

CHAPTER 4

Results and Discussions

This chapter contains the results from studying the effect on the film from various parameters; oxygen doping pressure, bias voltage, film's annealing and deposition time. Moreover, the power conversion efficiency of the film is also measured.

4.1 TiO₂ Film Preparation

4.1.1 Distance between Filter Exit and Sample Surface

The different distance between the filter exit and the sample surface shows different uniformity and thickness of the coated film. The shorter distance causes thicker but worse uniformity of the film. However the longer distance causes better uniformity but thinner film. Therefore the deposited film with higher uniformity is preference in this study. As a result, the distance between the filter exit and the sample surface as 3 cm is required after comparing the film deposited with 1 cm as shown in Figure 4.1.

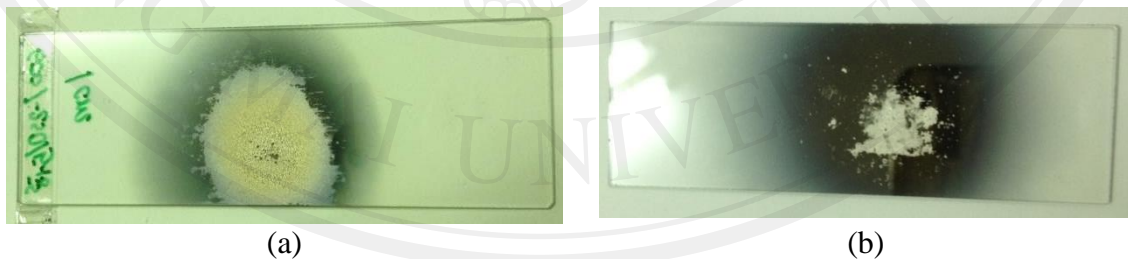


Figure 4.1 The deposited film on varying distance (a) 1cm. and (b) 3cm, with arc voltage 600 V, bias -250 V, pressure 4.2×10^{-3} for 20 minutes.

4.1.2 Oxygen partial pressure

The SEM, EDS, Raman spectroscopy and AFM are applied to study the effect from varying of the oxygen pressure in TiO₂ film. The TiO₂ coated substrates with different oxygen doping pressure at 1×10^{-1} torr, 1×10^{-2}

torr, 1×10^{-3} torr, 1×10^{-4} torr and non-doped with their constant deposition parameters; base pressure at 5×10^{-5} torr, -250 V biased substrate, arc voltage at 600 V with 20 minutes deposition time. For SEM and EDS, TiO₂ is deposited on glass. Moreover for Raman analysis and AFM, TiO₂ is deposited on silicon wafer as shown in Table 4.1.

The deposition time does affect the film's transparency and film's thickness as shown in Figure 4.2 and Figure 4.3. The increasing of O₂ causes thinner deposited film. The thickness of the films at 10^{-1} , 10^{-2} and 10^{-3} torr are unable to define their difference by the SEM at 10,000X, however the AFM can measure their thickness with more reliable as shown in Figure 4.4 and the set of films' thickness measured by AFM is also plotted in Figure 4.5. The Figure 4.6 shows an example of information obtained from EDS and the whole information from the 5 deposition conditions are shown in Table 4.2, which shows that the film deposited at a low working pressure with O₂ contains a low percentage of oxygen and tended to be increased while the working pressure is increased. Although every percentage amount of each element in the film are change, the standard deviation shows that only the amount of oxygen and titanium are varied significantly over the various working pressure of O₂. After applying the lowest percentage amount of oxygen in Figure 4.6 to be a reference amount, the relative percentage amount of oxygen for each deposition condition is concluded in Table 4.2. As a result, the most suitable oxygen pressure deposition condition is at the 1×10^{-3} torr, because it provides the ratio between oxygen:titanium nearest to 2:1, which is expected that it does contain the highest amount of TiO₂ as shown in Figure 4.7.

Although the deposited film with different O₂ pressure levels are affected as the varied the thickness and the ratio of oxygen:titanium, they do not provide a spectrum of anatase structure at 639 cm^{-1} after being analyzed by Raman spectroscopy analysis as shown in Figure 4.8.

Table 4.1 A summary of the deposition and characterization of the 20-min deposited TiO₂ film for SEM, EDS, Raman analysis and AFM. Y: done for the specified analysis, N: not done for the specified analysis.

| Sample No. | Substrate | Deposition Time (mins) | Base Pressure (torr) | Working Pressure with O ₂ (torr) | SEM | EDS | Raman analysis | AFM |
|------------|-----------|------------------------|----------------------|---|-----|-----|----------------|-----|
| 1g | Glass | 20 | 5×10^{-5} | 0 | Y | Y | N | N |
| 2g | Glass | 20 | 5×10^{-5} | 1×10^{-4} | Y | Y | N | N |
| 3g | Glass | 20 | 5×10^{-5} | 1×10^{-3} | Y | Y | N | N |
| 4g | Glass | 20 | 5×10^{-5} | 1×10^{-2} | Y | Y | N | N |
| 5g | Glass | 20 | 5×10^{-5} | 1×10^{-1} | Y | Y | N | N |
| 1s | Si | 20 | 5×10^{-5} | 0 | N | N | Y | Y |
| 2s | Si | 20 | 5×10^{-5} | 1×10^{-4} | N | N | Y | Y |
| 3s | Si | 20 | 5×10^{-5} | 1×10^{-3} | N | N | Y | Y |
| 4s | Si | 20 | 5×10^{-5} | 1×10^{-2} | N | N | Y | Y |
| 5s | Si | 20 | 5×10^{-5} | 1×10^{-1} | N | N | Y | Y |

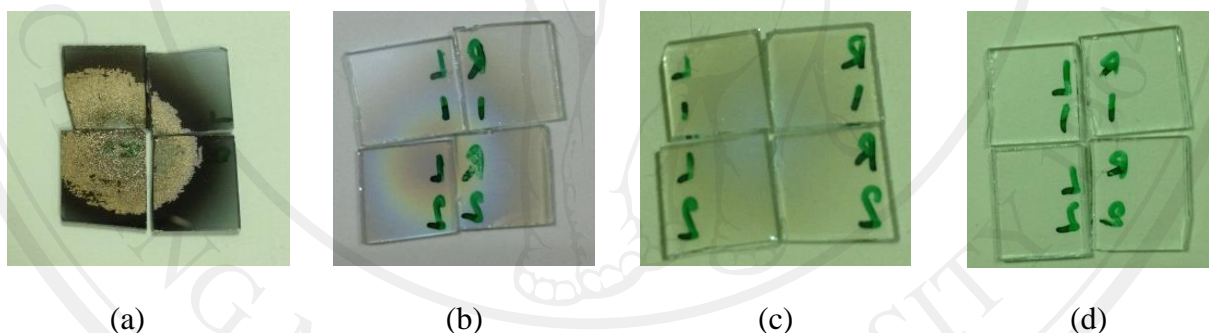


Figure 4.2 The film transparency as a function of the working pressure.

