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Polystyrene Micro-pools Distribution on Quartz Crystal Microbalance (QCM) Surface using Ultrasonic Atomization Spray Coating

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Abstract. Surface morphology of polystyrene thin film is one of the significant factors to be take into account in the development of quartz crystal microbalance (QCM) as biosensor and chemical sensor. Many coating methods were developed to modify the morphology of polystyrene thin film surface. Our previous study showed that ultrasonic atomization spray coating (UASC) is a promised coating method to produce a rough polystyrene thin film on QCM sensor with patterns called micro-pools. There are many parameters that can affect the uniformity of micro-pools produced by UASC. In this work, 0.5% polystyrene solution which was solved in toluene was used as material coated onto a QCM sensor using UASC method. The effect of the distance variation between the spray nozzle and specimen towards the surface morphology of polystyrene thin film was observed. The surface morphology of the coated polystyrene and the micro-pools distribution were characterized by an optical microscope and Scanning Electron Microscope (SEM). The electrical impedance of the QCM was measured and characterized using Impedance Analyzer. The result showed that the optimum distance of the spray nozzle and specimen is between the range of 15 until 24 cm. At this optimum distance, the uniform micro-pools distribution was formed on the QCM surface without influencing the QCM acoustic impedance.

1. Introduction

Quartz Crystal Microbalance (QCM) is widely utilized as a biosensor and chemical sensor over the past decade. The QCM sensor has high sensitivity. It can detect changes in mass with sub-nanogram sensitivity which is nearly 1000 times greater than an electronic mass balance with 0.1 μg sensitivity [1]. As a biosensor and chemical sensor, QCM can be used to detect the existence of substances concentration as well as biochemical reaction among molecules by direct as well as indirect method [2].

Generally, the surface morphology of QCM used as biosensor and chemical sensor is made as smooth as possible to avoid damping effect [3]. However, it affects sensor immobilization ability. In smooth surface, the biosensitive layer mostly forms a monolayer of a biomolecule, so the target molecule is only limited to the vertical direction attachment to the sensitive layer as one-by-one pair per surface area. In our previous study, the rougher surface increased the surface area of the sensitive layer, so that increasing the surface roughness of the sensor resulted in increasing number of the immobilized biomolecule on the sensor surface [4]. Moreover, the surface roughness should be controlled because rougher surface yields more trapped water that can shift down resonance frequency and increase the electrical impedance value of the QCM.

Surface modification methods to enhance the selectivity and sensitivity of the QCM sensor were widely developed. One of these modification methods is surface roughness and structure of the coated material on top of the QCM electrode. Ultrasonic Atomizer Spray Coating (UASC) is one method which was developed nowadays. Using UASC method has been used to coate a thin film in the order of nanometer. The surface roughness of a deposited film was higher than the surface roughness produced using spin coating [5]. Using the UASC coating, the produced polystyrene film formed many different morphology which can be controlled by the coating parameters [6]. According to our last study, polystyrene deposition onto QCM surface using UASC method produceed thinner, rougher and more porous polystyrene thin film surface with micro-pools without affecting the QCM acoustic impedance. Comparing to the spin coating method, the UAS has the advantages for the ability to produce a structured surface, such as micro-pools.

UASC has some parameters that affect the result of polystyrene micro-pools such as the concentration of polystyrene solution and the solvent used, the flow rate of the polystyrene solution, the number of spray passes, and the nozzle-to-specimen-distance. The large numbers of parameters indicated the need for systematic process optimization [7]. Nozzle-To-Specimen-Distance was one of the main factor affecting film uniformity [8]. It also had a great impact on the morphology of deposited layer [9]. Furthermore, from our last study, we found that there was another factor which could also affect the polystyrene micro-pools formed on the QCM surface, that was, spraying time of polystyrene solution. Thus, in order to get the best result of polystyrene micro-pools formed on QCM surface, in this experiment, we have been developed UASC system with spray controller to define the optimum distance between nozzle and specimen used in UASC method.

