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Morphology and Wettability of Polystyrene film on QCM Sensor Caused by Oxygen Plasma with DC Bias

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Abstract

Surface wettability and morphology are important aspects of developing QCM sensors for chemical sensors and biosensors. The functionality and morphology of the sensitive coating on the sensor surface affect the sensor sensitivity and selectivity. Various materials and methods to improve the functionality and morphology of the sensor surface have been developed, one of which is plasma. Species and parameters of the generated plasma play an important role in the treatment. One parameter is the DC-bias voltage of RF plasma, which plays an important role in plasma generation and bombardment on the surface being modified. This work shows the effect of the DC bias of the 2 MHz RF plasma with oxygen species. Surface functionality and morphology modification of the polystyrene film on the QCM sensor was done by surface modification using oxygen plasma. Partial etching of the polystyrene film occurred when treated with oxygen plasma generated using 2 MHz with negative DC-bias. C^{II}, CO+, and CO were detected during the exposure of oxygen plasma on polystyrene film, indicating a chemical reaction between the plasma species, oxygen plasma, and the polystyrene. Observation by optical microscope and SEM showed the occurrence of partial etching on the polystyrene film. As there is no masking, the partial etching occurred randomly. The average size of the etched film increased with the DC bias voltage, but the percentage of the etched area was not. The oxygen plasma converts the polystyrene film from hydrophobic to hydrophilic, but hydrophobicity increases with the DC bias voltage.

Keywords: Oxygen plasma, Negative DC bias, Etching, Polystyrene, Hydrophobicity, ImageJ

Introduction

A sensor surface's chemical and physical properties are crucial in developing a chemical sensor or biosensor. Materials and methods were developed to achieve a degree of selectivity and sensitivity. For the quartz crystal microbalance (QCM) sensor, the role of chemical and or physical surface properties was important. Metal [1], polymer [2-4], biological materials [5], and nanomaterial [6,7] were used as a sensitive layer or supporting matrix for the sensitive layer.

A polymer is used because of its availability as a coating material and the possibility of further modification. Polystyrene has been modified its surface to achieve the intended property by UV radiation [8,9], and plasma treatment [10-12].

Surface modification using plasma treatment has been used widely. Low-pressure plasma is employed to modify the surface polymer coating as it only affects the surface property without changing its bulk characteristic [13,14]. The plasma treatment on the polymer surface produces a functional group, changes the surface wettability, and modifies the polymer surface morphology and other phenomena. Plasma treatment was reported to improve the binding efficiency of the surface of a biosensor to the immobilized biomolecule [15]. Oxygen plasma treatment on the polydimethylsiloxane film affect the surface hydrophobicity and doesn't affect the modulus young of the film [16].

Oxygen plasma on a film leads to surface functionalization or surface etching [13]. The dominant mechanism depends on the material and the plasma parameter. A synthetic polymer such as polystyrene riches in the carbon atom; therefore, oxygen plasma treatment on a polystyrene film will dominantly produce carbon-oxygen functional groups such as C-O, C=O, O-C=O, and C-O-O.

Polystyrene etching using plasma was extensively used [17]. Change in the surface wettability after plasma treatment was reported, showing the reaction of the plasma with the polystyrene surface [10,18-20]. Oxygen plasma treatment on the polystyrene surface increases the surface energy and changes the polymer surface wettability [20,21].

Gas composition, which forms the ion species, pressure, temperature, generation method, generator power, and DC-bias are the parameters that affect the polymer surface modification process using plasma. The ion species responsible for the chemical reaction during the etching process should be selected according to the etched material. Reactive gases such as fluoride, oxygen, hydrogen, and methane are used [19,22-24].

Duration of the plasma treatment affect the surface property of the polystyrene [25] and its resistance to the solvent, however the effect of the DC bias not yet explored. In the RF plasma, the DC bias in the plasma treatment is one important aspect of controlling the modification rate. DC bias affects plasma density and chamber pressure [22,26]. The reactive gas percentage and the chamber pressure also affect the surface modification rate. Therefore, the DC bias is expected to affect the surface modification process, such as the etching area. By slightly etching the polymer film of the QCM sensor without removing the whole film, for example, one can get a polymer layer with additional surface area caused by the partial etching of the film.

