Swelling Effect Observation of The Copper Phthalocyanine Layer on QCM and Its Effect on Surface Roughness and Morphology Changes

Rahmad Oktafiansyah$^{1,2}$, D J Djoko Herri Santjojo$^{1,2}$, Setyawan P Sakti$^{1,2}$, Tyas N Zafirah$^{1,2}$, Muhammad Ghurmon$^{1,2}$, N F Khusnah$^{2,3}$ and Masruroh$^{1,2}$*

$^1$Department of Physics, Brawijaya University, Malang, 65145, Indonesia
$^2$Collaborative Research Group for Advanced System and Material Technology (ASMAT), Brawijaya University, Malang, Indonesia
$^3$Laboratorium Sentral Ilmu Hayati (LSIH), Brawijaya University, Malang, 65145, Indonesia

*Corresponding author: ruroh@ub.ac.id

Abstract. Copper Phthalocyananine (CuPc) is one material often used for the active layer on Quartz Crystal Microbalance (QCM) sensor. One important mechanism which can shorten the recovery time in the sensor is the swelling effect. The swelling effect is studied by observing the morphology of the layer and subsequent changes in QCM frequency during surface contact with three kinds of solution. The solutions used in this study were distilled water, phosphate-buffered saline (PBS) and Tris-HCl. The results of frequency measurements indicate a swelling effect which was shown by the decrease of the frequency change after the injection process. The most significant change in frequency occurs in PBS solutions. This change occurs as PBS has a higher molecular weight and ionic strength than distilled water and Tris-HCl. SEM results show that the swelling of the CuPc layer changes the microstructure layer. A decrease in the roughness of the CuPc layer was also observed due to the presence of buffer solution molecules that diffuse through the layer. Upon diffusion of the solution molecules into the CuPc layer, a continuous decrease in the QCM frequency occurs. Further, the diffusion caused the CuPc microstructure to become more tenuous.

1. Introduction

Quartz Crystal Microbalance (QCM) is a device that is sensitive to changes in the mass of up to $10^{-4}$ ng, making QCM a vital device and well applied as a gas sensor base. In its usage, the sensitivity and selectivity of the QCM sensor can be increased by coating certain materials on its surface [1]. Copper Phthalocyananine (CuPc) is one of the materials that is often chosen as a thin layer on the surface of QCM because it is chemically and thermally very stable. Moreover, CuPc is proven to increase the number of gas molecules detected by sensors [2,3]. CuPc is composed of Phthalocyananine chains that bind to the Cu cation as its core metal. Generally, CuPc has two structural phases, namely the metastable α-phase and also the more stable β-phase [4]. The structure of CuPc can be conditioned by giving heat treatment to the layer, where the α-phase is found in heat treatment below 200°C, and the β-phase structure is found when heat treatments are above 200°C [5].
One criterion of good coating for gas sensors is the existence of a swelling effect. A high swelling effect can shorten the gas sensor recovery time [6]. Swelling occurs due to the interaction of the thin layer with the solution, causing the solvent molecules to diffuse into the layer creating the thin layer to experience additional volume [7]. The diffusion of liquid into the thin layer tends to balance the tensile and repulsive force between the liquid mixture and the layer thermodynamically. Upon reaching the driving force equilibrium of the liquid with the force that holds the diffusion from the layer, the swelling process will stop [8]. Several factors affect swelling, including layer microstructure, the affinity between solution and layer, the porosity of layers, temperature and ionic strength [9]. Specific buffer solutions i.e. PBS and Tris-HCl, which have ionic strengths of 2.434 M and 0.086 M, are used for swelling observation. The diffusion process in swelling mechanism is categorized in non-Fickian diffusion, making the decrease in diffusion rate proportional to its depth. Observation of the swelling effect of a layer can be done by measuring changes in deposited QCM frequency which are then given a liquid on its surface [9].

