	3	600	0	10	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BA2	Silicon	3	600	0	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BA3	Silicon	3	600	0	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BA4	Silicon	3	600	0	40	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BB1	Silicon	3	600	-250	10	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BB2	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BB3	Silicon	3	600	-250	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BB4	Silicon	3	600	-250	40	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BC1	Silicon	3	600	-500	10	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BC2	Silicon	3	600	-500	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BC3	Silicon	3	600	-500	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
BC4	Silicon	3	600	-500	40	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
B3	Silicon	3	600	-250	10	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
C3	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
C4	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-2</sup>	N
D3	Silicon	3	600	-250	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
B3a	Silicon	3	600	-250	10	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	Y
C3a	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	Y
C4a	Silicon	3	600	-250	20	5x10 <sup>-5</sup>	1x10 <sup>-2</sup>	Y
D3a	Silicon	3	600	-250	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	Y
GH06	FTO	3	600	-250	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
GH06a	FTO	3	600	-250	30	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	Y
GG05	FTO	3	600	0	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	N
GG05a	FTO	3	600	0	20	5x10 <sup>-5</sup>	1x10 <sup>-3</sup>	Y

### 3.3 Analysis of the thin film

Specific analysis techniques required a specific substrate to be analyzed in TiO<sub>2</sub> film. Moreover the deposited glass slide must be measured its mass after the deposition to calculate a weight of the thin film. In spite of the DLC film, only Raman spectroscopy is applied in the study. Therefore, the DLC is needed to be deposited on a silicon substrate.

#### 3.3.1 Scanning Electron Microscopy and Energy-Dispersive Spectroscopy

To begin with titanium coated glass substrate must be coated by gold as shown in Figure 3.10, in order to do the analysis. While some of them are installed on the SEM's stubs, the other must be attached on the stubs' side in order to be analyzed their cross section. The prepared stubs are all installed in the machine before being vacuumed as shown in Figure 3.11.

After bombarding an electron beam, the scattered secondary electrons will be detected and produce a raster information of the film's surface. Moreover, the characteristic X-ray is also detected to define the percentage amount of each element which is consisted in the film.



Figure 3.10 Gold-coated TiO<sub>2</sub>-deposited substrates attached on top and side of SEM's stubs.





Figure 3.11 The JEOL® JSM 6335F is being used for analyzing the film by both SEM and EDS techniques in this study.

### 3.3.2 Raman Spectroscopy

After Raman laser incidents on a sample which is installed in the Raman spectrometer in Figure 3.12, a wide range of emitted spectrum appeared. By scanning the obtained spectrum between 300 and 1,200  $\text{cm}^{-1}$  is suitable for defining the anatase structure of  $\text{TiO}_2$ . Differently for DLC, the scanning range between 1,100 and 2,000  $\text{cm}^{-1}$  is required.



Figure 3.12 Renishaw InVia Reflex Raman spectrometer with an Ar laser at a wavelength of 514 nm as the excitation source is using in the study.

### 3.3.3 Atomic Force Microscopy

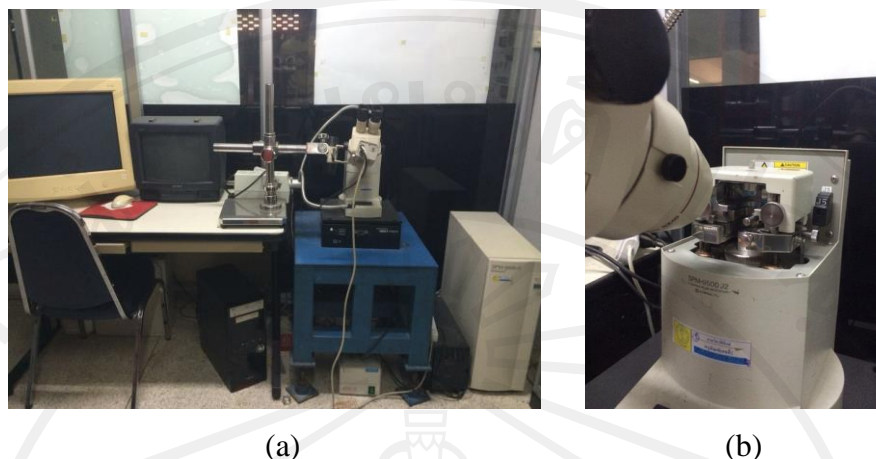


Figure 3.13 AFM system (a) Shimadzu SPM-9500J2 is being used for analyzing the  $\text{TiO}_2$  film's surface and thickness (b) a sample is placed on a sample's stand and being analyzing.