Polymer plasma etching formed various nanostructure forms observed using SEM and AFM [27]. Analysis of the formed structure was done qualitatively. This work used an optical microscope and image analysis to measure the polystyrene etched area caused by RF plasma and DC bias. This paper shows that the DC bias affects the polystyrene surface modification using oxygen plasma.

Materials and methods

The polystyrene film was made by solving polystyrene with a molecular weight of 35 kDa in Toluene solution at a concentration of 9 % w/w. Sonication was applied to the solution for 10 min. A 50 μL polystyrene solution was dropped on top of a QCM sensor in the spin coating apparatus. The rotation speed of the spin coater during the coating was 1800 rps. Both sides of the sensor surface were coated with the same procedure. The film's drying process was done by letting the coated sensor overnight and heating at 200 °C for 1 h. The polystyrene (CAS number 9003-53-6) and Toluene (ACS Reagent, CAS number 108-88-3) were purchased from Sigma-Aldrich, and the QCM sensor was bought from PT Great Microtama, Surabaya, Indonesia.

Plasma treatment was done by exposing the QCM sensor coated with polystyrene film in an RF plasma chamber. A 2MHz RF-DC plasma system was used. The plasma system is a capacitively coupled plasma with 2 upper rod electrodes on top of the base plate. The base plate was connected to the negative

DC bias to the ground, as depicted in **Figure 1**. The QCM sensor was placed on top of the base plate under the RF plasma generator electrode facing the RF generator electrodes.

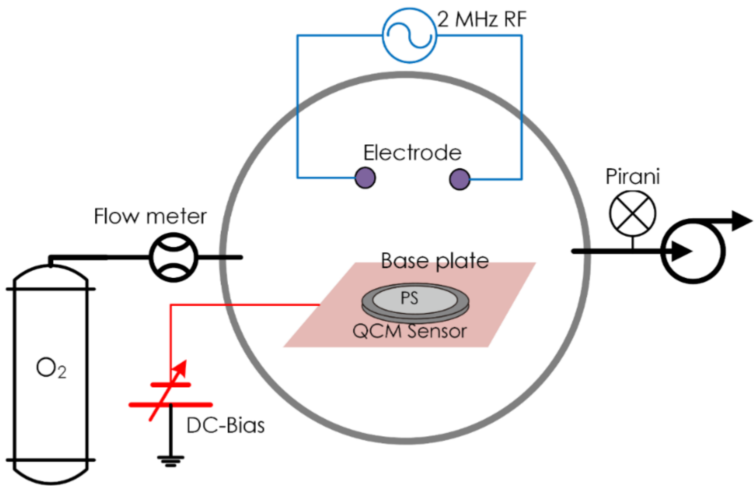

Figure 1 Schematic diagram of the 2 MHz RF-DC and the sensor placement.

After being pumped into a vacuum condition at 2×10^{-3} Pa, the chamber was filled with oxygen gas. Oxygen gas has surged into the chamber with a flow rate of 70 sccm. The chamber pressure with the oxygen gas was maintained at 15 Pa. The 2 MHz RF power with a voltage of 150 V was applied to the electrode for 5 s to generate oxygen plasma. At the same time, the DC-bias voltage was applied.

Plasma species generated between the RF electrode showed a glowing discharge according to plasma materials. The color formed by oxygen plasma is a purple glow. The resulting plasma ion was observed using optical emission spectroscopy (OES) measurement. The plasma spectrum was captured using an Aurora-4000GE200-1100nm spectrometer, which can detect the wavelength from 200 to 1100 nm with a resolution of 0.75 nm.

The surface film was observed using SEM QUANTA 650-FEG and an optical microscope Olympus BX 51. For the BX 51 image, based on the digital image's scale bar, each pixel represents an actual size of 1.75 μm. The sensor's image with polystyrene film was captured before and after plasma treatment. The etched area of the polystyrene surface caused by the plasma treatment was analyzed based on the image captured using an optical microscope. Image analysis to identify the etched area was done using ImageJ.