In this research, the effect of affinity between the solution of distilled water, PBS, and Tris-HCl with the CuPc layer on the swelling effect was studied by observing frequency changes. The effect of swelling on changes in microstructure (morphology and surface roughness) of CuPc layers is also discussed.

2. Materials and Method
Samples were prepared by superimposing Polystyrene on the surface of a quartz crystal microbalance (QCM) sensor with a frequency of 10 MHz. QCM was obtained from Great Microtama Surabaya. Polystyrene layer with a molecular weight of 192 kDa was made from polystyrene grains obtained from Sigma-Aldrich dissolved in toluene solvent to obtain a solution with a concentration of 6%. Then the solution is homogenized with an ultrasonic cleaner, and coated with a spin coater, then heated in an oven for 60 minutes at 200°C. CuPc deposition was carried out by the thermal evaporation method, in which QCM-coated Polystyrene was used as a substrate, and CuPc Powder (purity 99%) obtained from Sigma-Aldrich was used as a vaporized material. CuPc coating deposition was carried out by setting up 1.5 A current and 28V voltage, with the CuPc deposition time being 5 minutes. After that, the samples were annealed at 220°C in the oven for 60 minutes.

QCM samples deposited with CuPc layers are placed in reaction cells connected with an oscillator to measure the QCM frequency. After the QCM frequency has stabilized, 50 µl of distilled water solution is injected into the QCM. The swelling effect of the CuPc layer was observed by observing changes in the QCM oscillation frequency after being injected with a distilled water solution. Then the same thing was conducted to observe the swelling effect of the CuPc layer from the buffer solution of Phosphate Buffered Saline (PBS), and Tris-Hydrochloride (Tris-HCl) obtained from GIBCO. Figure 1 is an illustration of a set-up tool for observing the swelling effect with QCM. The morphology of the CuPc layer was observed using SEM-EDS (FESEM, FEI, Quanta 650 FEG), in the LSIH, Brawijaya University, and the roughness value of the CuPc layer was measured using the Topography Measurement System (Polytech TMS 1200), in the Material Physics laboratory, Department of Physics, Brawijaya University. Morphological observations and roughness measurements of the CuPc layer were carried out before and after the swelling process for all buffer solutions.
3. Result and Discussion
Swelling effect arises as a result of the diffusion of molecules from the solution injected onto the surface of the QCM thin layer. A sudden injection of the solution on the QCM surface causes a mass increase in the QCM sensor, causing the QCM frequency to drop dramatically. The repulsion of the QCM surface layer will increase the QCM frequency on a small scale. Diffusion that occurs in a thin layer of QCM will result in a continuous decrease in the frequency of QCM until saturation conditions are reached, and the solvent molecules are unable to diffuse again.

Figure 2. QCM frequency response after injection of the solution on the surface of CuPc.

Figure 2 shows the decrease in the QCM oscillation frequency after the injection process of the solution on the surface of the CuPc layer. The change in QCM frequency indicates the presence of buffer solution molecules that diffuse into the thin layer of CuPc, causing loading on the QCM sensor. After
more in-depth observation, the CuPc layer that was injected using PBS solution experienced a more significant decrease in frequency compared to Tris-HCl and distilled water injection, and this is due to the higher weight of the PBS molecular than the molecular weight of Tris-HCl and distilled water. Thus, the mass of loading received by QCM is greater. Also, PBS has a higher ionic strength compared to Tris-HCl and distilled water. Ionic forces cause electrostatic repulsion when buffer molecules interact with the CuPc layer. As the repulsion force of the CuPc layer will be more tenuous, the PBS molecules will be easier to break into the CuPc layer. Molecular diffusion of buffer solution in the CuPc layer results in changes in the microstructure and morphology of the layer, as shown in Figure 1.

