Effect of Evaporation Deposition Time on Thickness and Impedance Value of Polyaniline Layers

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Abstract. Quartz Crystal Microbalance (QCM) works by using the principle of frequency shifting in quartz crystals due to mass deposition on the surface of the crystals. QCM sensors can be applied as chemical sensors and gas sensors. To increase its sensitivity and selectivity, QCM must be coated with active ingredients, one of which is Polyaniline (Pani). There are several methods for the Pani layer deposition above QCM. In this study, the evaporative deposition method was carried out. The purpose of this study was to analyse the effect of deposition time on the thickness and impedance value of the Pani layer. Before being coated by Pani, QCM was given a polystyrene coating to increase its adhesion. The variation of deposition time used was 10; 15; 30 and 60 seconds. The characterization carried out was measured the impedance of the layer by using an impedance analyser, observing the layer morphology by using an optical microscope, and determining the thickness of the layer using the Saurbrey equation approach. The results showed that the longer the deposition time caused the Pani layer to be deposited thicker and had a more even morphology. The layer impedance value was also getting bigger. The maximum thickness obtained at the deposition time of 60 seconds was 32.21 μm with a layer impedance value of 891.57 Ohm. With a huge impedance value, the Pani layer provides a substantial damping effect on QCM.

1. Introduction
Polyaniline is one of the most studied conductive polymers due to its ease of synthesis and stability at room temperature. Based on the stability aspect in air, polyaniline (Pani) has better stability when compared to other conductive polymers such as polyacetylene (PA), polyacetylene (PdA), polythiophene (PT) and polypyrrol (Ppy) [1]. Apart from several superior properties when compared to other conductive polymers, Pani can also be adjusted to the level of conductivity by adding dopants [2]. Due to its good properties, Pani has a wide range of applications including battery cathodes, anti-corrosion coatings, and sensor alternatives. Many studies have been conducted regarding the application of Pani as an active ingredient in sensors, including H2S gas sensors [3], ammonia gas [4], humidity sensors [5], acid sensors [6], and alcohol sensors [7]. As the active ingredient of the sensor, Pani needs to be synthesized in the form of a thin layer to make it more applicable.
The ease of Pani synthesis can be seen from the many Pani synthesis methods. Pani can be synthesized by a chemical method that will produce Pani powder, also can use an electrochemical method to directly produce a product in the form of a Pani thin layer that is deposited on the substrate. To obtain a thin layer of Pani can also use a stepwise method, namely synthesizing Pani powder first, then depositing it on the substrate by using the spin coating or evaporation method. The deposition of Pani thin layer by spin coating method has several limitations, including the need for nonorganic solvents and the insoluble nature of Pani (non-soluble), as discussed in the previous article [8]. This research will discuss another deposition method, namely using the evaporation method. The substrate used is QCM because it is known as a simple, cheap and easy to use sensor system.

Quartz crystal microbalance (QCM) is a sensor that has a working principle based on changes in oscillation frequency which is proportional to the change in mass deposited on its surface, following the Saurbrey equation [9]. The use of QCM as a gas sensor has been widely studied, including as a gas alcohol sensor [10], a free radical sensor [11] and an HCl sensor [12]. The sensitivity and selectivity of QCM can be increased by selecting the right layer of active ingredients. With low operating temperatures, conductive polymers are better candidates for active ingredients when compared to metal oxide-based sensor materials [13].

The evaporation method is a method that has been commonly used to deposit a thin layer on the substrate surface. The active material is evaporated in a vacuum so that the particles can move towards the substrate surface, which then sticks to the substrate surface. There are two basic processes in the evaporation method, namely the active material that has been heated will evaporate. Then the particles will stick to the surface of the substrate. The substrate as a deposition target must have a flat surface so that the active ingredients can be deposited properly. A rough surface will cause a step coverage or shadowing effect, where the active ingredient will stick to a more prominent surface. The advantages of the evaporation method are that the layer can be deposited with a high speed, low atomic energy so that it can minimize damage to the substrate surface and increase the purity of the active layer material [14].

