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A Study of the Effect of Zinc Organic Metal Composite Layers on the Frequency of Quartz Crystal Sensor

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Abstract

The performance, sensitivity, and corrosion protection on the QCM sensor requirement be improved to maximize the value. Therefore, the functional material coating was carried out. The addition of the polystyrene and ZnPc deposited using the vacuum evaporation method. This study intends to the morphology structure and effect of the coating, to improve performance through the annealing process based on the impedance value at QCM. The frequency measurement before and after the coating process was carried out with a variation of the deposition time, which is 1 minute 30 seconds, 1 minute 45 second, 2 minutes, 2 minute 20 seconds, and 4 minutes. The coating and annealing resulted from the surface structure of the QCM sensor are smooth, small porous, and homogeneous. In addition, the impedance to frequency graph indicates a low damping effect means the QCM sensor does not respond viscoelasticity.

Keywords: Frequency, Impedance, QCM, Sensor.

Abstrak

Performa, sensitivitas dan ketahanan korosi pada sensor QCM perlu ditingkatkan untuk memaksimalkan kebermanfaatannya. Maka dari itu dilakukan pelapisan material fungsional yaitu polistiren dan ZnPc yang dideposisi menggunakan metode pengupan vakum. Penelitian ini bertujuan untuk mengetahui morfologi dan pengaruh pelapisan serta peningkatan performa melalui proses perlakuan panas berdasarkan nilai impedansi pada QCM. Pengukuran frekuensi sebelum dan sesudah proses pelapisan dilakukan dengan variasi waktu deposisi yaitu 1 menit 30 detik, 1 menit 45 detik, 2 menit, 2 menit 20 detik, dan 4 menit. Hasil pelapisan dan perlakuan panas menunjukkan struktur permukaan sensor QCM yang halus, berpori kecil dan homogen. Selain itu grafik impedansi terhadap frekuensi menunjukkan bahwa redaman pada sensor QCM sangat kecil sehingga sensor QCM tidak mengalami viskoelastisitas.

Kata Kunci: Frekuensi, Impedansi, QCM, Sensor.

1. Introduction

New technology in biosensors facilitate fast measured and highly sensitive needed to detect small masses in various fields like in biomedical fields (Rahman, 2018), chemical fields (Vashist, 2011), and environment fields (Guo, 2021). QCM is one type of biosensor that works based on the piezoelectric properties of quartz crystals (Novianti, 2013)(Santjojo, 2015)(Khusnah, 2018). This sensor can detect mass changes on the surface allows measurement in the gas phase (Hori, 2020) and liquid phase (Liang, 2014)(Wu, 2019)(Didik, 2014). The small mass adsorbed on the electrode surface will lead to a QCM frequency decrease causes the magnitude for a frequency shifted (Asai, 2017)(Pan, 2019).

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QCM can detect the mass change when mechanical forces are applied to the sensor produce deformation crystalline structure (Itoh, 2010). A dipole moment currents can flow across external circuits. On the other side, using alternative voltages to the crystal induces mechanical oscillations of the crystal lattice. The resonant frequency is established by the thickness of the surface with thin-film deposition results a shift of the resonant frequency (Mista, 2016). The electrode surface of the QCM sensor is quickly corrosion because of the material used (Didik, 2020). This result decreases the sensor’s performance and unpredictable shifts in the calibrated value of the mass. The solution is to use well-characterized resonance-based sensor that can go with masses to provide an indication of mass change (Stambaugh, 2019). The material used to modify QCM sensors is polymers, metal oxide, and other functional materials, which large specific surface area (Hu, 2015).

In this study, polystyrene and ZnPc layer deposition on the QCM surface using the vacuum evaporation method (Robiandi, 2014). The addition of polystyrene and ZnPc on the sensor surface aims to protect the electrodes from corrosion and bind the detected molecules to improve the performance of QCM (Sutantri, 2014). The addition of mass affects the deposition layer to dampen QCM oscillations because of the viscoelastic properties. Viscoelastic properties are known of impedance measurements because the load on the QCM surface was determined so that the sensor continues to oscillate (Fitriani, 2014)(Masruroh, 2015)(Nurramdaniyah, 2017). Morphology was analyzed using SEM and optical microscopy to determine the deposited structure and viscoelastic properties analyzed by the impedance value changed to variations in the addition of layers.

