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The Role of DC Biased Plasma Treatment of Polystyrene on the Formation of the C≡N Functional Group Controlling Its Hydrophobicity

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Abstract. Nitrogen plasma treatment was carried out to modify the surface of polystyrene film deposited on a quartz crystal microbalance (QCM) sensor. The modification was intended to enhance the wettability of the film by inducing the formation of CN functional group on its surface. This work investigated the effect of DC bias controlling N* in the plasma on the effectiveness of the nitrogen plasma treatment. The polystyrene was deposited by a spin coating method on the surface of a quartz crystal normally used in an electronic resonator. The nitrogen plasma was generated in an aluminium vacuum chamber using a 2 MHz radio frequency (RF) generator. The vacuum pressure and the gas flow rate were kept constant during the experiments. The plasma character in the chamber was controlled by applying a DC bias between the RF electrodes and the sample stage. The DC voltage was varied from 100 to 500 volts at 100 volts' step, while maintaining the RF voltage constant. During the process, the species in the plasma was characterized using an optical emission spectroscopy (OES). The wettability of the treated samples was tested using a contact angle measurement system. FTIR measurement was utilized to study the polar functional groups on the surface of the polystyrene before and after the treatment. The OES identified the existence of N radical (N*). The reduced intensity of emission line of the N* increased with the increase of the DC voltage. However, a small decrease was also evidence at DC voltage higher than 400 volts. The decrease of the line intensity was directly related to the decrease of the contact angle (CA < 40°). The relation of the N* and the resulted wettability is related to the polar functional group of the C≡N bond found in the treated polystyrene's surface.

1. Introduction

Quartz Crystal Microbalance (QCM) is a device that can detect a change of mass that adsorbed or deposited on its surface. The device consists of a thin quartz and electrodes on the both sides. The sensing mechanism is related to the change of shear resonant frequency due to the change of mass on its surface. The amount of this frequency change is proportional to the change of mass, and is described by the Sauerbrey equation. One utilization of the QCM can be found in many design of biosensors. In the biosensor application, a matrix layer is needed to immobilize biomolecules at the surface. Immobilization of biomolecule on QCM surface is realized mostly via covalent bonding and physical adsorption on the surface of the matrix. One of the many materials which can be used as immobilization matrix for the QCM biosensor is a polystyrene thin film. Polystyrene has been used conventionally as the immobilization matrix because of its hydrophobic properties leading to hydrophobic adsorption. However, in order to improve the biomolecules immobilization by the polystyrene, the surface was modified using a UV radiation [1], and a plasma treatment [2 - 5]. The modification by the UV radiation resulted in the decreased of the polystyrene's hydrophobicity [1]. On the other hand, the modification using the plasma treatment resulted in the further decrease of the hydrophobicity due to the change of the surface's microstructure and functionality [6]. Recently, modification the surface of the polystyrene has been carried out using oxygen plasma [7] and atmospheric plasma [5].

From a number of studies on the plasma treatment, discussions on the effect of DC biased nitrogen plasma treatment on the decrease of hydrophobicity are very limited. This study will try to investigate the effect of the DC bias on the plasma species during the treatment process which in turn affect the hydrophobicity.

2. Materials and Method

Samples were prepared by coating QCM sensor with polystyrene thin film. The film was produced using a raw polystyrene (*Sigma-Aldrich*) with 192 kDa molecular weight. A 6% concentration of polystyrene solution was made by mixing 0.06-gram of the polystyrene and 1 ml toluene. An ultrasonic bath was used to homogenize the solution. The polystyrene solution was then coated to the surface of the QCM by means of a spin coating method for 1 minute at 3000 rpm. The coated QCM was baked in the oven for 60 minutes, with 100^{o} C temperatures after the coating procedure.

This study utilized a vacuum plasma reactor to treat the polystyrene thin film's surface. The reactor consists of two electrodes (anode) and a base plate (cathode) contained in a cylindrical vacuum chamber. The plasma was generated by a 2 MHz RF generator with an automatic impedance matching system. A variable high voltage DC can be applied between the anodes and cathode. Figure 1 shows a schematic drawing of the system.