Results and discussion

Optical emission spectroscopy analysis

The optical emission spectrum of the generated plasma in the chamber was measured for the oxygen plasma only and the generated plasma with the QCM sensor placed in the chamber. The spectrum pattern of the oxygen plasma and the resulting species when the plasma reacts with the polystyrene was identified by checking the spectrum to the NIS database and other works.

The OES measurement of the generated oxygen plasma spectrum is depicted in **Figure 2**. The measured oxygen plasma using the spectrometer shows a peak at 558.3, 654.7, 775.8 and 843.1 nm. The strongest peak occurs at 775.8 nm, and the second-highest peak at 842.8 nm corresponds to O^{I}'s oxygen species [28,29]. According to Fukunaga *et al*. [30], the generated plasma species of oxygen plasma are dominated by a spectral line at 776.9 and 843.9 nm. It showed that the intensity of the species increased with the RF power with a frequency of 13.56 MHz.

The 558.5 and 655 nm peaks show the oxygen ion-molecule (O^{II}) [28]. The oxygen species' different peaks indicate that the reactive oxygen molecule ion O^{I} dominates the oxygen plasma. It is expected that the abundance of the reactive oxygen molecule ion will take effect when the sensor with polystyrene coating is placed in the chamber.

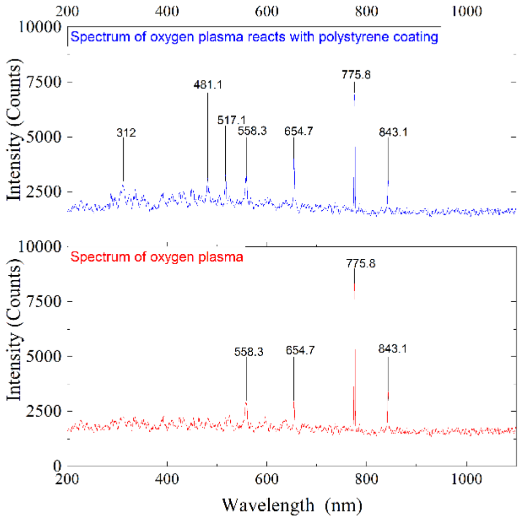

Figure 2 OES spectrum of plasma before and after the QCM sensor with polystyrene coating was placed inside the chamber.

The QCM sensor with polystyrene film changed the plasma species. Additional peaks were observed in the spectrum. There were new peaks at 312, 481.1 and 517.1 nm. Simultaneously, the peak intensity of the O^{II} at 775.8nm species decreased, while the intensity of O^{I} at 654.7nm increased. The new peak at 312 nm relates to the C^{II} line, 481.1 nm relates to CO^{+} [31], and 517.1 nm relates to the CO [32,33]. As there were no trace carbon species before the QCM sensor was placed inside the chamber, it is evident that the origin of the carbon ion species occurred because of the reaction between the oxygen ion and the polystyrene. The reaction's existence was supported by the decreasing intensity of the O^{2+}, which means there was a probability that the O^{2+} reaction with the polystyrene's carbon forms a carbon-oxygen ion species. The CO formation on the polystyrene surface after oxygen RF plasma with 13.6 MHz was reported [30].

As the QCM sensor's surface with polystyrene film is exposed directly to the plasma generator (paired electrodes), the plasma and the polystyrene film's reaction exists on all surfaces. An optical microscope observation showed the ion bombardment effect on the film surface. The effect was analyzed based on the image captured using the microscope.

Surface morphology change

The effect of the oxygen plasma on the polystyrene film surface was observed using optical and scanning electron microscopes. **Figure 3** depicts the optical microscope images. **Figure 3(a)** shows the polystyrene surface before plasma treatment observed using the optical microscope. The polystyrene film is homogeneously distributed over the sensor surface with no defect. In contrast, **Figures 3(b)** and **3(c)** show the polystyrene surface after being treated with RF plasma without DC and with a DC bias at -150V, respectively.