(a) 1×10^{-4} torr. (b) 1×10^{-3} torr. (c) 1×10^{-2} torr. (d) 1×10^{-1} torr

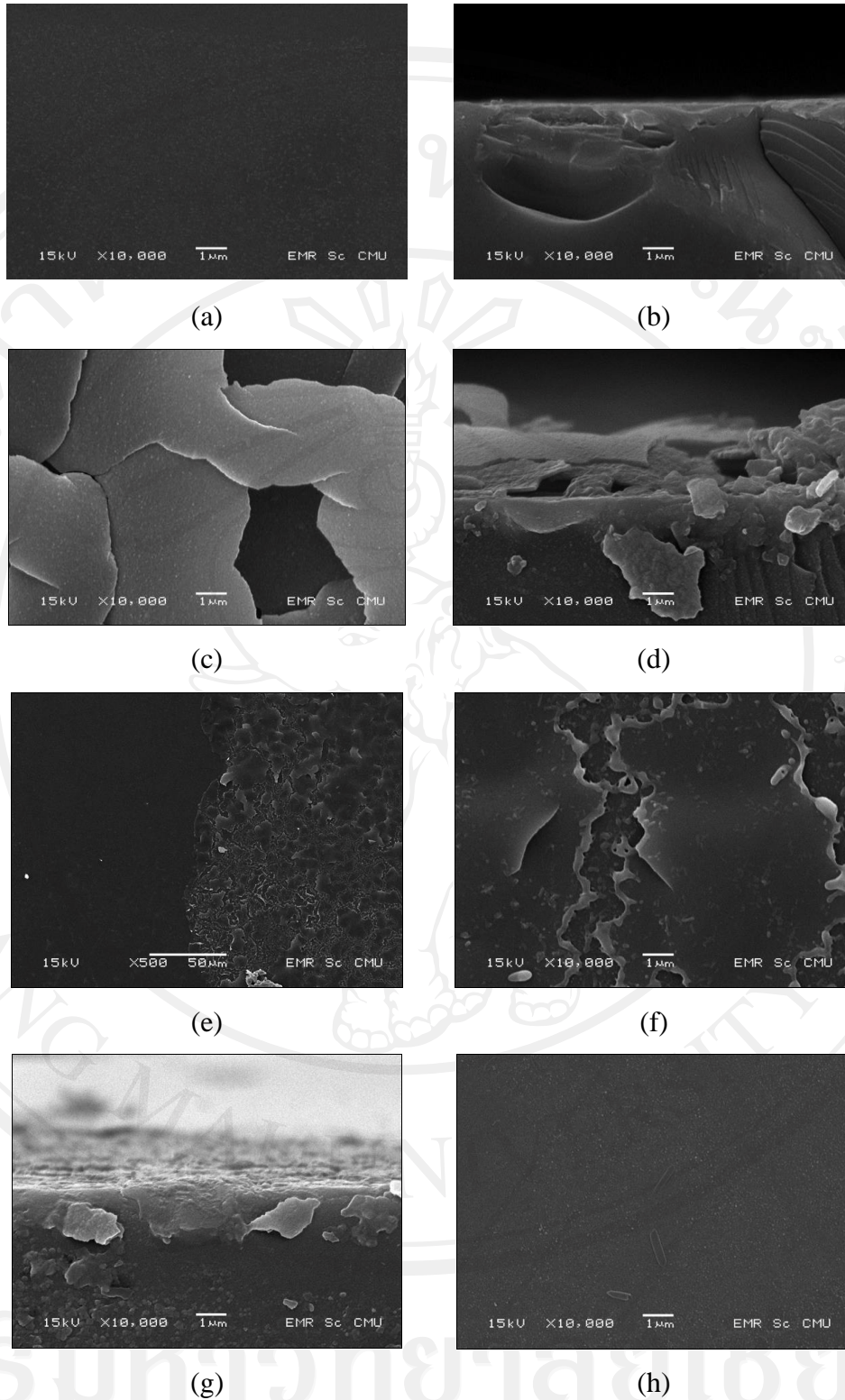


Figure 4.3 SEM images of the films. (a) (top view) and (b) (cross section): glass without film. (c) (top view) and (d) (cross section): Ti film deposited at the base pressure. (e), (f) (top views) and (g) (cross section): pressure 1×10^{-4} torr. (e) shows a border section between the coated (right) and uncoated (left) areas. (h) (top view): pressure 1×10^{-1} torr.

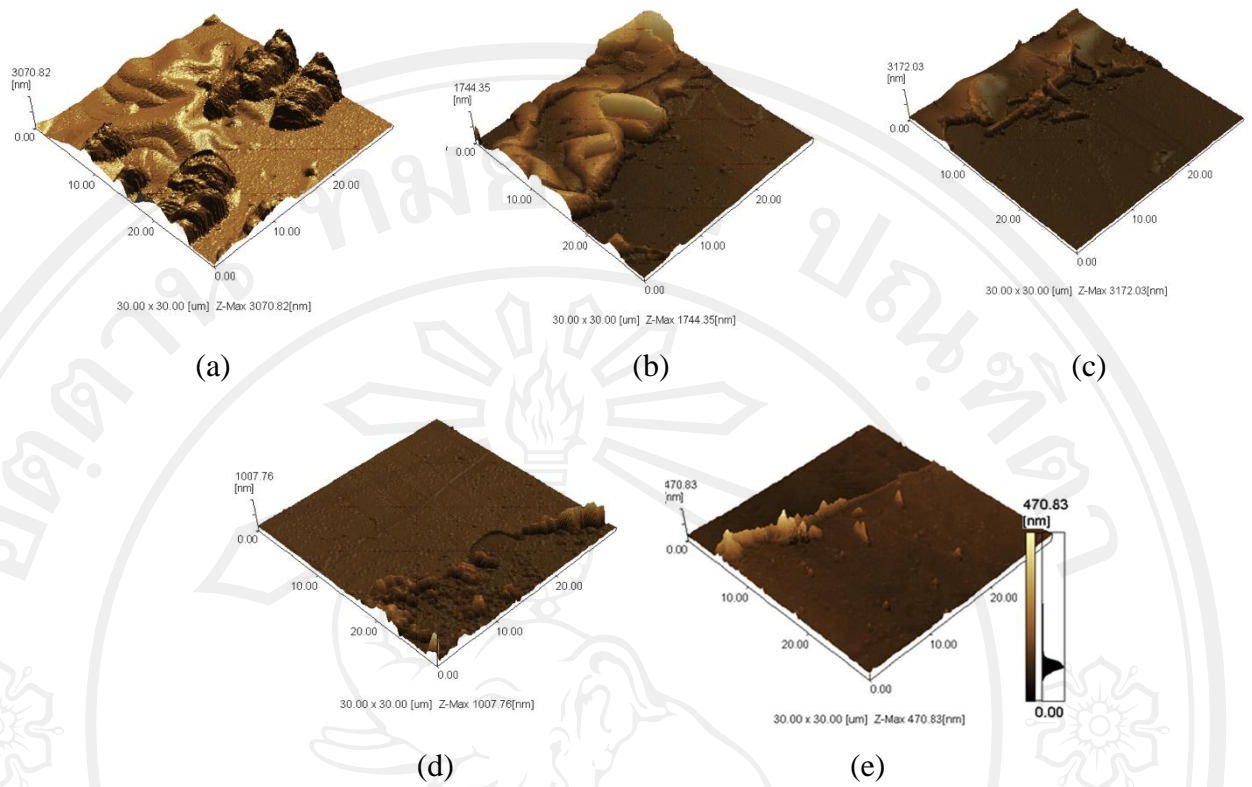


Figure 4.4 AFM-measured film surface morphology across the boundary between the film and the substrate as a function of the working pressure. (a) Base pressure 5×10^{-5} torr (b) 1×10^{-4} torr (c) 1×10^{-3} torr (d) 1×10^{-2} torr (e) 1×10^{-1} torr

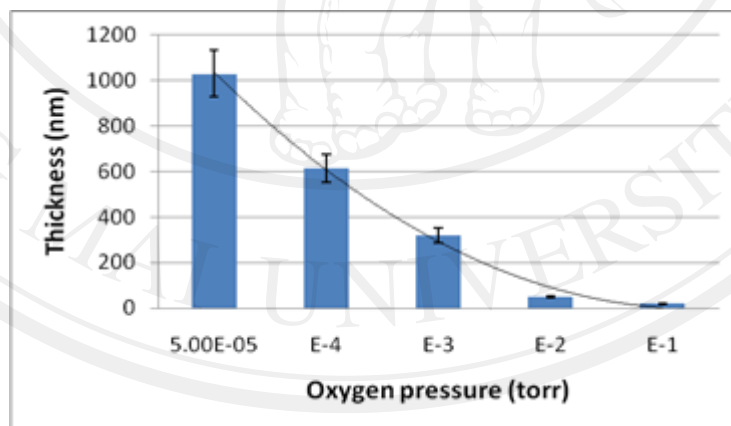


Figure 4.5 The thickness of films deposited at different oxygen doping pressure. The film deposited for 20 minutes with base pressure 5×10^{-5} torr, O_2 doped 10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} torr have their average thickness as 1,030 nm, 615 nm, 320 nm, 50 nm and 19 nm respectively.