Pulling of a transparent tape from a substrate slowly is necessary in order to get a sharp edge of the film. Sticking the substrate with a small magnetic plate is required then installing the plate into an AFM's sample stands in Figure 3.13. Try to adjust the AFM's cantilever to reach the film edge and scan around the film edge to measure its thickness.

### 3.3.4 Power Conversion Efficiency Experiment

The experiment is consisted of two parts: preparation of the DSSC and analysis the DSSC power conversion efficiency.

#### 1) Preparation of the dye-sensitized solar cell

Soaking the  $\text{TiO}_2$  coated glass into a benchmark sensitizer N719 dye solution in Figure 3.14 for 1 hour and anneal the soaked glass at  $500^\circ\text{C}$  for 2 hours.



Figure 3.14 N719 dye solution soaked annealed TiO<sub>2</sub> coated FTO glasses.

To make a Platinum coated counter electrode, transparent tape is attached on a non-deposited conductive glass to reserve a space as 0.5x2.0 cm<sup>2</sup>. Drop a 10 μm<sup>3</sup> droplet of H<sub>2</sub>PtCl<sub>6</sub> solution on to the reserved space. Attach 2 pieces of plastic paraffin film on the soaked glass. Then attach the Platinum coated glass and the N719 dye soaked glass together. Blow the attached glasses with hot air for 30 seconds.

## 2) Analysis of the dye-sensitized solar cell

Fill a droplet of iodine electrolyte into a small gap between the attached glasses by a syringe as shown in Figure 3.15.

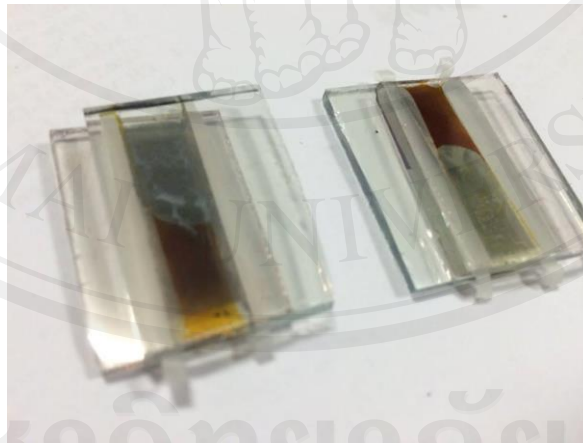


Figure 3.15 Iodine half-filled after testing DSSC.

Put a DSSC into a blue box where the light source is installed in Figure 3.16, where has its simple schematic as Figure 3.17.