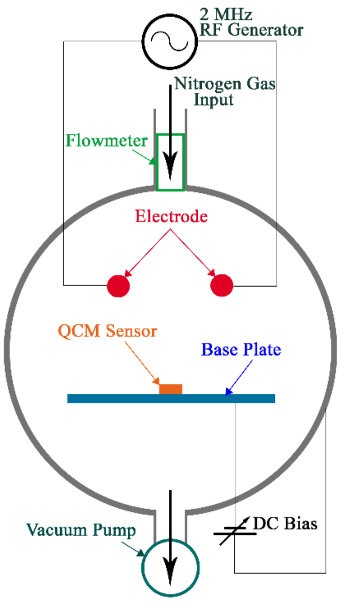

Figure 1. Plasma reactor scheme for nitrogen plasma treatment.

A high purity nitrogen gas was used to produce the nitrogen plasma. The RF power was kept constant during the treatment by adjusting the generated RF voltage at 90 volts. A constant 60 ml/minutes flowrate of the nitrogen gas and a subsequent pumping was applied to keep the pressure of chamber at 40 Pa.

The nitrogen plasma treatments were carried out for 2 minutes with the variation of the DC bias at 100, 200, 300, 400, and 500 volts. During the treatment, the nitrogen plasma was diagnosed using a spectrometer (Aurora 4000) which have a resolution up to 0.75 nm. The wavelength scanning range used in this study was from 200 nm to 1000 nm.

The effect of the DC biased plasma treatment on the hydrophobicity of the polystyrene film was evaluated by measuring the contact angle between a drop of water and the surface at the atmospheric environment. Further analysis related to changes of bonding due to the treatment was carried out by performing Infrared spectroscopy (8400S/Shimadzu) characterization.

3. Result and Discussion

The effect of the DC biased nitrogen plasma treatment on the change of the polystyrene hydrophobicity was first investigated by diagnosing the plasma state. The plasma state depends on the species generated during the process. The optical emission spectrum of the plasma can be used to identify the species.

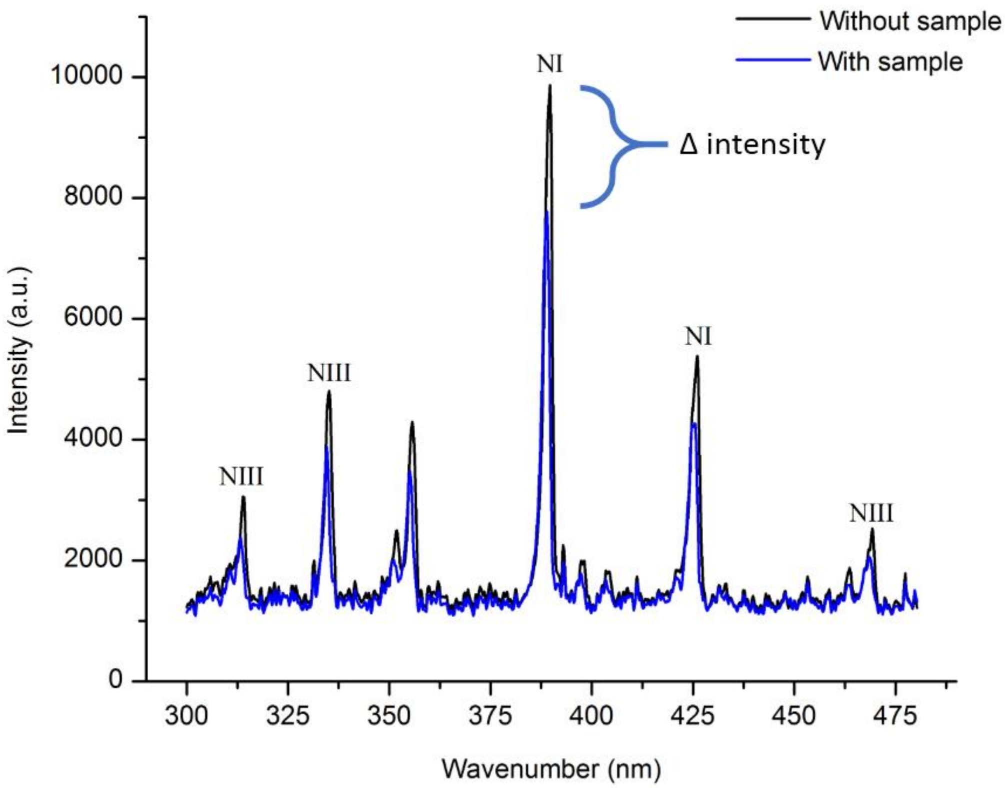

Figure 2. Nitrogen plasma spectra at -400 volts DC bias.