(a) (b) (c)

Figure 3 Polystyrene film surface image (a) before plasma treatment, (b) oxygen plasma without DC bias, and (c) oxygen plasma with −150 V DC bias.

Under the same optical illumination, the captured image of the polystyrene film after oxygen plasma treatment shows a change in the captured surface color. The image color changes from a yellowish color to reddish color. It seems that there are changes on the film's surface property related to the oxygen plasma treatment. After plasma treatment, the etching process may also be related to the phenyl ring's damage [11].

A significant change in the optical image is observed on the polystyrene film after oxygen plasma treatment with DC bias (**Figure 3(c)**). Black spots can be seen on the QCM sensor surface with polystyrene film after plasma treatment with 150 V negative DC bias.

Further analysis using a scanning electron microscope supports the occurrence of the etching. **Figure 4** shows the SEM BSE image on the surface of the black spot area. The image was taken at 1000× magnification. As we know that the polystyrene was coated using spin coating on top of the silver electrode, and beneath the silver electrode is SiO_2 (quartz), we expected that the backscattering image should show a contrast between silver and polystyrene or silver and Si. The gray color in **Figure 4** shows the silver, and the darker (black) area is the SiO_2. It shows that the polystyrene and the silver electrode were etched from the sensor surface. In some areas, we can see a small spot of silver in the form of a dot (ball-like) shape. Based on the SEM image, we are convinced that the black spot area observed using the optical microscope is an etched area by the oxygen plasma; therefore, the measurement of the etched area based on the optical microscope image can be applied.

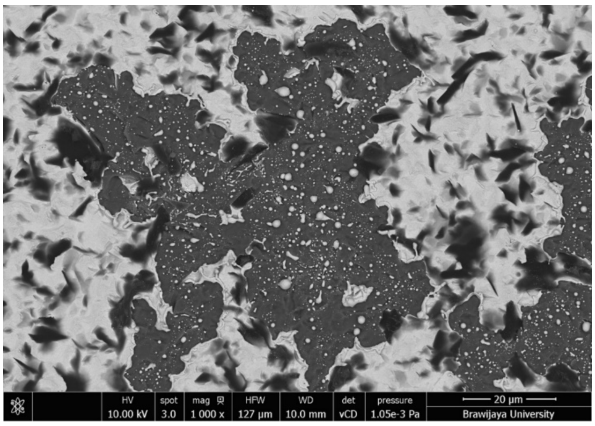

Figure 4 BSE image of the QCM sensor with Polystyrene film after RF plasma treatment with 150 V negative DC-bias (Quanta-650 FEG, 1 K magnification).

Measurement using energy dispersive spectroscopy confirms the etching area of the QCM sensor surface as depicted in **Figure 5**. The image was taken using Quanta-650 FEG with a magnification of 4000×. The detector is X-Act from Oxford Instrument with AZtecOne software.

The etched area can be seen in the middle of the image as a dark background area. The etched area comprises the silicone (Si, red color) and oxygen (O, aqua color) atoms. Silicone and oxygen exist from the quartz material (SiO_2). In the left and right areas, the image shows silver (green color), which is the electrode material. The carbon (magenta color) area is the carbon as a composing atom of polystyrene. In the middle, we can see some silver spot scattered on top of the SiO_2.

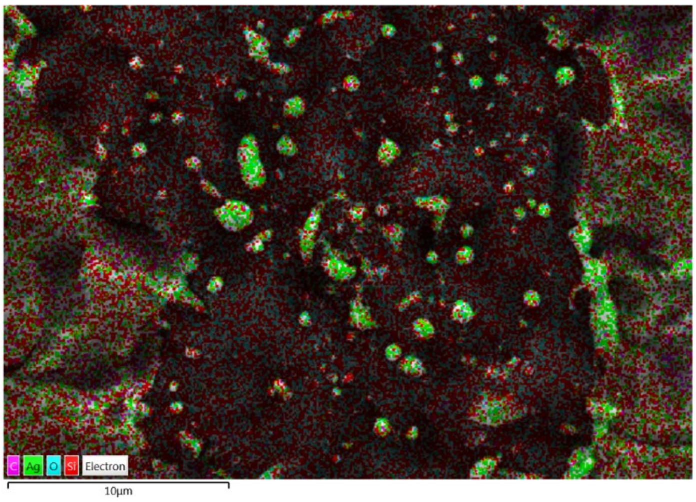

Figure 5 EDS image of the sensor surface with polystyrene film after 150 V negative DC-bias

