Oxygen Plasma Effect on QCM Sensor Coated Polystyrene Film

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Abstract. Hydrophobicity property of polystyrene (PS) thin film is one of the essential factors to be considered in the development of quartz crystal microbalance (QCM) biosensor using polystyrene as matrix layer. Many methods were developed to improve the immobilization rate of the biomolecule on the sensor surface without affecting the QCM essential works. Surface modification of the sensor surface aims to modify the physical and or chemical property of the surface. A straightforward method, the fast, environmentally-friendly, and low-cost solution to modify the sensor surface coated with polystyrene film is using oxygen plasma. In this experiment, the polystyrene film was spin-coated on both surface of QCM electrodes and then heated at 100 °C. The specimen is then placed for 5 min long in a chamber filled with oxygen plasma generated by 2 MHz RF-DC high-density plasma system. The relationship between DC-bias used and the changes in morphology properties of the coated film was characterized by Topography Measurement System (TMS) and Contact Angle Measurement. The electrical characteristic of QCM was also characterized using Impedance Analyzer. It was revealed that the contact angle of oxygen plasma treated film is changed and depicted the hydrophobic character. Also, there is an increasing resonance frequency of the sensor after oxygen plasma treatment indicates an etching mechanism occurs during plasma treatment.

Keywords. Oxygen plasma effect, polystyrene film, QCM sensor

1. Introduction
A quartz crystal microbalance (QCM) is a piezoelectric mass-sensing device which has been used widely for physical sensors, chemical sensors, and biosensors. The typical applications of the QCM sensor are based on the gravimetric methods as described by the Sauerbrey equation. The frequency shift of the sensor is proportional to the amount of mass deposited on the sensor surface. The main advantageous of QCM that support its rapid development in various disciplines, i.e., low-cost, modifiable substrate, label-free, real-time measurement, and quick response.

In the chemical and biosensor application, the QCM sensor surface is covered with a layer which is selective to the target molecule being detected. The selective layer can be coated directly on the sensor surface, i.e., on top of the sensor electrode or a matrix layer. The behavior of the selective layer and also any matrix layer must satisfy the requirements to works in gravimetric modes.

The polymer film can be used as a matrix layer or as a sensitive layer. Its function depends on the polymer surface property as well as the nature of the target molecule. Polystyrene can be used as a
matrix layer in the biosensor application. On top of the polystyrene layer, a particular biomolecule was immobilized. Furthermore, the polystyrene was interested to be studied as coating layer because it acted as the protective film for the sensor electrode. However, in some conditions, the surface behavior of the polystyrene need to be modified to a specific condition which satisfies to the application. To be used as a coating film of QCM sensor in the application for chemical sensor or biosensor, the surface property such as hydrophilic/hydrophobicity, roughness, and chemical composition of the polymer is one of the crucial factors to be considered. For example, to increase the sensitivity of QCM sensor to hydrocarbons pollutant, hydrophobic polymer coatings are often chosen [1].

One important aspect to be considered during polymer film surface modification is the rigidity of the film. The shear moduli of the film must be high enough to keep the coating layer in a glassy condition to avoid damping to the sensor. The excellent bulk physical and chemical properties, inexpensive, and easy to process are a few factors that made polystyrene successfully applied in many QCM sensor developments. Surface modification is needed to alter the polystyrene chemical and physical properties without affecting the bulk properties.

Among many methods, low-pressure plasma processing is widely used to modify polymer material due to their ability to alter the outermost substrate without affecting its bulk properties [2, 3]. This treatment has been employed to achieve some purposes such as to produce specific functional group, increase surface energy, increase hydrophobicity/hydrophilic, modify surface morphology, and much more. Oxygen plasma treatment, for example, can increase the surface energy of polymers which can alter the hydrophobicity of the surface. For the biosensor application, plasma treatment has been used to improve the binding efficiency of the biomolecule on the sensor surface [4].