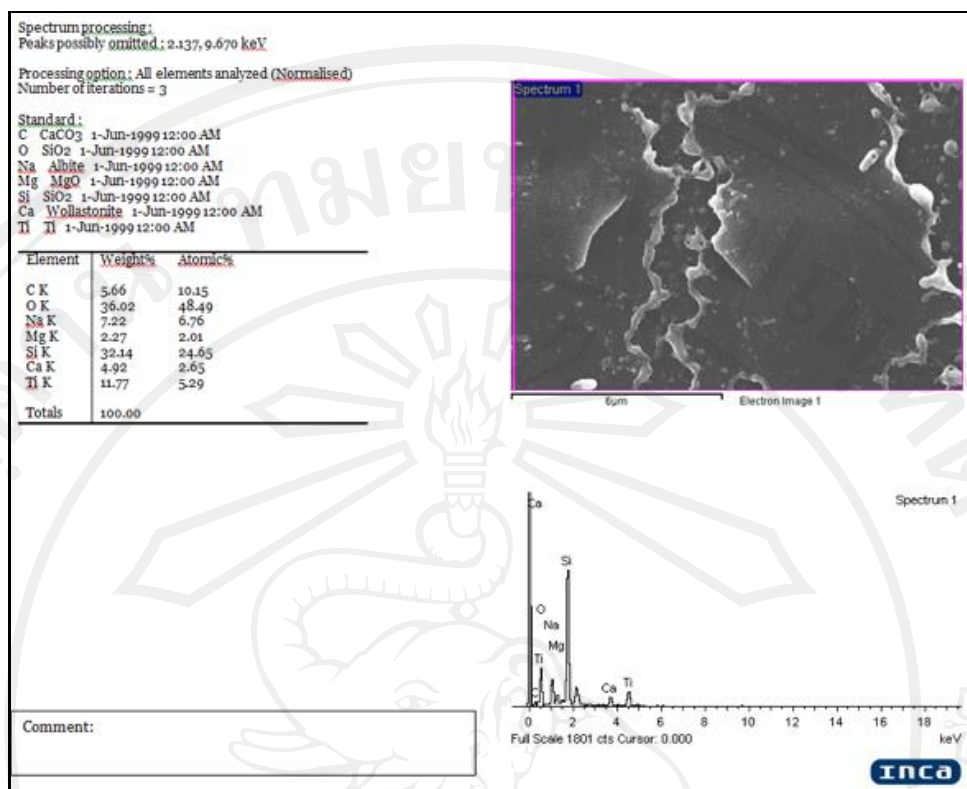


Figure 4.6 An example of the EDS information of the titanium dioxide thin film which is deposited at 10^{-4} torr, arc 600 V and -250 V biased with 20 minutes deposition

Table 4.2 The atomic percentage of elements in film on various O₂ pressures.

| Element | Percentage of elements in film on various O ₂ pressure (% atomic) | | | | | |
|---------|--|----------------|----------------|----------------|----------------|--------------------|
| | 5×10^{-5} torr | 10^{-4} torr | 10^{-3} torr | 10^{-2} torr | 10^{-1} torr | Standard Deviation |
| C | 8.36 | 10.15 | 7.25 | 9.73 | 5.78 | 1.607 |
| O | 49.26 | 48.49 | 53.03 | 53.54 | 56.97 | 3.086 |
| Na | 6.44 | 6.76 | 7.43 | 7.23 | 7.76 | 0.471 |
| Mg | 1.48 | 2.01 | 1.85 | 1.91 | 1.86 | 0.180 |
| Al | 0.00 | 0.00 | 0.53 | 0.00 | 0.46 | 0.244 |
| Si | 23.01 | 24.65 | 25.24 | 23.94 | 24.73 | 0.772 |
| Ca | 2.23 | 2.65 | 2.39 | 2.36 | 2.41 | 0.136 |
| Ti | 9.22 | 5.29 | 2.28 | 1.28 | 0.02 | 3.298 |

Table 4.2 shows the standard deviations of the amount of both oxygen and titanium are changed significantly while the others are not, which means that the varying of the oxygen pressure causes varying of oxygen and titanium significantly. After taking the percentage of oxygen at 10^{-5} torr as the reference,

the relative oxygen atomic percentage of each condition shown as Table 4.3. For example, the 3.77 and 7.71 in the below table comes from 53.03 – 49.26 (reference) and 56.97-49.26 respectively, while the Titanium’s information is directly duplicated from its raw data.

Table 4.3 The relative atomic percentage varied by varying O₂ pressure, which making use of the non-doping condition as a reference.

| Element | Relative Atomic% of varying O ₂ pressure | | | | |
|---------|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | 5×10 ⁻⁵ torr (1s) | 1×10 ⁻⁴ torr (2s) | 1×10 ⁻³ torr (3s) | 1×10 ⁻² torr (4s) | 1×10 ⁻¹ torr (5s) |
| O | 0 | 0 | 3.77 | 4.28 | 7.71 |
| Ti | 9.22 | 5.29 | 2.28 | 1.28 | 0.02 |
| O/Ti | 0.00 | 0.00 | 1.65 | 3.34 | 385.50 |

From the Table 4.3, the plotted information is shown in Figure 4.7 which contain the ratio of O:Ti as 2:1 is between the O₂ doped deposition condition at 10⁻³ torr to 10⁻² torr.

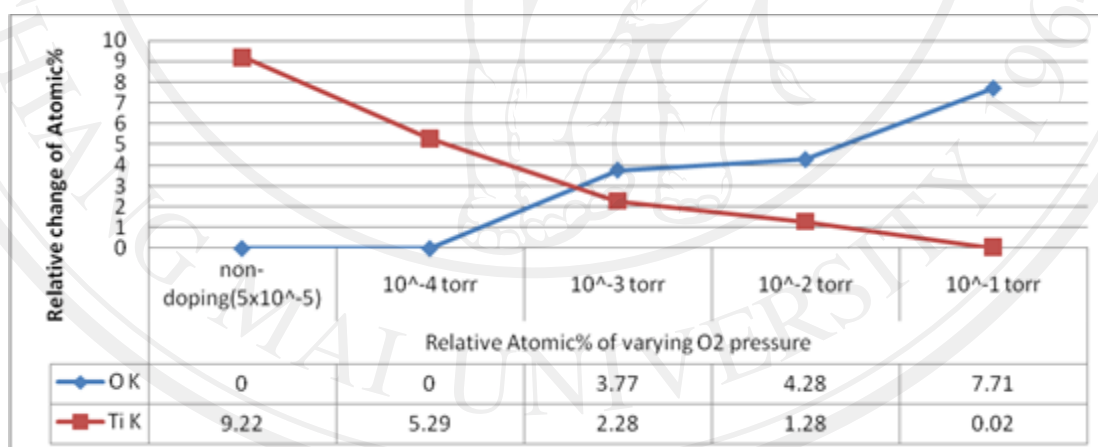


Figure 4.7 The plotted relative atomic percentage varied by varying of O₂ pressure with making use of the non-doping condition as a reference.