Figure 3 shows the morphological changes in the CuPc layer due to injection of buffer solution. Figure 3 (a) shows that the CuPc layer has fibrous characteristics that are interconnected with one another. There are no visible interrelated fibers observed after the surface was injected with the buffer solution. However, from Figure 3 (c) and (d), the CuPc fibers are scattered and do not accumulate like the one before injection. The scattered microstructure is possible due to the diffusion of buffer solution molecules that break through the CuPc layer, resulting in the widening of the CuPc layer.

Figure 4 shows that the Na and Cl spectra appear from the results of the EDS analysis of the CuPc layer injected with PBS solution, where Na and Cl are the constituent elements of PBS, thus confirming the existence of a PBS molecule that diffuses into the CuPc layer. The swelling effect that occurs in the CuPc layer results in changes in the properties of the CuPc layer, one of which is the roughness of the CuPc layer. The results of roughness analysis using TMS (Topography Measurement System) are listed in Figure 5.
Figure 4. EDS results of CuPc coating after PBS solution injection.

Figure 5. Roughness value of CuPc layers before injection and after injection with Distilled water, PBS and Tris-HCl.

Figure 5 shows a decrease in the level of roughness of the CuPc layer after injection of buffer solution in the CuPc layer. This decrease in roughness is caused by the diffusion of buffer molecules that relax the CuPc layer. The characteristics of the CuPc layer in the form of fibers are interrelated, resulting in a coarser CuPc layer. However, due to the widening of the CuPc layer, the CuPc molecules do not
accumulate any more, thus decreasing the layer's roughness. The roughness value of CuPc layers for all buffer solutions shows almost the same value. This similarity shows that the CuPc layer has reached saturation condition, indicating that diffusion occurs at a certain depth. Therefore, swelling that occurs in the CuPc layer is categorized in the case of non-fickian diffusion, where the diffusion rate slows following the deeper layers. Moreover, because of this swelling effect, the CuPc coating can improve QCM's ability to detect gases.

4. Conclusion
The swelling effect occurs in the CuPc layer when it comes in contact with distilled water, PBS, and Tris-HCl solutions as indicated by observations on the changes in QCM frequency. The most significant change in the frequency takes place in the CuPc layer injected with PBS solution, due to the higher PBS molecular weight compared to distilled water and Tris-HCl solutions. The swelling of the CuPc layer causes a decrease in the surface roughness and microstructure changes of the CuPc layer.

References
[1] D V Ivanov, A Yelon 1996 J. Electrochem. Soc. 143 2835–2841
[2] A Arnau, Y Jimenez, R Fernández, R Torres, M Otero, E J Calvo 2006 J. Electrochem. Soc. 153 C455
[3] Singh, Sukhwinder, G S S Saini, and S K Tripathi 2014 Sensing Properties of ZnPc Thin Films Studied by Electrical and Optical Techniques Sensors & Actuators B. Chemical 203. Elsevier B.V.: 118–21
[4] El-Nahass, M M, F S Bahabri, a a Al Ghamdi, and S R Al-Harbi 2002. J. Sol 25 2 307–21
[5] Grobosch, M C Schmidt, R Kraus, and M Knupfer 2010 Organic Electronics 11 9. Elsevier B.V.: 1483–88
[6] Rianjanu A, S N Hidayat, T Julian, E A Suyono, A Kusumaatmaja, and K Triyana 2018 IOP Conf. Ser. Mater. Sci. Eng. 367 012020
[7] Shinkai, Tomoaki, Kohzo Ito, and Hideaki Yokoyama 2014 J Supercritical Fluids 95. Elsevier B.V.: 553–59
[8] Sukhorukov, Gleb B, and J Schmitt 1996 Reversible Swelling of Polyanion/ Polycation Multilayer Films in Solutions of Different Ionic Strength J 953 6 948–53
[9] Tyas N Z, D.J.D.H. Santjojo, Masruroh and S.P. Sakti 2019 Mater. Today Proc 13 18-23.

Acknowledgements
This work was partly supported by RISTEKDIKTI for PDUPUT Grants through LPPM of Brawijaya University.