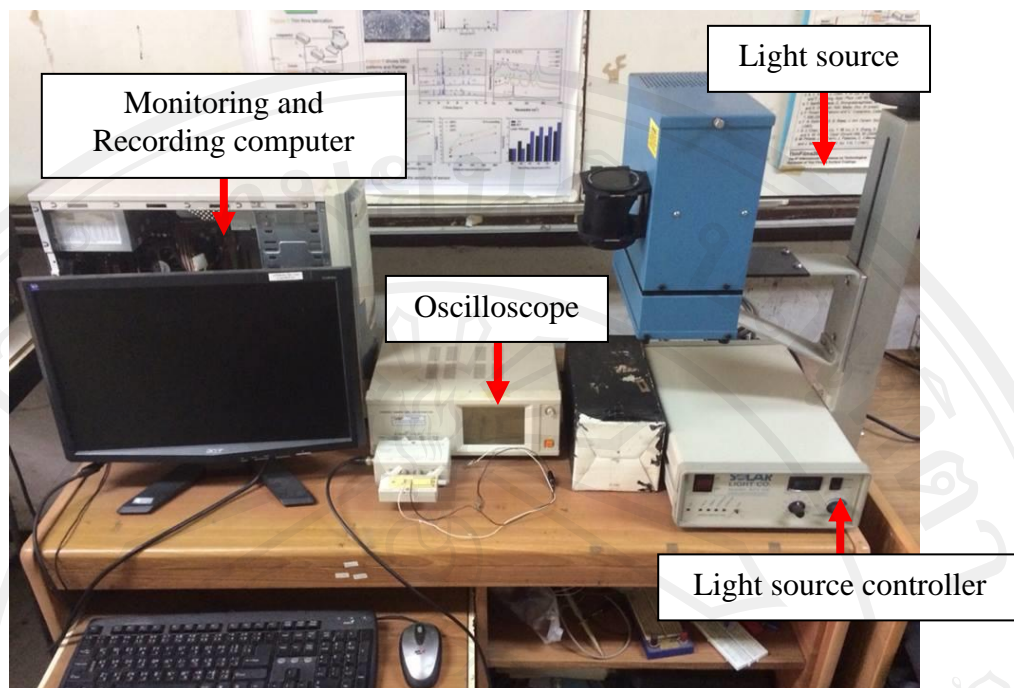


Figure 3.16 The power conversion efficiency test system.

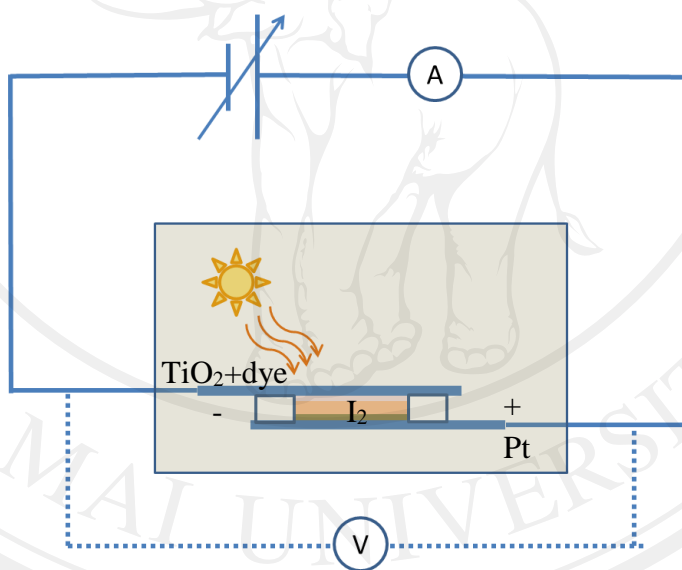


Figure 3.17 Schematic of the power conversion efficiency experiment circuit.

Turn on a light source with its power per area as  $100 \text{ mW/cm}^2$  and vary the input voltage from  $0 \text{ V}$  to  $0.7 \text{ V}$  as well as record the varied current of the circuit by computer. Moreover, the solar power conversion coefficient can be calculated as an area under the relationship between the varied voltages and current.

A TiO<sub>2</sub> deposited FTO glass has soaked in N719 dye solution for an hour while a non-deposited glass is coated by platinum via dropping several drops to become a DSSC. The DSSC is installed as a part of an electric circuit which absorbs photon from 100 mW light source as the same time as increasing the voltage of an electric circuit power supply from 0 V, keep recording the circuit's current between increasing the voltage until the current has reached 0 A.

### 3.3.5 Photocatalytic antibacterial test

Some TiO<sub>2</sub> films deposited on Si were tested for photocatalytic antibacterial effect. In the test, an ultraviolet (UV) lamp was installed at the top of a black paper box and the box was put in an incubator. Tubes of bacterial *E. Coli* solution of 200 ml were shaken by a shaker in the black box under the UV light inside the incubator at 37°C for overnight. Figure 3.18 shows the testing setup. After a certain time period, the TiO<sub>2</sub> soaked bacterial solution was being applied on the 16 replicate agar plates which play a role culture medium. The bacteria applied agar was left in the incubator at 37°C for 2 nights are measured by counting the bacterial colonies after further culturing.



(a)

(b)

Figure 3.18 Photograph of the setup for TiO<sub>2</sub> film photocatalytic antibacterial effect.

(a) The black box placed inside the incubator. (b) Inside the box: the UV lamp  
(at the top of the box) and the shaker.