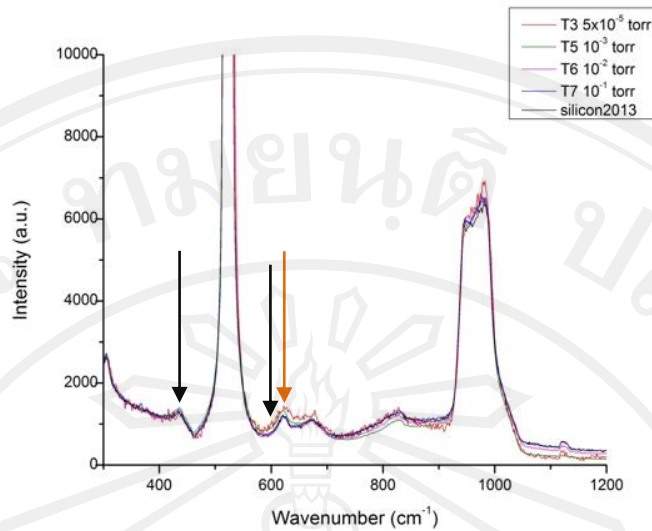


Figure 4.8 The deposited TiO₂ film with different oxygen doping pressure 10⁻¹, 10⁻², 10⁻³ torr and non-oxygen doped at the base pressure 5x10⁻⁵ torr. Black and orange arrows show the peaks of rutile and anatase respectively.

4.1.3 Bias voltage

The TiO₂ films are deposited on a glass slide at the three different bias voltages; 0 V, -250 V and -500 V with fixed arc voltage at 600 V for 10, 20 and 30 minutes deposition time at 10⁻³ torr O₂ doped pressure on silicon wafer. The glass slide is partly pasted by transparent tape and also measured its mass before deposition and after deposition in order to calculate the film's mass. Consequently, the films are calculated their volume and density as shown in Table 4.4.

The varying of the bias voltage from 0 V, -250 V and -500 V causes varying of Film's mass, thickness and Density as shown in Figure 4.9, Figure 4.10 and Figure 4.11 respectively. The Figure 4.9 shows the film's mass is increasing with increasing of deposition time between 0 to 40 minutes of deposition which is well fitted to the logarithm trend line. Moreover, the more magnitude of negative voltage biasing causes more amount of titanium deposit on substrate. The Figure 4.10 shows the film's thickness which is increasing with the increasing of the deposition time, however, the varying of bias voltage is not effectively causing any changes for the thickness. Moreover the Figure 4.11 shows the density of

the film which is not significantly changed over varying deposition time but effectively changed over varying the bias voltage.

Table 4.4 The varied bias voltage and deposition time TiO₂ deposited substrate's calculated thickness and density.

| No. | Bias Voltage (V) | Time (mins) | Substrate mass (g) | Post-deposited Substrate mass (g) | Film's Mass (g) | Average thickness (nm) | Volume (x10 ⁻⁵ cm ³) | Density (g/cm ³) |
|-----|------------------|-------------|--------------------|-----------------------------------|-----------------|------------------------|---|------------------------------|
| BA1 | 0 | 10 | 4.8459 | 4.8460 | 0.0001 | 42.50 | 4.373 | 2.286 |
| BA2 | 0 | 20 | 4.8167 | 4.8169 | 0.0002 | 54.52 | 5.610 | 3.564 |
| BA3 | 0 | 30 | 4.9467 | 4.9471 | 0.0003 | 80.45 | 8.278 | 3.623 |
| BA4 | 0 | 40 | 5.1360 | 5.1362 | 0.0003 | 87.69 | 9.023 | 3.324 |
| BB1 | -250 | 10 | 4.6518 | 4.6520 | 0.0002 | 54.14 | 5.571 | 3.589 |
| BB2 | -250 | 20 | 4.8123 | 4.8126 | 0.0003 | 64.58 | 6.645 | 4.514 |
| BB3 | -250 | 30 | 5.1439 | 5.1443 | 0.0003 | 75.24 | 7.742 | 3.874 |
| BB4 | -250 | 40 | 5.1489 | 5.1494 | 0.0005 | 90.82 | 9.345 | 5.350 |
| BC1 | -500 | 10 | 5.2241 | 5.2244 | 0.0003 | 54.65 | 5.623 | 5.334 |
| BC2 | -500 | 20 | 5.1818 | 5.1819 | 0.0004 | 62.18 | 6.398 | 6.251 |
| BC3 | -500 | 30 | 5.1989 | 5.1993 | 0.0005 | 84.27 | 8.671 | 5.765 |
| BC4 | -500 | 40 | 5.1607 | 5.1612 | 0.0005 | 83.82 | 8.625 | 5.796 |

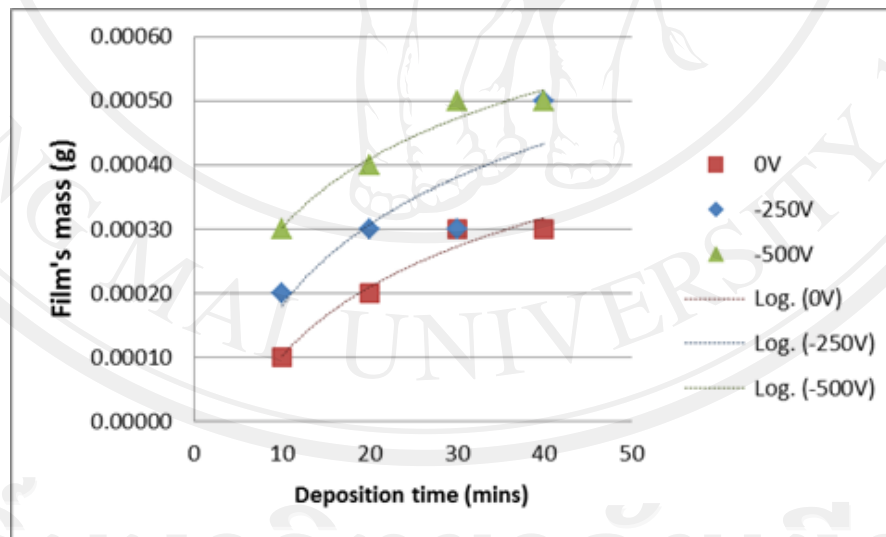


Figure 4.9 The relationship between film's mass and deposition time.

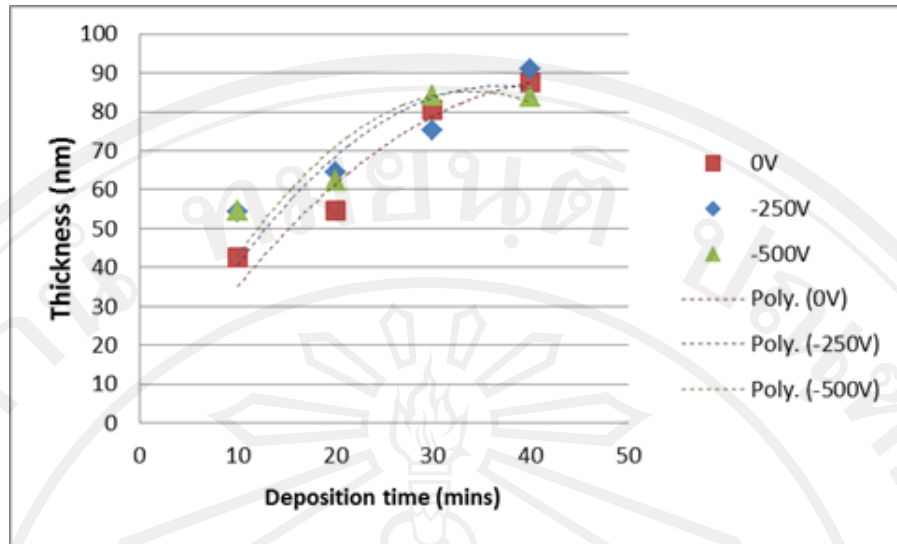


Figure 4.10 The relationship between film's thickness and deposition time.