A variety of oxygen functional groups such as C-O, C=O, O-C=O, and C-O-O will be produced at the polymer surface when oxygen plasma or oxygen-containing plasma is employed for polymer modification. Functionalization [4] and etching [5] process may occur during the oxygen plasma treatment of polymers. The process depends on plasma parameter. Etching of the polymer is occurred through the reaction of atomic oxygen with the carbon atoms at the surface of a film, giving the volatile product such CO. Surface functionalization such as a functional group of oxygen is formed through the reaction between the active species from plasma and the surface atoms.

Polystyrene has been used as a coating material in QCM sensor development for biosensor application. This film used with or without any surface modification. Polystyrene acts as a matrix layer during immobilization of some biomolecule. Biomolecule immobilization on top of polystyrene surface works through physical adsorption. Physical adsorption consists of hydrophobic interactions or hydrophobic/ionic interactions between the biomolecule and the polystyrene surface. However, the degree of the hydrophobicity needs to be optimized for the immobilization. Therefore it is essential to explore a method to modify the hydrophobicity of the polystyrene surface. In this experiment, polystyrene thin film is adjusted by oxygen plasma to alter the hydrophobicity and surface roughness of polystyrene as a coating layer of the QCM sensor. For the biosensors application, the change of the surface hydrophobicity and roughness alters the biomolecule immobilization. Therefore understanding the DC bias effect of oxygen plasma generated by 2 MHz RF-DC high-density plasma system to hydrophobicity and surface roughness of the polystyrene coated QCM is an attractive method as it can be done with better controllability.

2. Materials and methods
The polystyrene film was prepared by solving a polystyrene grain with a molecular weight of 192 kDa in Toluene solution at 3 w/w%. The solution then was ultra-sonicated for about 10 min to accelerate the dissolution process. A 50 µL of the polystyrene solution was coated onto 10 MHz AT-cut silver electrode QCM sensor using spin coating method at 3000 rpm. The coating was applied to both sides of the sensor. The polystyrene-coated sensor was heated at 100 °C for an hour in an oven at the atmospheric condition to vaporize the solvent.
The experiment was carried out by exposing one side of polystyrene coated QCM sensor in 2 MHz RF-DC high-density plasma chamber generator as shown in Figure 1 for 5 min. This system is a capacitively coupled discharge which upper electrode (anode rod) was connected to RF generator power supply, and the lower plate electrode (cathode plate) was connected to DC generator power supply. The oxygen plasma is generated with RF voltage of 60 Volt and current 0.5 A while the DC bias voltage was varied from –100 V to –500 V. The oxygen inlet flows into the chamber was controlled at 50 sccm at 60 Pa. The negative DC bias at the lower electrode where the sample was put is aimed to accelerate the generated ion by the upper electrode to bombard the polystyrene film surface.

Figure 1. 2 MHz RF-DC High-Density Plasma System Schematic.

The water surface contact angle, surface roughness, and resonance frequency of the sensor before and after plasma treatment were measured. The measurement of the water surface contact angle was carried out by using self-developed goniometer based contact angle measurement system [6]. Surface roughness was measured using non-destructive surface profilometer TMS-1200 TopMap µLab from Polytec. The plasma spectrum also measured without and during sample treatment using fiber optic spectrometer Aurora 4000 from CNI Laser with a wavelength scanning range from 200 nm to 1000 nm with an optical resolution of 0.75 nm.

3. Results and discussion
Oxygen plasma is mostly used in polymer modification by functionalizing it surface with polar oxygen group and slow etching. The typical species formed in oxygen plasma glow discharge generated by 2 MHz RF-DC plasma system is shown in Figure 2. Two atomic lines are detected, i.e., 775 nm and 842 nm which corresponding to OI [7,8]. During plasma treatment of polystyrene, there are no peaks changes identified from plasma spectrum except decrease of intensity.

The plasma spectrum which remains before and during the plasma treatment indicated that there were no new species existed during the polystyrene plasma treatment. These indicated there was no atom nor molecule released from the polystyrene surface to the chamber.