2. Method
The materials used in this study were the monomer aniline (Merck), APS, HCl, acetone, polystyrene, toluene and QCM substrate. To synthesize Pani powder, researchers used a chemical synthesis method, namely the oxidation method. The oxidation method was chosen because it is a simple and easy method to obtain Pani powder. The aniline and APS solutions were mixed with 0.2 M HCl solution and allowed to stand for 1 hour, then stirred with a magnetic stirrer for 1 hour until the solution was blackish green. The solution is filtered, and then the precipitate is washed with HCl and acetone. The washed precipitate is then dried using an oven at 60°C for 5 hours to dry. The Pani powder was then crushed using a mortar and sieved with a 350 mesh sieve to obtain a powder with uniform particle size.

To reposition PANi on the QCM substrate, the substrate was previously coated with polystyrene so that it could increase its adhesion. 0.06 grams of polystyrene dissolved in 1 ml of toluene, then deposited on top of QCM using the spin coating method with a rotating speed of 3000 rpm. QCM was then dried at 100°C so that the polystyrene was evenly deposited on the surface of the substrate. Before and after the polystyrene coating, the impedance of the QCM substrate was measured to get the initial QCM impedance value and the polystyrene layer impedance value. Impedance measurements use an impedance analyzer.

Pani deposition above QCM uses the evaporation method with a vacuum evaporator (illustration of the evaporator can be seen in Figure 1). The distance between the crucibles containing Pani powder and QCM is set to 1.5 cm. Before the evaporation process is carried out, the evaporator is first vacuumed for 1 hour. The current and voltage are slowly increased to 30 mA and 1.3 V. After that the shutter glass cover is opened and the deposition time is varied for 10 seconds, 15 seconds, 30 seconds, and 60 seconds. Furthermore, the sample was heated in an oven at 100°C for 1 hour.
The characterization includes measuring the impedance value using an impedance analyzer and morphological observations using an optical microscope. The deposited layer thickness was predicted using the Saurbrey equation approach below,

$$\Delta f = \frac{-2(\Delta \rho \mu_q)^2 \Delta m}{A \rho_q \mu_q}$$  \hspace{1cm} (1)

where
- $\Delta f$ = frequency changes (Hz)
- $\Delta m$ = mass changes (g)
- $f_0$ = QCM’s resonance frequency (Hz)
- $A$ = QCM’s surface area (m$^2$)
- $\rho_q$ = QCM’s density (2.684 g/cm$^3$)
- $\mu_q$ = QCM’s modulus ($2.947 \times 10^{11}$ g/cm.s

Pani layer thickness calculation using the equation

$$\Delta h = -\frac{\Delta \rho \mu_q}{2f_0^2 \rho a}$$  \hspace{1cm} (2)

where $\Delta h$ is deposited layer thickness, and $\rho a$ is the density of the deposited material.

3. Results and Discussion

3.1. Effect of deposition time on the thickness of the Pani layer
Deposition time affects the amount of Pani formed and the thickness of the Pani layer. Pani powder changes from a solid phase to vapour due to the heat source that comes from the electricity in the evaporator filament. Pani, which is in the vapour phase, moves leave the heat source towards the QCM substrate, which has a lower temperature. The longer the evaporation time, the more Pani solids were deposited on the QCM/polystyrene surface. The calculation results of the Pani layer deposited thickness are shown in Table 1.

| Deposition time (t) | Frequency of QCM + polystyrene (Hz) | Frequency of Pani (Hz) | $\Delta f$ (Hz) | $\Delta m$ Pani (μg) | $\Delta h$ (μm) |
|---------------------|------------------------------------|------------------------|----------------|-------------------|----------------|
| 10                  | 9989.11                            | 9987.84                | 1.27           | 0.89              | 3.20           |
| 15                  | 9978.86                            | 9975.84                | 3.02           | 2.14              | 9.29           |
| 30                  | 9987.83                            | 9979.67                | 8.16           | 5.78              | 25.00          |
| 60                  | 9987.83                            | 9977.35                | 10.48          | 7.40              | 32.21          |
From the calculation results in the Table 1, it can be seen that with more Pani powder deposited, the thickness of the Pani layer also increases. This is following the opinion of Ohring (2002) which states that one of the factors affecting the thickness of the deposited layer using the evaporation method is the deposited solid mass [15].