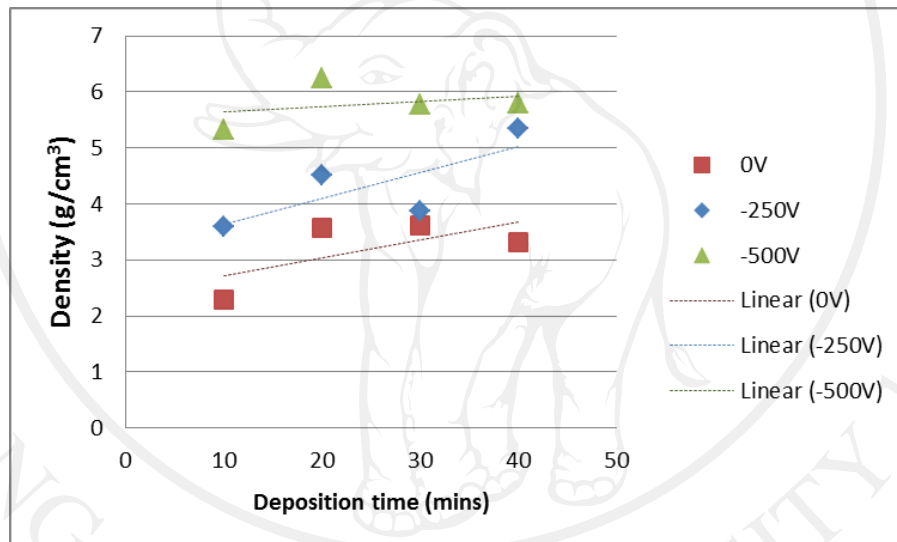


Figure 4.11 The relationship between film's density and deposition time.

4.1.4 Annealing and deposition time

After being deposited for 10, 20 and 30 minutes deposition time with 0 V and -250 V biased at 10^{-2} and 10^{-3} torr O_2 doped pressure, the half of each deposition condition substrates are annealed with 400°C for 2 hours as shown in Table 4.5.

Table 4.5 The summary of deposition condition for the annealing and deposition time effect on film experiment.

| No. | Arc Voltage (V) | Bias Voltage (V) | Deposition Time (mins) | Working Pressure with O ₂ (torr) | 400°C 2 hours Annealing |
|-----|-----------------|------------------|------------------------|---|-------------------------|
| B3 | 600 | -250 | 10 | 10 ⁻³ | N |
| C3 | 600 | -250 | 20 | 10 ⁻³ | N |
| C4 | 600 | -250 | 20 | 10 ⁻² | N |
| D3 | 600 | -250 | 30 | 10 ⁻³ | N |
| B3a | 600 | -250 | 10 | 10 ⁻³ | Y |
| C3a | 600 | -250 | 20 | 10 ⁻³ | Y |
| C4a | 600 | -250 | 20 | 10 ⁻² | Y |
| D3a | 600 | -250 | 30 | 10 ⁻³ | Y |

Without annealing, the film with 10 minutes, 20 minutes and 30 minutes deposition time do not offer any differences in their Raman spectrum as shown in Figure 4.12. However, the annealing process increases the anatase's peak intensity around 639 cm⁻¹ of the films with 20 minutes and 30 minutes deposition time, while the annealing process does not significantly increase the peak on film with 10 minutes deposition time as shown in Figure 4.13.

The deposited TiO₂ film with doped oxygen at 10⁻² torr and 10⁻³ torr are re-deposited on a different manufacture's silicon from the deposited silicon in (4.1.2) Figure 4.8 but the other parameters are remained the same as shown in Table 4.5. Moreover some of the deposited substrates are annealed with 400°C for 2 hours. The Raman spectroscopy analysis result from the non-annealed film is still the same as the experiment in (4.1.2), that it is difficult to identify the difference between the films as shown in Figure 4.14. However the Figure 4.15 and Figure 4.16 show that the annealed film with oxygen doped pressure at 10⁻³ torr show a significantly increased of the anatase peak at 639 cm⁻¹ while for the annealed film at 10⁻² torr does not show the peak respectively. It can be concluded that the annealing of the film does affect to the film's structure on 10⁻³ torr oxygen doped condition but does not affect the film's structure on 10⁻² torr because its thickness is

too small. This result is according to the experiment result in (4.1) that the most suitable oxygen doped pressure is 10^{-3} torr.

It can be concluded that the 400°C with 2 hours annealing boosts up the forming of TiO_2 film into the anatase structure.

The non-annealed TiO_2 films are also tested their photocatalytic properties by depollution bacterial contaminated water but they do not effective in depollute the water. Possibly, the film does not contain the anatase phase TiO_2 and the film is too thin.

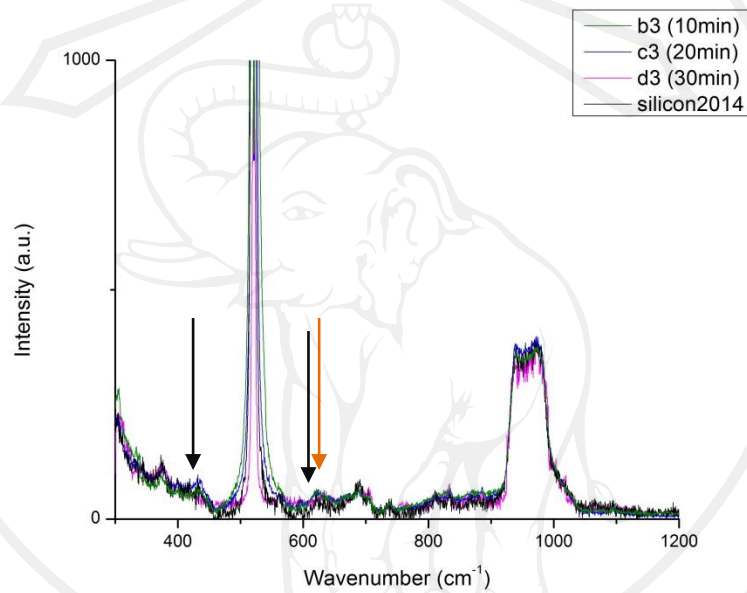


Figure 4.12 The not annealed TiO_2 film deposited with O_2 doped pressure at 10^{-3} torr for 10 minutes, 20 minutes and 30 minutes deposition time. Black and orange arrows show the peaks of rutile and anatase structure respectively

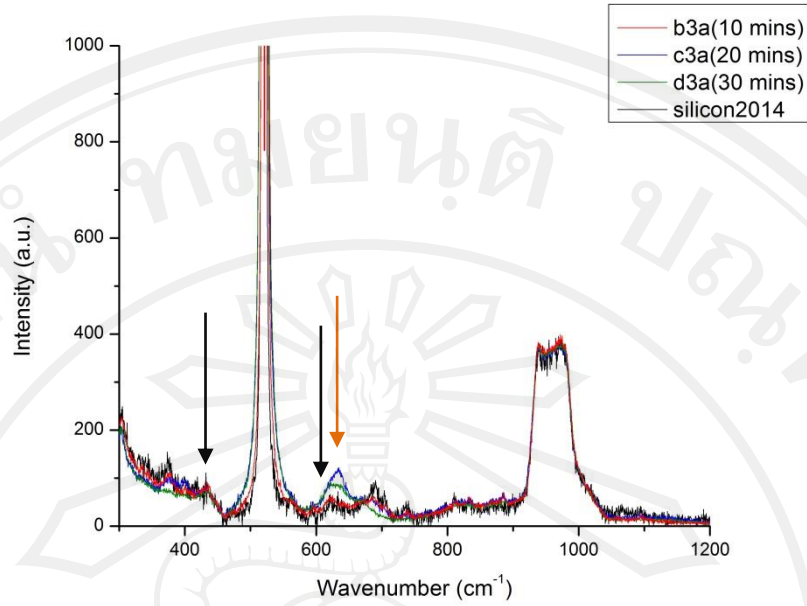


Figure 4.13 The annealed TiO₂ film deposited with O₂ doped pressure at 10⁻³ torr for 10 minutes, 20 minutes and 30 minutes deposition time. Black and orange arrows show the peaks of rutile and anatase structure respectively