The effect of the plasma treatment to the polystyrene surface property was analyzed by measuring the contact angle of the surface before and after plasma treatment. Figure 3 shows the water contact angle measurement of polystyrene film before and after oxygen plasma treatment. This graph shows after plasma exposure the sample hydrophobicity increased slightly compared to native polystyrene film (from around 85° to 95°). The trend of the graph shows the surface became more hydrophobic by an increase of negative DC Bias starting from –200 V to –500 V. However, different case happened for low DC bias, i.e., –100 V. The contact angle measurement showed the polystyrene coating became
hydrophilic. It is probably due to low ion flux and energy bombardment to the polystyrene surface. Because of it, the oxygen ions/atoms and the outermost atoms are chemically reacted or diffuse. While the changes of a more hydrophobic surface are probably due to functionalization or etching mechanism that works dominantly so the surface profile of the polystyrene coating changes during the ion bombardment.

**Figure 2.** Typical Plasma Oxygen Spectrum

Further analysis was performed by measuring the surface roughness of the coating layer before and after plasma treatment. Figure 4 shows the surface roughness of the polystyrene coating before and after plasma treatment. This graph showed that the increase of surface roughness only happens from DC bias by $-200 \, \text{V}$ to $-500 \, \text{V}$ but slightly decrease for $-100 \, \text{V}$. This results correlated with the surface hydrophobicity as shown in Figure 3. The increase of surface roughness is as if confirm that the formation of surface structure occurred during the process. These possibly occur through functionalization and etching mechanism. The etching mechanism occurred as the ion has adequate energy caused by the DC bias voltage which accelerates the ion. Higher DC bias voltage results in the higher kinetic energy of the ion in the plasma chamber.

**Figure 3.** Water contact angle surface of the polystyrene coating before and after plasma treatment.  
**Figure 4.** Polystyrene surface roughness before and after plasma treatment.
The impedance measurements were performed before and after plasma treatment to investigate the effects of the plasma treatment on the QCM sensor coated with polystyrene. Figure 5 and Figure 6 shows the minimum impedance and series resonant frequency trends of the sensor before and after plasma treatment. Almost all the sample, except with parameter –300 V, shows an increase of frequency which could be associated with deposited mass reduction. As described by Sauerbrey equation for the gravimetric condition, the resonance frequency of the sensor decreases when the deposited mass on the sensor is increased and vice versa [9]. The condition is also valid as long as the deposited mass, in the case of the experiment was polystyrene coating, behaves as a rigid material [10].

Figure 5. Series resonant frequencies of the QCM coated polystyrene before and after plasma treatment.

Figure 6. QCM sensor minimum impedance before and after plasma treatment.

Figure 7. Optical Photograph of QCM coated polystyrene electrode area a) before O₂ plasma treatment and b), c), d), e), f) after O₂ plasma treatment with -100 V, -200 V, -300 V, -400 V, -500 V of DC bias respectively.
The mechanical bulk property of polystyrene layer after ion bombardment in the plasma chamber remained. It was supported by the data as depicted in Figure 6 which showed that the minimum impedance of the sensor after plasma treatment remained low. The low impedance of the sensor indicated that the coating layer remains rigid. It means that ion bombardment of the oxygen plasma did not change the shear modulus of the coating layer.

Qualitatively the changes to polystyrene coating surface could be observed by using an optical microscope. Some black dots are formed on the surface of QCM especially on the electrode area as shown in Figure 7. The increase of the DC Bias proportionally increases the number of black dots itself. This black dots as if indicates the ion bombardment strongly occurs when higher DC Bias is used. The number of black dots also seems to affect the changes to surface hydrophobicity.

4. Conclusions
This experiment revealed that processing Polystyrene coating surface in RF-DC oxygen plasma by varying the DC Bias leads to the changes of its hydrophobicity. The water contact angle dependence on DC bias is highly related to surface chemical composition and the surface morphology. Thus, functionalization and etching mechanisms are suggested taking place during the treatment. Increases of the sensor resonance frequency indicated etching mechanism after plasma treatment which is related to decreasing of deposited mass on the sensor surface. Higher energy of oxygen ion bombardment to the polystyrene surface leads caused by DC bias increased the surface roughness.

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