DC Bias effect to affected surface area and hydrophobicity

Based on the resulting optical and SEM analysis above, we can use the image from the optical microscope to calculate the etched area caused by the oxygen plasma treatment on the polystyrene film. **Figure 6** shows the different of the polystyrene film after oxygen plasma treatment with negative DC bias and without DC bias. The image of the polystyrene without DC bias look as it has no black spot, while the image of the polystyrene film after oxygen plasma with DC bias show the existence of many black spot.

After image pre-processing process by separating the RGB component of the optical image, the black dot size analysis was calculated. By applying the particle size analysis tools on the image from the polystyrene film before plasma treatment, we found that the black spot area with a 1-pixel threshold was 0.04 % and omitted when the threshold was 20 pixels with a covered area of 0.002 %, as seen in **Figure 7**. At pixel area of 25 pixels, there is no black dot area counted. This criteria is then used to calculated the etched area of the polystyrene film.

The black spot area analysis was conducted using a minimum pixel area size of 25. The number of etched areas was affected by the DC-bias. As the DC-bias applied, the bombardment of the plasma ion to the polystyrene has adequate energy to etched the polystyrene film. It is indicated by the significant change of the black spot area from 22 to more than 300 spots. **Figure 8** shows the step change of the black spot (etched are). The number of the isolated etched area remains constant until −350 V DC-bias.