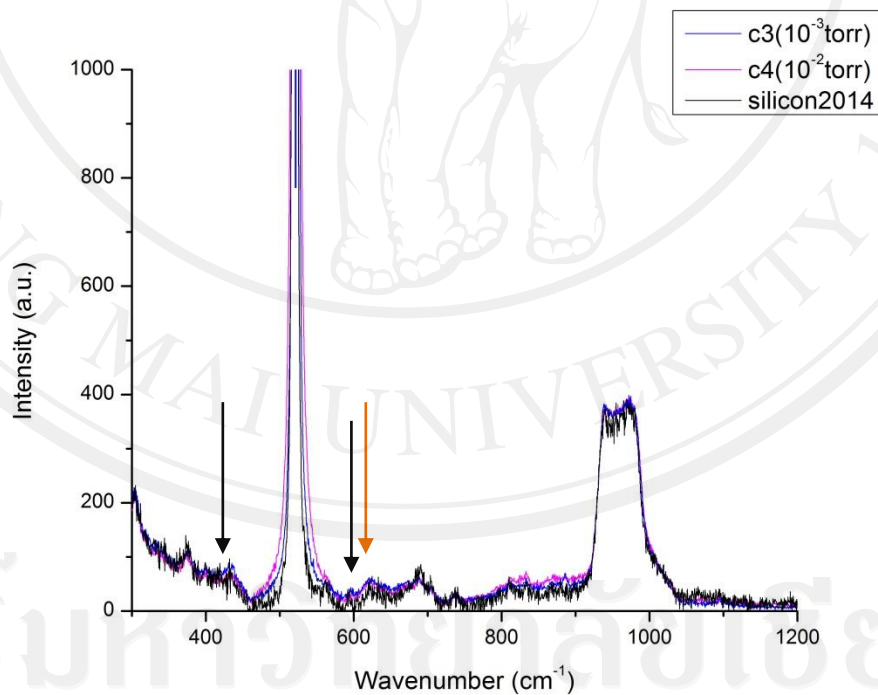


Figure 4.14 The deposited TiO₂ film with different O₂ doped pressure 10⁻³ torr and 10⁻² torr. Black and orange arrows show the peaks of rutile and anatase structure respectively.

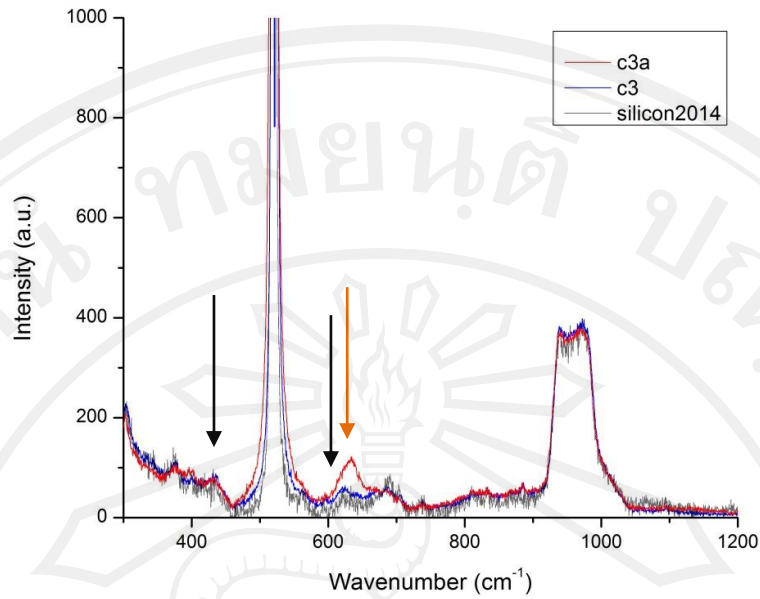


Figure 4.15 The deposited TiO₂ film with annealed and not annealed condition deposited with O₂ doped pressure at 10⁻³ torr. Black and orange arrows show the peaks of rutile and anatase structure respectively.

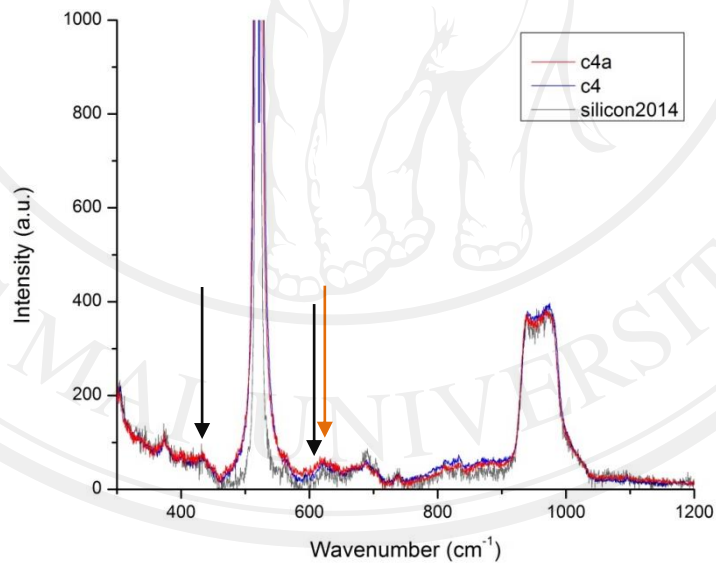


Figure 4.16 The deposited TiO₂ film with annealed and not annealed condition deposited with O₂ doped pressure at 10⁻² torr. Black and orange arrows show the peaks of rutile and anatase structure respectively.

4.2 Application as a solar cell

There are 3 comparisons of the varying annealing, biasing and deposition time on the solar conversion efficiency by 6 TiO₂ coated FTO glasses with different deposition conditions as shown in Table 4.6.

Table 4.6 The 6 deposition conditions of TiO₂ deposited FTO glass to be assembled as the DSSC.

| No. | Arc Voltage (V) | Bias Voltage (V) | Deposition Time (mins) | Working Pressure with O ₂ (torr) | 400°C 2 hours Annealing |
|-------|-----------------|------------------|------------------------|---|-------------------------|
| GG05 | 600 | 0 | 20 | 10 ⁻³ | N |
| GG05a | 600 | 0 | 20 | 10 ⁻³ | Y |
| GH05 | 600 | -250 | 20 | 10 ⁻³ | N |
| GH05a | 600 | -250 | 20 | 10 ⁻³ | Y |
| GH06 | 600 | -250 | 30 | 10 ⁻³ | N |
| GH06a | 600 | -250 | 30 | 10 ⁻³ | Y |

With emitting 100 mW from light source into the films; GH06 and GH06a, the annealed deposited film (GH06a) provides solar conversion efficiency as 0.0249 %, however the non-annealed (GH06) deposited film provides 0.0155 % which can be calculated from the area under the spectrum in Figure 4.17 comparing with the constant input power of a light source with 100 mW. The Figure 4.18 shows that the GH05a and GG05a are annealed at the same annealing process at 400°C for 2 hours but different by their bias voltage -250 V and 0 V provide their power conversion efficiency as 1.72×10^{-7} % and 27.1×10^{-7} % respectively. As a result, the more negative bias voltage causes lesser efficiency because more negative biased substrate provides a higher density of the TiO₂ film which causes lower amount of dye attached on the film. Moreover the increasing of the deposition time does effectively increase the efficiency as shown in Figure 4.19, the 30 minutes deposition time (GH06a) provides the efficiency as 0.0249 %, while the 20 minutes deposition time (GH05a) provides very low efficiency around 1.72×10^{-7} %.