2. Material and Methods

2.1. Materials
The QCM sensor with silver electrodes used as the specimen in this experiment was an AT-cut 10 MHz of HC 49/U (PT Great Microtama, Surabaya, Indonesia). The 192 kDa polystyrene as solved in toluene with a concentration of 0.5%. Polystyrene and toluene was purchased form Sigma Aldrich.

2.2. Polystyrene Film Fabrication
In order to observe the polystyrene micro-pools, this experiment focused on polystyrene deposition using UASC method on the upper side of the QCM sensor surface. One side of the QCM sensor was coated with polystyrene.

2.2.1. Ultrasonic Atomization Spray Coating
The upper side of QCM was coated with 0.5% of polystyrene solution. The coating of polystyrene was done by using UASC method. The schematic system of UASC is illustrated in Figure 1. Our UASC system was completed with a self-developed spray controller which could control the spraying time and time between sprays. In this study, spraying time was constant. The frequency change of the coated sensor was measured in realtime [10].

In this experiment, the nozzle-to-specimen-distance (15, 18, 21, and 24 cm) varied, with the number of spray passes was set at 8 times, 50 ms of spraying time and 800 ms interval between sprays. The solution flow rate was set up at 2 rpm and at minimum power of ultrasonic generator. All the deposition process was done at room temperature and at atmospheric condition.

2.3. Characterization
Some characterization techniques were used to observe the surface properties of the polystyrene micro-pools formed by ultrasonic atomization spray coating and QCM electrical properties. An optical microscope (Olympus BX 51) was employed to examine the coverage of micro-pools distribution and

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2D structure of polystyrene coating on the QCM surface. The morphology of polystyrene micro-pools formed was observed in high resolution by using a Scanning Electron Microscope (FEI-SEM Quanta 650 FEG). The QCM electrical impedance before and after coating process was measured by using a Bode 100 impedance analyzer commercially produced by Omicron-Lab.

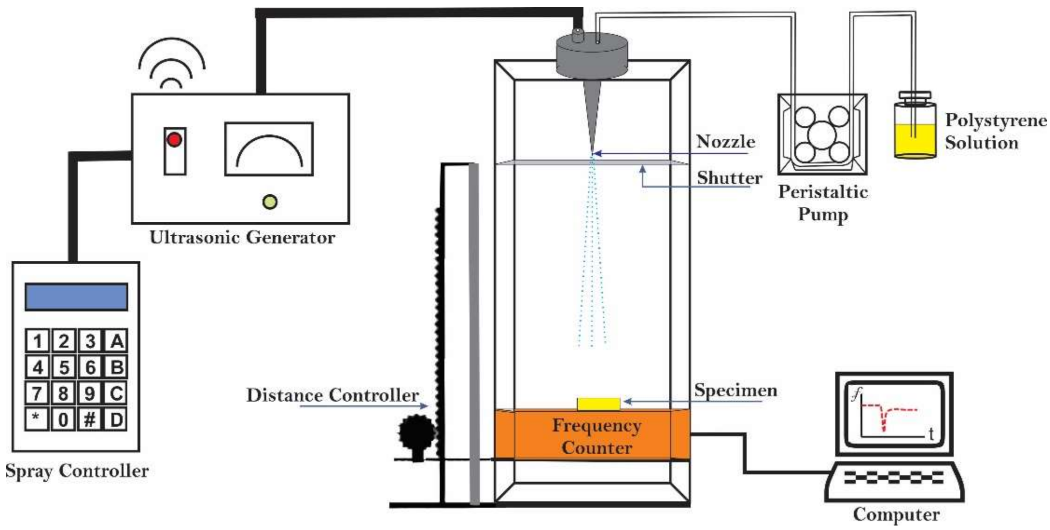


Figure 1. Ultrasonic atomization spray coating schematic system

3. Result and Discussion

The optical microscope images of the polystyrene film growth on the QCM surface with various nozzle-to-specimen-distance (NSD) are shown in Figure 2. From the optical microscope images, the yellowish color indicates the QCM electrode part, while the greyish or lighter color indicates the QCM quartz. By using the new self-developed UASC system with a spray controller, we obtained a different result of polystyrene film formed in each NSD variation.

