Uneven Coating Influences on Electrical Impedance of Quartz Crystal Microbalance

S P Sakti$^{1,2}$, D D. Kamasi$^{1,2}$, S A Nuha$^1$, M Setiana$^{1,2}$

$^1$ Department of Physics, Brawijaya University, Jl. Veteran Malang, 65145, Indonesia
$^2$ Collaborative Research Centre for Advanced Systems and Material Technology, Brawijaya University, Jl. Veteran Malang, 65145, Indonesia

E-mail: sakti@ub.ac.id

Abstract. High shear modulus coating material does not provide loading effect to the Quartz Crystal Microbalance sensor. The condition is met when the coating material was glassy and the layer was homogeneous. Polystyrene is considered as a glassy coating material when used on 10MHz Quartz Crystal Microbalance. Homogeneous and compact polystyrene coatings that are glassy can be obtained using the spin coating method. The film's rigid condition is shown by the sensor impedance value at the series resonance frequency after coating. However, using ultrasonic spray coatings, it was known that polystyrene films are formed not as homogeneous as when coated using spin coatings. We observed that Quartz Crystal Microbalance was damped by the polystyrene film when the coating film was not evenly distributed over the sensor surface, especially on the sensor surface above the electrode. The minimum impedance of the QCM sensor increased significantly. The unevenness of the coating causes the damping effect on the QCM sensor. The minimum sensor impedance before coating was less than 15 Ohms. When the polystyrene layer was uneven, we found that the impedance increased by more than 25 Ohms. The results showed that the distribution of polymer layers on the sensor surface is one of the important factors that must be considered to avoid the effect of damping on the sensor. The measurement results showed that the sensor has a negative mass effect.

1. Introduction

Coating on the Quartz Crystal Microbalance is one of an importance part for the biosensor and chemical sensor application, especially for the detection of target molecule in liquid medium. The condition of the sensor after coating was aimed to have an electrical property as closed as to the sensor before coating. QCM electrical impedance is the main property of the sensor condition. The impedance of the sensor at series resonance frequency after coating was attempted to be low as the impedance value of the sensor before coating.

Polystyrene is known as a glassy material which can be used as a coating material for QCM sensor [1], [2]. The common method to coat the QCM sensor using polystyrene was by utilizing the spin coating method. The spin coating was known as a good method to achieved a homogenous coating thickness, especially for thin film. The glassy property of the polystyrene was proven by the fact that the impedance minimum of the sensor after polystyrene coating developed using spin coating was not different from its value before coating.

The QCM sensor was known as a mass sensitive device where the resonance frequency decreases with increasing deposited mass perpendicular to the sensor surface. Studies showed that the sensitivity of the QCM sensor depend on position of the deposited mass to the center of the circular electrode [3]
The sensitivity distribution of the QCM sensor was also affected by the electrode geometry [5]. The measurement and the model developed by a single spot mass deposition. In addition it was also known that a punctual load to the sensor resulted a negative mass effect to the sensor [6]. The loading effect to the sensor due to the mass distribution was not reported. This work show that the geometrical structure of the coating material as mass on top of the QCM sensor affected the electrical impedance of the sensor.

2. Material and Method
A 10 MHz quartz crystal resonator was used. The resonator has a diameter of 8.7mm. Impedance measurement was done using the Bode 100 vector Network Analyzer. Surface observation was done using optical microscope Olympus BX51. Polystyrene with a molecular weight of 192KD was purchased from Sigma Aldrich. The polystyrene was solved in toluene. Coating was done using an ultrasonic spray working at 125KHz.

Before coating process, the impedance of the sensor was measured. The coating process was done by praying the polystyrene solution on top of the sensor surface for a few seconds. The distance between the ultrasonic nozzle to the sensor surface was set to 25cm. The coated sensor was place in room temperature for more than one hour to let the toluene evaporated and followed by measuring the electrical impedance of the sensor. Optical observation was done to see any non-uniformity of the coating layer.

3. Result and Discussion
The impedance spectrum of the QCM sensor before and after coating was measured and compared. The impedance spectrum of the sensor before coating showed impedance value at series resonance frequency varied from 8 to 15 . The minimum impedance at series resonance frequency of the sensor with polystyrene coating up to few m by spin coating did not change.

Figure 1 shows an example of a QCM sensor before and after coating with polystyrene. The impedance curved of the sensor with coating shifted to the left because the polystyrene coating is considered as a glassy material. There was no minimum impedance different between the sensor with coating and sensor without coating. The frequency different between the parallel resonance frequency and the series resonance frequency of both sensors were similar.

![Figure 1. Impedance curve of the QCM sensor without coating and with polystyrene coating using spin coating](image)

Ultrasonic spray coating gives a different mechanism of the coating layer formation during the coating process. The layer is formed through the process of accumulation of polystyrene solution granules on top of the sensor surface. The size of the granules was in the order of micrometer to
depending on the ultrasonic frequency [7]. The polystyrene solution granules sprayed from the ultrasonic spray nozzle have a distribution that is determined by the ultrasonic generator frequency. For 125KHz frequency, it is estimated that the grain size of the sprayed solution is around 100 μm. The overlapped granules joined together formed the film.