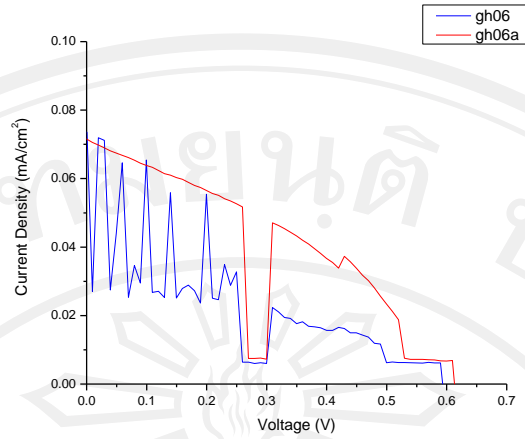


Figure 4.17 The altered circuit's current density affected by varying the electricity source's voltage in annealed and non-annealed TiO₂ deposited FTO glasses.

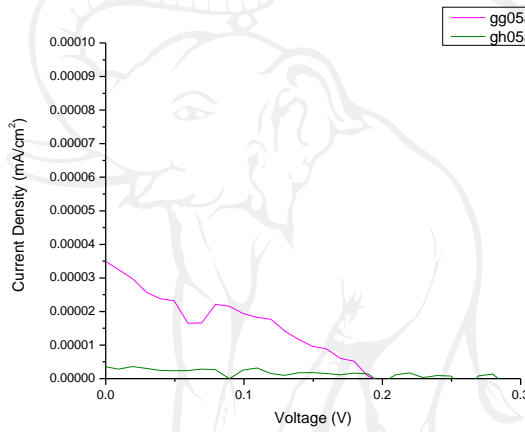


Figure 4.18 The altered circuit's current density affected by varying the electricity source's voltage in non-biased and -250 V biased TiO₂ deposited FTO glasses.

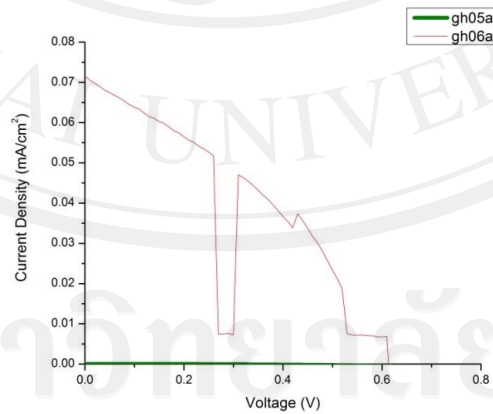


Figure 4.19 The altered circuit's current density affected by varying the electricity source's voltage in 20 minutes and 30 minutes deposition time of TiO₂ deposited FTO glasses.

It can be concluded that the film annealing is required to boost up solar conversion efficiency. Although the annealed film can convert photon into electricity as 0.0249 %, it is far from maximum efficiency of the dye-sensitized solar cell. Because the films deposited by other technique are drastically thick (above microns) compared to the film deposited by FCVAD (a few tenth nanometers), which means that the thicker films provide more surface area to be attached by dye-sensitized particles which offer higher chance of more energy conversion.

Biassing substrate causes reducing of the efficiency. Even if the efficiency of the film with non-biased substrate is 27.1×10^{-7} % and 1.72×10^{-7} %, they are too low to be considered as a dye-sensitized solar cell. Moreover, the non-biased substrate provides higher efficiency than the -250 V biased substrate can be explained by the AFM result that the -250 V biased substrate contains denser TiO₂ film, which offer a smaller amount of surface area compared to the non-biased substrate.

Deposition of the film at least 30 minutes is necessary. The study of the 20 and 30 minutes film deposition shows that the 20 minutes deposition provides a very low efficiency compared to the 30 minutes deposition.

4.3 Application as an antibacterial compound

Preliminary test result of the photocatalytic antibacterial effect of the film is shown in Table 4.7. The bacterial survivals looked very close. The non-annealed deposited film at 10^{-3} torr, -250 V biased, arc voltage 600 V, 20 minutes deposition did not have anatase and hence there was no photocatalytic effect. This result demonstrated again that the anatase was necessary for photocatalytic and photovoltaic applications.

Table 4.7 The raw data of the photocatalytic antibacterial test result. Two replicates were used. Bacteria *E. coli* solution was incubated at 37°C for overnight to count the number of colonies.

| Replicate 1 | | | |
|--------------------|------------------|---------------|------------------|
| Condition | Number of colony | Condition | Number of colony |
| Control 1/1 | 125 | Treatment 1/1 | 76 |
| Control 1/2 | 125 | Treatment 1/2 | 132 |
| Control 1/3 | 105 | Treatment 1/3 | 88 |
| Control 1/4 | 102 | Treatment 1/4 | 98 |
| Control 2/1 | 118 | Treatment 2/1 | 169 |
| Control 2/2 | 118 | Treatment 2/2 | 203 |
| Control 2/3 | 222 | Treatment 2/3 | 106 |
| Control 2/4 | 222 | Treatment 2/4 | 176 |
| Control 3/1 | 78 | Treatment 3/1 | 130 |
| Control 3/2 | 44 | Treatment 3/2 | 126 |
| Control 3/3 | 87 | Treatment 3/3 | 135 |
| Control 3/4 | 110 | Treatment 3/4 | 129 |
| Control 4/1 | 23 | Treatment 4/1 | 150 |
| Control 4/2 | 59 | Treatment 4/2 | 148 |
| Control 4/3 | 73 | Treatment 4/3 | 92 |
| Control 4/4 | 67 | Treatment 4/4 | 99 |
| Mean +-SD | 104.9+-52.82 | Mean +-SD | 128.6+-33.90 |
| Replicate 2 | | | |
| Condition | Number of colony | Condition | Number of colony |
| Control 1/1 | 121 | Treatment 1/1 | 112 |
| Control 1/2 | 132 | Treatment 1/2 | 118 |
| Control 1/3 | 117 | Treatment 1/3 | 117 |
| Control 1/4 | 121 | Treatment 1/4 | 110 |
| Control 2/1 | 125 | Treatment 2/1 | 123 |
| Control 2/2 | 153 | Treatment 2/2 | 127 |
| Control 2/3 | 122 | Treatment 2/3 | 140 |
| Control 2/4 | 134 | Treatment 2/4 | 121 |
| Control 3/1 | 115 | Treatment 3/1 | 117 |
| Control 3/2 | 118 | Treatment 3/2 | 114 |
| Control 3/3 | 87 | Treatment 3/3 | 114 |
| Control 3/4 | 139 | Treatment 3/4 | 110 |
| Control 4/1 | 120 | Treatment 4/1 | 116 |
| Control 4/2 | 117 | Treatment 4/2 | 114 |
| Control 4/3 | 132 | Treatment 4/3 | 115 |
| Control 4/4 | 126 | Treatment 4/4 | 121 |
| Mean +-SD | 123.69+-13.508 | Mean +-SD | 118.06+-7.224 |

4.4 DLC Film Preparation

4.4.1 Bias voltage

In the study of the effect of bias voltage on a film, the DLC films are deposited follow the Table 4.8 below; moreover, The Raman spectrum of the films and their ratio of I_D/I_G are shown in Figure 4.20 and Figure 4.21 respectively.