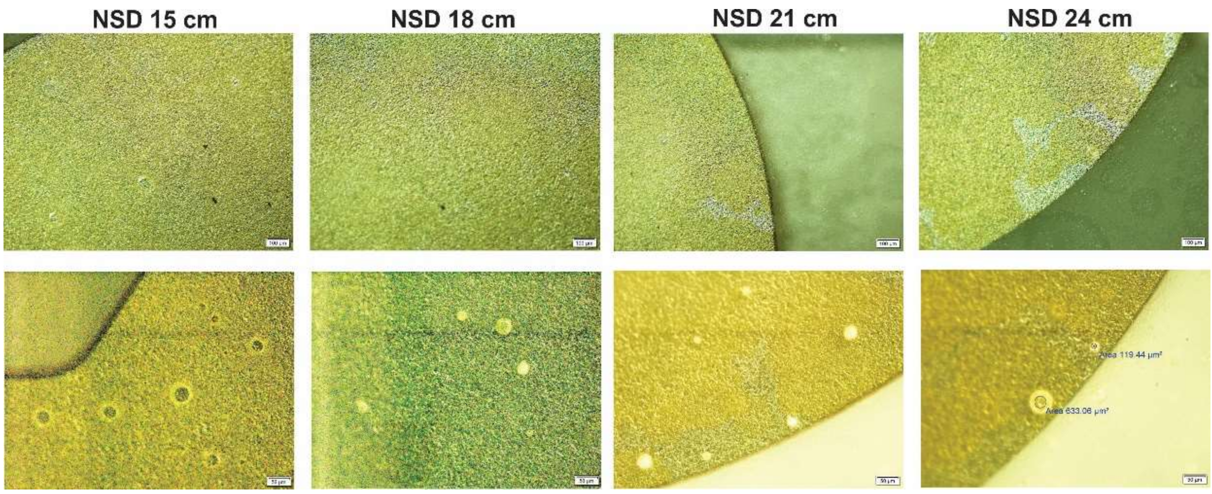
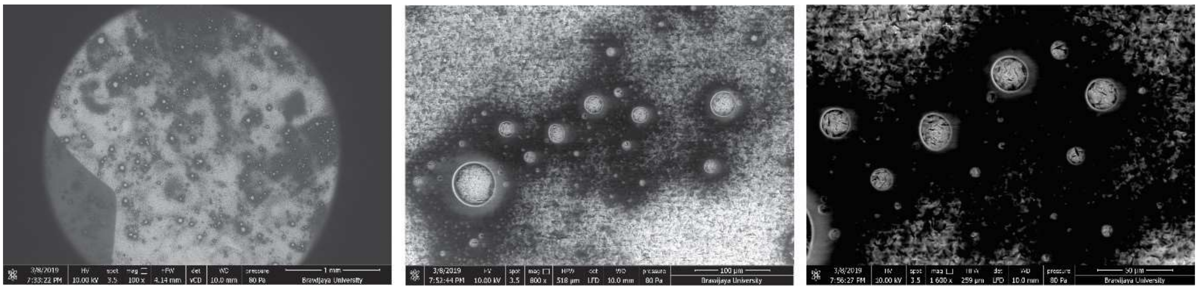


Figure 2. Optical microscope image of polystyrene film on QCM surface

In the NSD 15 cm, the polystyrene thin film was spread off homogeneously on the QCM electrode and there are micro-pools on it. Conversely, in the other NSDs, further distance produced inhomogeneous polystyrene film and some polystyrene lumps on it. It occurred because further distance increases the amount of evaporation of the polystyrene solution, so the polystyrene film formed on QCM was not evenly deposited. Furthermore, during spraying process, further distance produced dryer polystyrene droplets dropped on QCM. Then, as a result of this, when a droplet overwritten by other droplets, it did not produce polystyrene micro-pools, but polystyrene lumps on it as seen on NSD 21 cm and NSD 24 cm.