Figure 2 shows two spectra representing the emission of the plasma with (blue) and without (black) sample. Identification of the peaks in the spectra was conducted by comparing the measurement to the data from the NIST atomic database [8]. According to the database the peaks in the spectra can be identified as NI which is the excited or radical N and NIII which is the N^{2+} ion. It can be seen from the figure that the plasma state was changed by the existence of the sample in the chamber. Generally, the intensity of the plasma spectrum was reduced. This indicates that chemical reactions were occurred during the treatment. The chemical reactions were expected to affect the functional property of the polystyrene surface. Firstly, it is important to identify the relation between the intensity reduction and the applied DC voltage.

Table 1. The relation between the DC bias voltage and the intensity reduction (Δ Intensity).

DC bias (-volt)	Δ Intensity (a.u.)
100	-450
200	-1294
300	-1543
400	-2215
500	-1668

Table 1 above shows the results of the intensity reduction measurement during the plasma treatment at various DC bias Voltage. It can be seen from the table that the higher DC voltage resulted in larger reduction of the intensity. However, smaller reduction was obviously noticed during the treatment at the DC voltage of 500 volts. The next results come from the contact angle measurements. The measurements were carried out for each sample before and after the plasma treatment. Figure 3 below shows change of the contact angle due to the plasma treatment.

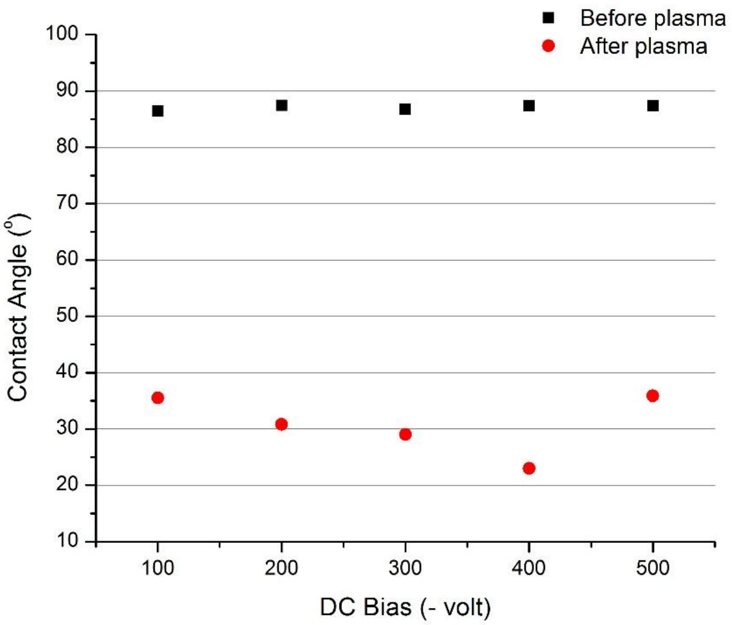

Figure 3. Contact angle value before and after plasma treatment.

It can be seen from Figure 3 that the plasma nitrogen treatment decreased the contact angle dramatically. The contact angles of the samples before the plasma treatment ranged from 85° to 90° indicating that the samples originally were hydrophobic. After the plasma treatment, the contact angle decreased dramatically according to the given DC bias voltage. The decrease of the contact angle is related to the change in the wettability level of the polystyrene film, which was originally hydrophobic to be more hydrophilic. The decrease of the contact angle was continued for the DC bias increase from -100 up to -400 volt. However, the increase of the DC bias from -400 to -500 volt resulted in slightly increase of the contact angle.

The decrease of the contact angle of the polystyrene film is due to the presence of N radical (NI) species interacting with the surface of the film. The interaction of the species with surface of polystyrene film is assumed to form a new chemistry-functional group which will reduce the value of the contact angle. This assumption is supported by the results from the FTIR measurement shown in figure 4.