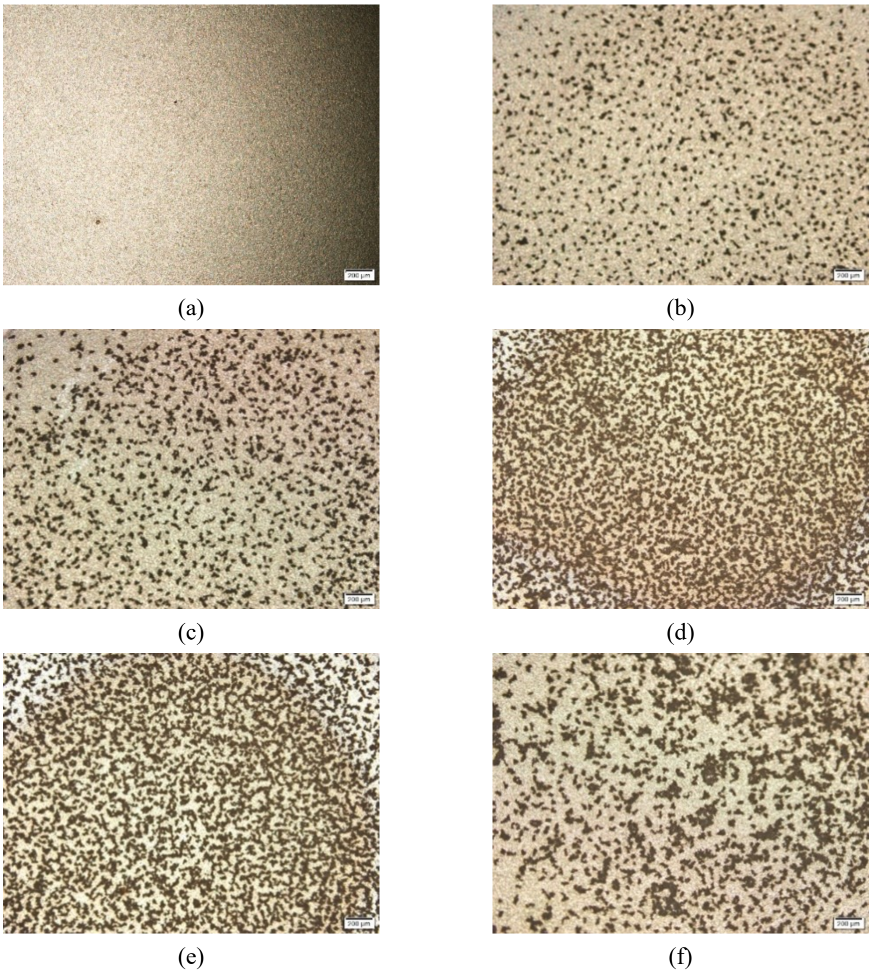

Figure 6 Optical image of polystyrene film after oxygen plasma treatment (a) no DC bias, (b) −150, (c) −250, (d) −350, (e) −450, and (f) −550 V DC bias.

The number of the isolated etched area decreased with the increasing DC-bias. The size of the isolated etched area increased with the DC-bias. At −150 V DC-bias, the average area size is 229. The area size increases up to 1156 at −450 V DC-bias.

The results show that the DC bias in the oxygen plasma play importance role in the polystyrene etching. The energy of the oxygen ion accelerated by the negative DC bias strong enough the etched away the polystyrene film. The oxygen plasma on the polystyrene film does not have adequate energy to etch the portion of the polystyrene film. The surface morphology of the polystyrene film was affected by the oxygen plasma bombardment with adequate DC-bias. In contrast the surface morphology change caused by ultraviolet is not significant, no part of the polystyrene film was etched [8,9].

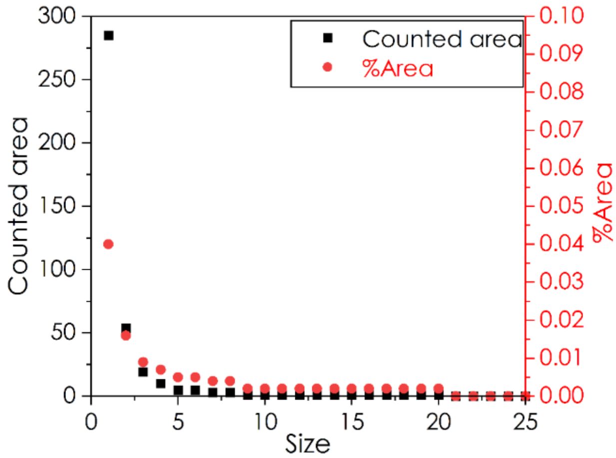

Figure 7 Counted area and percentage area of black spot for polystyrene film without plasma treatment.

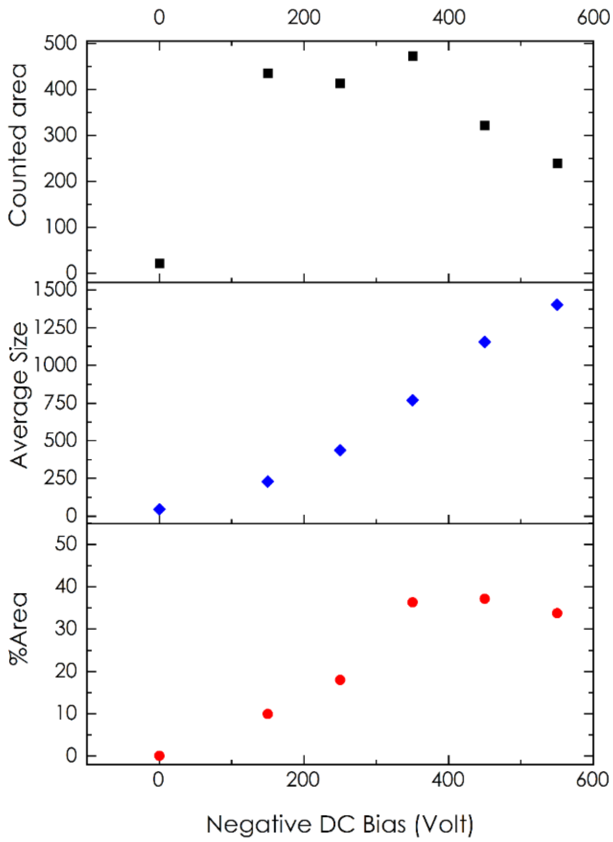

Figure 8 DC-bias effect on the polystyrene film etched area.