SEM images of polystyrene micro-pools formed on QCM surface are shown in Figure 3. In the NSD 15 cm with 100x magnitude, the image shows that many formed polystyrene micro-pools covered almost all the electrode region. In the 800x and 1600x magnitude, it can be seen that the micro-pools were still in diverse sizes, but were not significant. The average size of the polystyrene micro-pools formed was about 22.76 µm. The EDS image of the micro-pools is presented in Figure 4. The figure shows that in the center of each micro-pools there was a hole resembling a pool with shallow depth that able to trap water.



(a) (b) (c)

Figure 3. SEM image of polystyrene micro-pools formed on QCM sensor in NSD 15 cm (a) 100x magnitude (b) 800x magnitude (c) 1600x magnitude

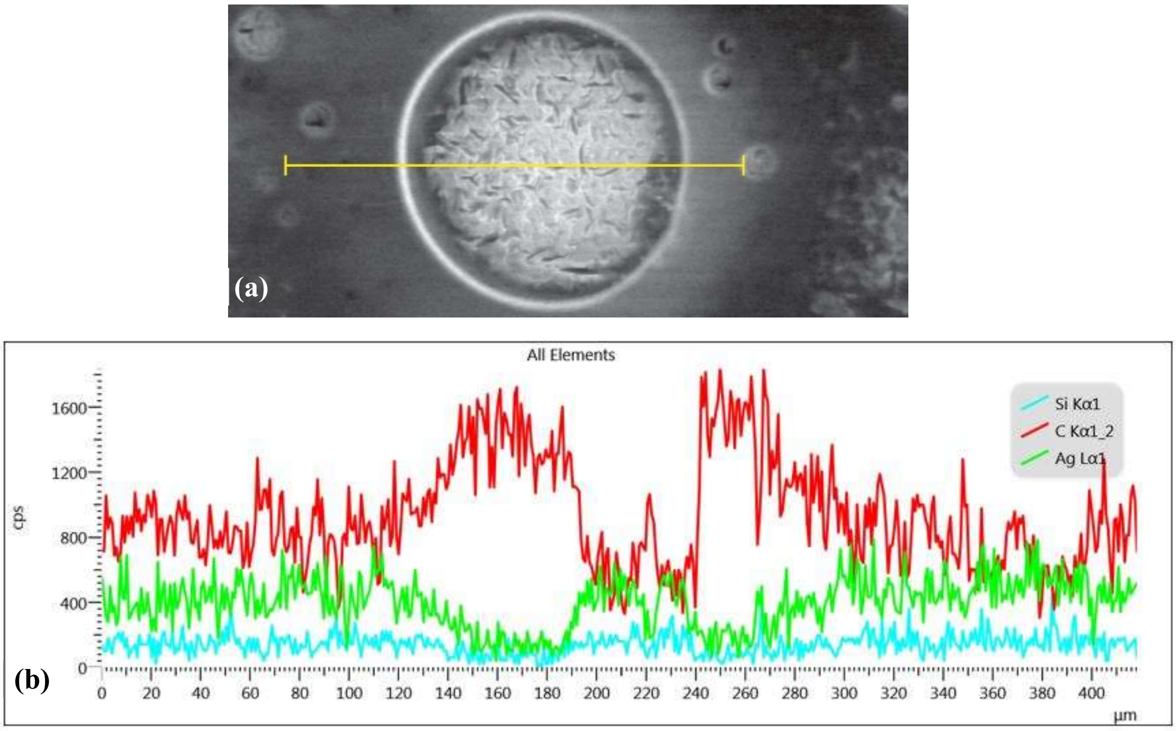


Figure 4. (a) SEM image of a micro-pool formed on QCM surface **(b)** The EDS profile of a micro-pool sampel in Figure 4a