After the polystyrene falls on the sensor surface, the solvent (toluene) evaporates and leaves the polystyrene. The mechanism of layer formation occurs from the process of accumulation and spread on the surface together with the process of evaporation of solvents. Polystyrene solution granules that touch the sensor surface spread around the point of fall due to gravitational force and impulse from the nozzle. The granules of solution which are close together converge and form a layer of polystyrene solution. At the same time the toluene evaporates. The rest was the well distributed polystyrene layer.

In a non-optimum condition of spray coating process, the polystyrene layer formed in the shape of islands as seen in Figure 2. In addition to being in the form of islands, it can be seen from the microscopic images that the surface of polystyrene is formed unevenly. Unlike the polystyrene layer through the spin coating process which forms a uniform layer nor resulted from a proper setup of the ultrasonic spray coating.

Figure 2. Microscopic image of the polystyrene layer formed an island like and wrinkles surface

Assuming that the polystyrene layer is a glassy material, the frequency change of the sensor after coating should be negative as described by Sauerbrey equation. In addition, the impedance curve should be shifted to the left only as depicted in Figure 1. However, the measurement of the impedance spectrum of QCM after the coating process with the surface formed island like, wrinkles and bumpy did not result as expected. Figure 3 shows the impedance spectrum of the sensor with the coating property as in Figure 2.
The impedance spectrum of the sensor before coating as depicted in Figure 3 shows a similar form condition. Sharp change of the phase occurs coincidently with the minimum impedance and maximum impedance. With the islands like coating layer and wrinkle surface, “negative mass” was observed. Instead of decreased, the series resonance frequency increases after coating. As the polystyrene is a glassy material, the negative mass effect caused by the mass distribution and geometrical shape of the coating surface. The impedance spectrum of the sensor was also affected. It can be seen that the minimum impedance at series resonance raised. In addition, the different between the parallel resonance frequency and the series resonance frequency of the sensor became smaller.

More dramatic case was observed in Figure 3d. The sensor was damped by the polystyrene coating. The minimum impedance at series resonance frequency increased significantly close to 1K Ω. Observing the coating distribution in Figure 2d, one can see that there is additional unevenly coating in the center of the island like film. More polystyrene was deposited in the center of the island like film. The magnitude of the sensor impedance at series resonance frequency raised 10 to 100 times from its original value.

4. Conclusion
This work shows that the electrical impedance of the QCM sensor with polystyrene coating was affected by the distribution of the coating and the geometrical property of the coating. Unevenly distribution of the polystyrene coating layer resulted in a negative mass effect to the sensor. The electrical impedance of the sensor at series resonance frequency increased, whilst the impedance at
parallel resonance decreased. In a worst condition of unevenly coating layer, the electrical impedance curve of the sensor changes significantly, where the minimum impedance value at series resonance can raised up to 100 times.

References
This work was funded by the Ministry of Research, Technology and Higher Education of the Republic of Indonesia under the research grant PDUPT scheme.

References
[1] S. P. Sakti, N. Chabibah, S. P. Ayu, M. C. Padaga, and A. Aulanni’am, “Development of QCM Biosensor with Specific Cow Milk Protein Antibody for Candidate Milk Adulteration Detection,” J. Sensors, vol. 2016, pp. 1–7, 2016.
[2] S. P. Sakti, F. Wahyuni, U. P. Juswono, and Aulanni’am, “Development of QCM immunosensor with small sample solution for detection of MMP-3 antibody,” Sensors and Transducers, vol. 149, no. 2, 2013.
[3] V. M. Mecea, “Loaded vibrating quartz sensors,” Sensors Actuators A Phys., vol. 40, no. 1, pp. 1–27, Jan. 1994.
[4] F. N. Dultsev and E. A. Kolosovsky, “Identifying a single biological nano-sized particle using a quartz crystal microbalance. A mathematical model,” Sensors Actuators, B Chem., vol. 143, no. 1, pp. 17–24, 2009.
[5] X. Huang, Q. Bai, W. Pan, and J. Hu, “Quartz Crystal Microbalance with Approximately Uniform Sensitivity Distribution,” Anal. Chem., vol. 90, no. 11, pp. 6367–6370, 2018.
[6] P. Castro, P. Resa, and L. Elvira, “Apparent negative mass in QCM sensors due to punctual rigid loading,” IOP Conf. Ser. Mater. Sci. Eng., vol. 42, no. 1, 2012.
[7] K. A. Ramisetty, A. B. Pandit, and P. R. Gogate, “Investigations into ultrasound induced atomization,” Ultrason. Sonochem., vol. 20, no. 1, pp. 254–264, 2013.