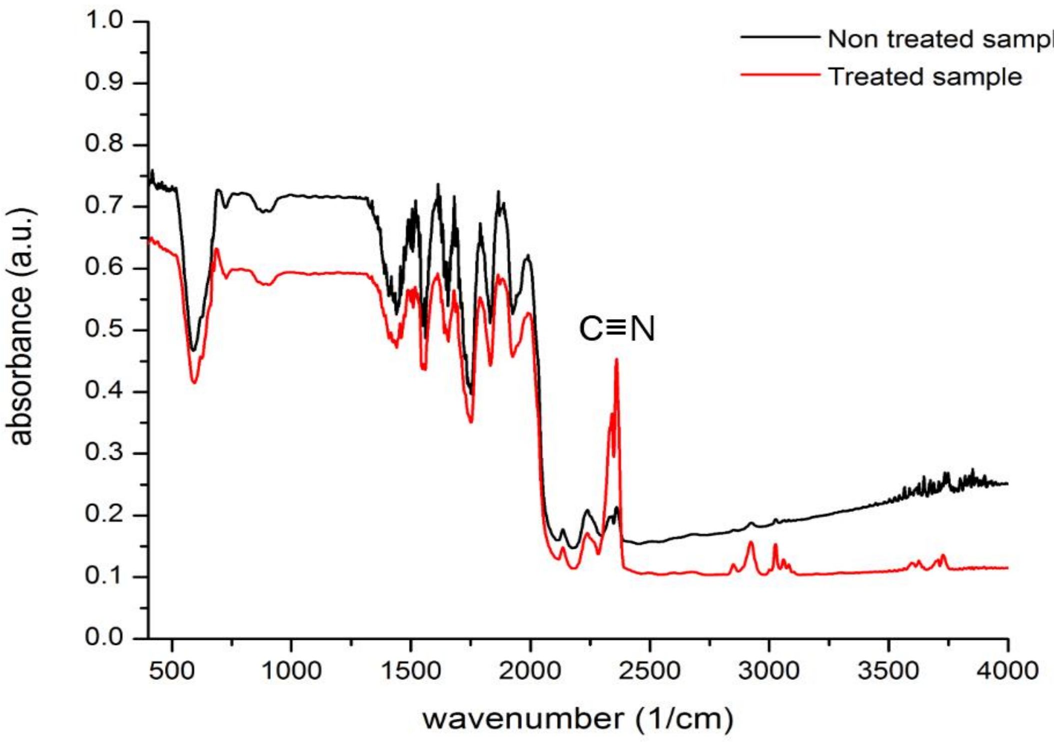

Figure 4. FTIR result for the sample before and after plasma treatment.

In Figure 4, it can be seen that the treated samples show new peaks in wavelength range of 2300 - 2400 cm^{-1}. Those peaks are related to C≡N functional group which has polar properties. According to the previous studies, this polar C≡N functional group has the tendency to interact with water molecules, thus increasing the wettability level of the polystyrene film [6].

The N radical species is generally neutral, but is reactive due to exited electronic state. However, whether the reactivity alone triggers the surface reaction is still debatable. It can be seen from Figure 2 that the nitrogen emission spectrum shows a number of peaks related to N^{2+} (NIII) species in the plasma. The ionic species are accelerated to the base plate when there is a DC bias applied. The kinetic of the ion can trigger surface ion bombardment mechanism. This mechanism can break the polystyrene chain, and raise the possibility of reaction between the radical (NI) species and the polystyrene surface. Furthermore, this ion bombardment can also modify the surface roughness. The change of the surface roughness alone does not seem to contribute much in the change of polystyrene surface wettability. It assumed that the wettability change cause by surface free energy rather than morphological change [5].

The radical NI species can be considered as the species which plays an important role in forming the C≡N functional group in the polystyrene film. Therefore, when there is more reduction of the NI in the plasma during the treatment, the more hydrophilic surface will be obtained. This relationship between the intensity reduction and the contact angle can be seen in Figure 5.

Figure 5 shows that the change of the Δ Intensity and the contact angle has a similar trend to the increase of DC bias. It can be seen that the increase the DC bias from -400 volts to -500 volts, resulted in the decrease of the NI intensity reduction and the increase of the contact angle. This phenomenon can be caused by the increase of the ion bombardments. Ion bombardment mechanism can break the polystyrene chain as well as the C≡N functional group. So, actually there must be a rate of the C≡N group forming and bond breaking which has to be optimized in the future. It assumed that between the

-400 volts to -500 volt of the DC bias, the bond breaking is greater than the group forming rate. This lead to the increase of the contact angle.