3.2. The effect of deposition time on the impedance value of the Pani layer

Impedance analyzer is used to measure the impedance value of QCM, both before coated and after coated with polystyrene and Pani. The results of the impedance measurement with the impedance analyzer can be seen in Table 2. With the increase in deposition time, the impedance value of the Pani layer also increases. The largest Pani layer impedance value was obtained when the deposition time was 60 seconds. The large impedance value can be affected by the density value (ρ) of the deposited material. Polystyrene has a smaller ρ value (1.05 g/cm³) when compared to Pani (1.44 g/cm³) so that the impedance value of the polystyrene layer is smaller and does not have a loading effect on QCM. The effect of loading on the QCM is enormous (above 100 Ω) will reduce the effectiveness and sensitivity of the QCM sensor [16].

| Deposition time (s) | QCM (Ω) | Polystyrene layer (Ω) | Pani layer (Ω) |
|--------------------|---------|-----------------------|----------------|
| 10                 | 11.15   | 0.55                  | 360.41         |
| 15                 | 7.97    | 0.14                  | 441.68         |
| 30                 | 8.12    | 0.14                  | 469.91         |
| 60                 | 7.97    | 0.29                  | 891.57         |

The curve of the relationship between the frequency and the impedance value can be seen in Figure 2. It can be seen that the polystyrene layer does not have a loading effect on QCM because the curve shape has sharp peaks, similar to the initial QCM impedance graph before coating. This indicates that the polystyrene layer can oscillate under the oscillation of QCM and has a minimal effect on QCM. In contrast, the Pani layer curve (in green) has a sloping peak and has a large impedance difference. This indicates that the Pani layer has a large damping effect on QCM.

![Figure 2. QCM Impedance Measurement Curves Before and After Polystyrene and Pani Coated After 60 Seconds](image-url)
3.3. The effect of deposition time on the Pani layer morphology

The results of Pani morphological observations that were deposited on the QCM/Polystyrene surface using an optical microscope can be seen in Figure 3. With increasing deposition time, the more Pani powder was deposited on the QCM surface. This has been confirmed by the larger frequency shift data (Table 1). There are some uncoated parts of QCM (blue area) proving that the spread of Pani powder is not evenly distributed. With the longer deposition time, the Pani powder spread evenly, as seen from the reduced empty area on the QCM surface. Apart from the uneven distribution, there was an agglomeration of Pani powder which was marked in red. This thickened Pani powder can cause QCM to fail to oscillate because it provides a large damping effect. This is in line with the results of the Pani layer impedance measurement (Table 2), where the increasing mass of Pani powder deposited will increase the impedance value.

![Figure 3. Morphological Observations (100x magnification) Pani Layer Deposited on the QCM/polystyrene Surface with Deposition Time: (a) 10 Seconds; (b) 15 Seconds; (c) 30 Seconds and (d) 60 Seconds.](image)

From the data that has been obtained, it can be seen that with the increasing time of evaporation deposition, the Pani layer that is deposited on the QCM/polystyrene surface has a more even morphology. However, there are still some uncoated surface parts. The Pani layer impedance value is also getting bigger, and the thickness calculated by the Saurbrey equation is also getting bigger. However, because the impedance value of the Pani layer is huge (above 100 Ω) even with the fastest deposition time (10 seconds), this evaporation method is not suitable for depositing the Pani layer above QCM. Several factors can cause the results to be less than optimal, including not using the vapour chopping technique. Vapour chopping technique was employed for thin film quality improvement [17]. Research that has succeeded in depositing the Pani layer on a substrate using this technique [18]. However, due to limited equipment in our laboratory, this technique cannot be used.

4. Conclusion

From the research that has been done, it can be concluded that the deposition time using the vacuum evaporation method can affect the morphological quality of the Pani layer deposited. The most uniform coating morphology was obtained when the deposition time was 60 seconds. The highest impedance
value and thickness of the Pani layer were also obtained at the deposition time of 60 seconds, which was 891.57 Ω with a thickness of 32.21 μm.

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