The effect of the coating to the electrical characteristic of the QCM sensor was analysed based on the minimum impedance of the sensor with coating. Low minimum impedance indicates a negligible damping effect to the sensor, which means that the film can be assumed behaving like a smooth glassy layer [11] . The minimum electrical impedance of QCM sensor after polystyrene deposition is represent in Figure 5. From the graphic below, the result of a repeating process for each varied NSD gained various impedance value. From 3 times repeating processes for each varied NSD, NSD 15 cm showed the best minimum impedance standard deviation values compared to the others. The NSD 15 cm showed a more consistent minimum impedance value. It means that the produced polystyrene layer was more consistent and distributed evently on the sensor surface. High variation of the minimum impedance at NSD greater than 15cm could be related to the unevent distribution of the polystyrene layer on top of the sensor. High minimum impedance indicated that the polystyrene surface was not considered smooth. Some thickness variation incresed the damping to the sensor which reflected by high minimum imnpedance. It was confirmed with the existenced of the lumps of the polystyrene (Figure 2). It could be caused by several reasons such as the vapor pressure of the solvent and unpredictable atomized volume that leads to unevenly polystyrene thin film and the growth of polystyrene lumps.

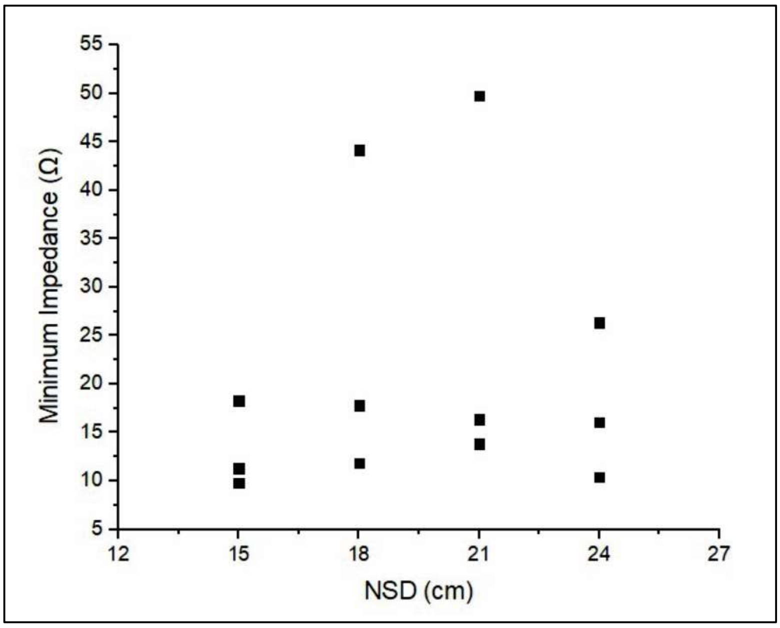


Figure 5. Minimum Impedance of QCM

4. Conclusion

The ultrasonic atomization spray of PS coating surface onto QCM with the variation of nozzle-to-specimen-distance was evaluated by using various characterization tools. The polystyrene film was affected by the nozzle to target distance. At a distance of 15 cm, a cluster of micro-pools polystyrene film was formed without heavily affecting the QCM minimum impedance. At longer distance some lumps polystyrene film was observed and the thickness of the film was varied. The lumps and polystyrene thickness variation affect the minimum impedance of the QCM sensor. It is required that the optimum spraying time and number of spray passes should be investigated further in the next experiment to achieved a better distribution of micro-pools and other surface strcuture of the polystyrene film.

Acknowledge
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