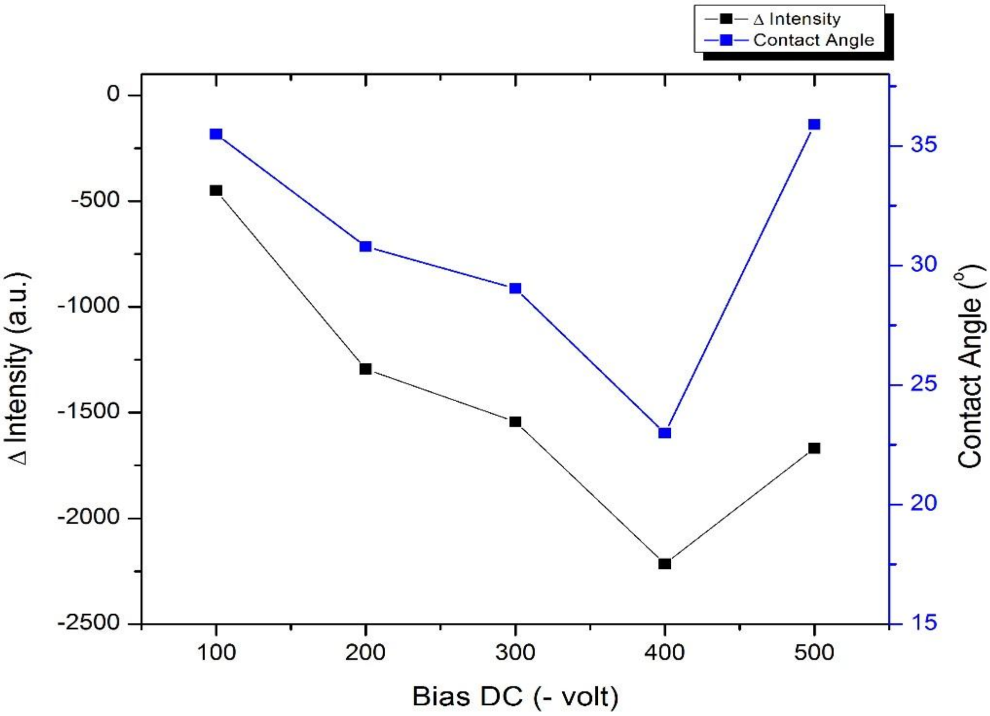

Figure 5. Effect of DC bias to the Δ Intensity, and contact angle drop.

4. Conclusion

The increasing DC bias (-100, -200, -300, and -400 volt), will increase the ion energy leading to sample, which indirectly increase the NI species that react with the sample. NI species that react with the polystyrene film will formed a C≡N functional group, it will increase the interaction between the film with water, and decreasing the contact angle. At the -500 volts DC bias, it assumed that the bond breaking rate of the C≡N group by the ion bombardment mechanism is greater than the formation rate resulting in an increase of contact angle and NI reduced intensity.

References

[1] Sakti SP, Amaliya L, Khusnah NF and Masruroh. 2017. *J. Teknol.* **79** 61.
[2] Nakhowong R, Srikhirin T and Osotchan T. 2008. *Adv. Mater. Res.* **55–57** 753.
[3] Vesel A. 2010. *Surf. Coatings Technol.* **205** 490.
[4] Guruvenket S, Rao GM, Komath M and Raichur AM. 2004. *Appl. Surf. Sci.* **236** 278.
[5] Sakti SP, Khusnah NF, Santjojo DJDH, Masruroh and Sabarudin A. 2018. *Mater. Today Proc.* **5** 15149.
[6] Masruroh, Zahirah TN, Aulanni'am, Sakti SP and Santjojo DJDH. 2018. *IOP Conf. Series: Mater. Sci. Eng.* **432** 012036.
[7] Khusnah NF, Sakti SP and Santjojo DJDH. 2018. *IOP Conf. Series: Mater. Sci. Eng.* **367** 012030.
[8] Kramida A, Ralchenko Y, and Reader J. 2018. NIST Atomic Spectra Database (ver. 5.6.1), [Online]