Table 4.8 The several DLC deposition conditions deposited at arc voltage 600 V, 10 minutes deposition time, base pressure at 5×10^{-5} torr with 0, -150, -250, -350 and -450 V biased.

| Sample No. | Arc Voltage (V) | Bias Voltage (V) | Deposition Time (min) | Base Pressure (torr) | Working Pressure with N ₂ (torr) |
|------------|-----------------|------------------|-----------------------|----------------------|---|
| 1a | 600 | 0 | 10 | 5×10^{-5} | 0 |
| 1b | 600 | -150 | 10 | 5×10^{-5} | 0 |
| 1c | 600 | -250 | 10 | 5×10^{-5} | 0 |
| 1d | 600 | -350 | 10 | 5×10^{-5} | 0 |
| 1e | 600 | -450 | 10 | 5×10^{-5} | 0 |

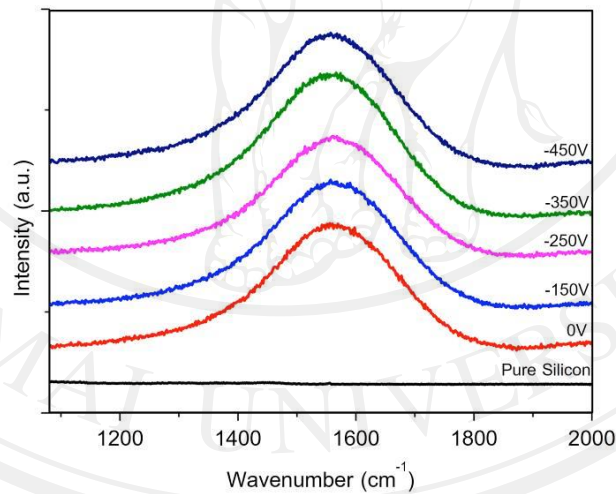


Figure 4.20 The Raman spectrum of DLC with varied bias voltage from 0 V to -450 V.

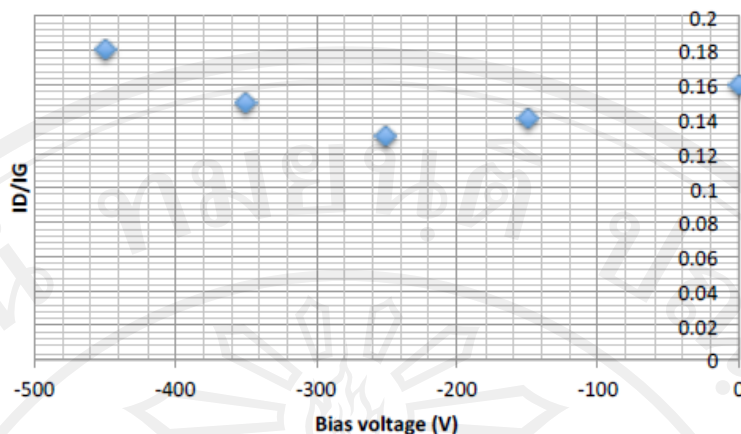


Figure 4.21 The plotted ratio of the intensity between D peak and G peak of the films with varied bias voltage from 0 V to -450 V.

It can be concluded that the lowest I_D/I_G of the DLC films can be achieved at the -250 V biasing. This indicates that the -250 V biased film has the highest sp^3 carbon content compared to the sp^2 .

4.4.2 Nitrogen partial pressure in DLC film

The Raman spectroscopy is the only one technique which applied in the study the effect of N_2 on DLC film. The DLC film is deposited follow the Table 4.9.

Table 4.9 The several DLC deposition conditions deposited at arc voltage 600 V, -250 V biased, 10 minutes deposition time, base pressure at 5×10^{-5} torr with different working pressure of N_2 .

| Sample No. | Arc Voltage (V) | Bias Voltage (V) | Deposition Time (min) | Base Pressure (torr) | Working Pressure with N_2 (torr) |
|------------|-----------------|------------------|-----------------------|----------------------|------------------------------------|
| 1 | 600 | -250 | 10 | 5×10^{-5} | 0 |
| 2 | 600 | -250 | 10 | 5×10^{-5} | 9×10^{-5} |
| 3 | 600 | -250 | 10 | 5×10^{-5} | 2×10^{-4} |
| 4 | 600 | -250 | 10 | 5×10^{-5} | 4×10^{-4} |
| 5 | 600 | -250 | 10 | 5×10^{-5} | 3×10^{-3} |

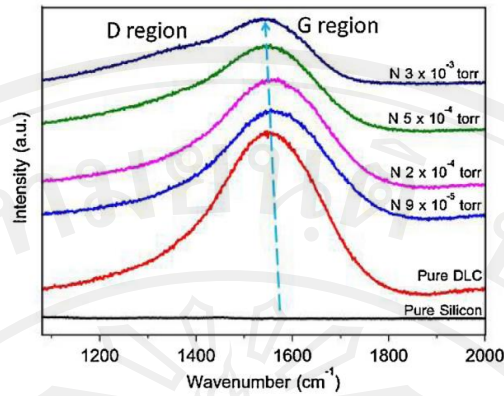


Figure 4.22 The Raman spectrum of the DLC with various working pressure of N₂.

The Raman spectrum of different levels N₂ doped pressure on DLC in Figure 4.22, shows that the peak of broad spectrum is slightly shift down while increasing the doping pressure of N₂. After applying a nano scratch test using a CSM Instrument scratch tester (Revetest Xpress), the hardness and the ratio of I_D/I_G of the film are displayed in Figure 4.23 below.

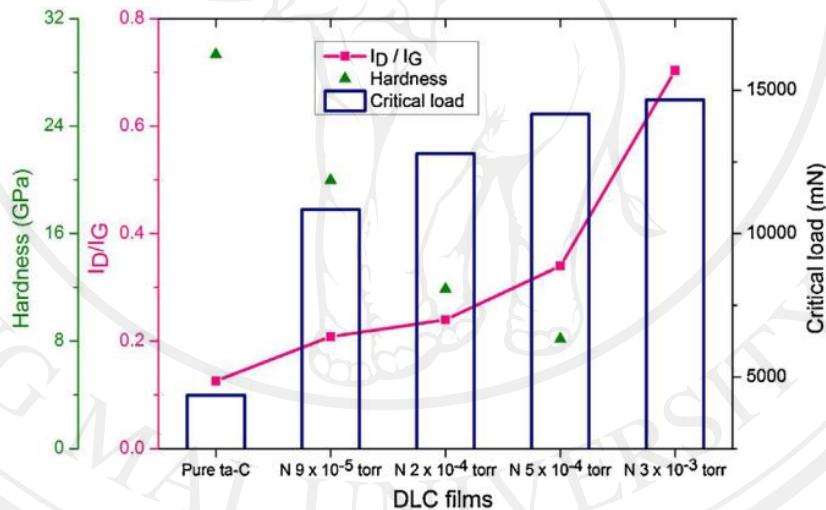


Figure 4.23 Summarized tested properties of DLC films; Hardness, Critical load and intensity ratio between D peak and G peak.

The scratch critical load of the ta-C film with various N₂ doping pressure is shown in Figure 4.23. The all ta-C:N films have a higher scratch critical load than the pure ta-C. The critical load tended to be increased while increase the N₂ doping pressure. The result confirmed with several literatures[30-32], which explained that the additional nitrogen gas improves adhesion or toughness of deposited ta-C films. The nitrogen also reduces the residual stress and increases

adhesion by reducing the formation of sp^2 and encourages the sp^2 to form clusters because of bonding with nitrogen[33].The literature[34] explains the mechanism of increasing critical load in the ta-C:N films with low nitrogen content that the C=C bonds have shorter bond lengths compared to the C-C bonds, therefore increasing of C=C bonds yields reduces the strain in the film, as a result the critical load increases. After the nitrogen added into the ta-C:N films, C=N bonds that have shorter bond lengths than either C=C bonds and C-C bonds will occur. As a result, the yielding of nitrogen increases the critical load by reducing the strain in the film.

It can be concluded that adding a low level of nitrogen content in the ta-C film to form ta-C:N decreases the hardness of the films. An additional nitrogen decrease the hardness in nitrogen doped diamond-like carbon and degrades mechanical properties[35] which show that nitrogen plays a role decrease the hardness in nitrogen doped diamond-like carbon and degrades mechanical properties of the film. The increase of the I_D/I_G ratio with addition of nitrogen also confirms the reduction in mechanical properties of nitrogen doped diamond-like carbon, however nitrogen increases the adhesion strength in nitrogen doped diamond-like carbon films as well as the critical load of nitrogen doped diamond-like carbon films when the added nitrogen pressure increased as shown in Figure 4.23.