Those 2 data show that the random oxygen ion bombardment to the polystyrene exists on all surfaces. As more and more polystyrene film reacted with the oxygen plasma ion, the etched area becomes wider. At a certain condition, the new etched area joined the neighboring etched area, resulted in a wider etched area, and reduced isolated ones. In our case, it started at −450 V DC-bias. At DC-bias

−450 and −550 V, the counted area decreased, and the average size increased. However, the percentage of etched area is saturated to around 37 %, as depicted in **Figure 8**.

The effect of the oxygen plasma with DC bias to the wettability of the polystyrene film was observed using the goniometry contact angle measurement [34]. **Figure 9** shows the contact angle of the polystyrene film on the QCM sensor. The polystyrene film changes from hydrophobic (contact angle = 85 °) to hydrophilic (contact angle less than 10 °) when exposed to plasma oxygen without DC bias. It seems that the substitution of C-H bonds with the C-OH group [35] contributed the change from hydrophobic to hydrophilic surface.

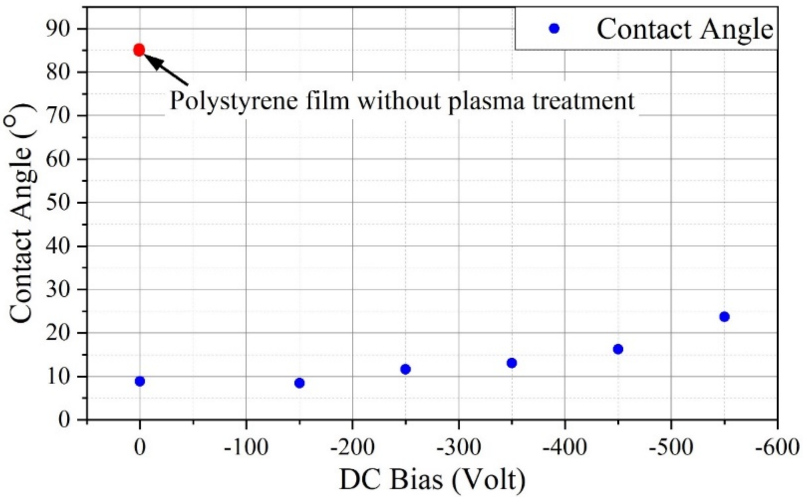

Figure 9 DC-bias effect on the polystyrene film hydrophobicity.

The contact angle increased slightly with increasing negative DC bias. Only at high negative DC bias (more than 250 V negative DC bias) is the change in contact angle observed. The slight change of the contact angle value related to the polystyrene film's morphological change, as there was a more etched area with increasing negative DC bias. Silver is known as a hydrophobic metal [36]; at higher negative DC bias, part of the polystyrene film was etched, and let the silver electrode was exposed, which contributed to the increasing contact angle. The effect to the surface wettability and morphology is stronger than caused by the ultraviolet radiation [9].

Conclusions

In this study, the effect of negative DC-bias in the oxygen plasma to the polystyrene film coated on QCM sensor was investigated. Optical emission spectroscopy showed that the oxygen plasma species generated by the 2 MHz RF plasma successfully reacted with the polystyrene film. The etched film spread over the sensor surface and was detected as a black spot by a reflectance optical microscope. The polystyrene etched area depends on the applied DC-bias that allows an ion bombardment with higher kinetic energy on the polystyrene film. Polystyrene surface change occurred significantly when the DC-bias was given. The average area of etched polystyrene depends on the DC-bias. Higher DC-bias resulted in a wider affected area. However, the total area of the etched film reaches a maximum of around 37 %.

The hydrophobicity of the polymer film decreased significantly with oxygen plasma treatment. Higher DC bias results in increasing contact angle of the polystyrene film.

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