2. Methods

2.1. Frequency Measurement

The frequency change received from the reduction of frequency before and after deposition. QCM, QCM with polystyrene coating, QCM with ZnPc coating, and QCM after annealing process were measured using an impedance analyzer bode 100. The minimum impedance value shows from the minimum impedance at the frequency data of sensors. The addition of layers to QCM describing the electrical behavior of a resonance by the Butterworth-Van Dyke (BVD) circuit with adding the resistor (R) and inductor (L) components decribed by Kanazawa et al and parlak et al.

2.2. Polystyrene Deposition

First, a 5% concentrated polystyrene was dissolved with chloroform using an ultrasonic cleaner. Polystyrene solution was deposited on the QCM surface using a vacuum spin coater VTC-100 with the speed of (ω1) 500 rpm and (ω2) 3000 rpm. Second, after coated the impedance of the QCM/Ps layer measured. Lastest, the morphology characterization using SEM.

2.3. ZnPc Deposition

ZnPc was deposited on the QCM/Ps surface using the Vacuum evaporation method according to previous research with deposition time of 1 minute 30 seconds, 1 minute 45 seconds, 2 minutes, 2 minutes 20 seconds and 4 minutes. Further, the deposition impedance layer was measured and characterized using optical microscopy and SEM.

2.4. Annealing Process

The annealing process uses a furnace for four hours at 170°C. After that, the impedance layer was measured and showed on the impedance to frequency graph.

2.5. Characterization

Microstructure, morphology, and cross-section of the layer of the QCM layer after the addition of polystyrene, Deposited of the ZnPc on the QCM surface, and annealing was investigated by scanning electron microscopy (SEM) and optical microscopy.

The stages in the research showed in the diagram below:

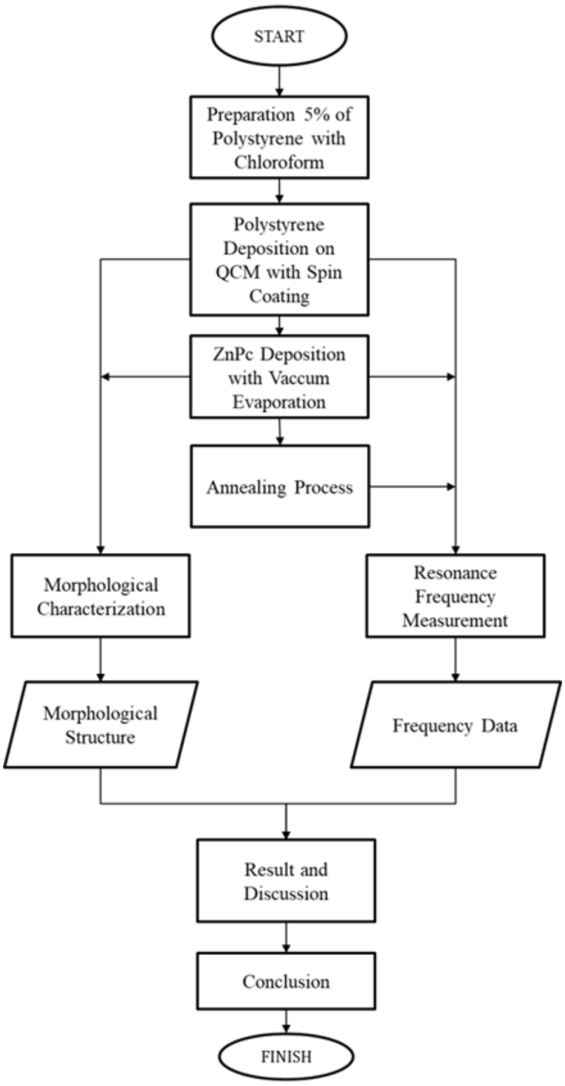

Figure 1: Research Stage Diagram.

3. Result and discussion

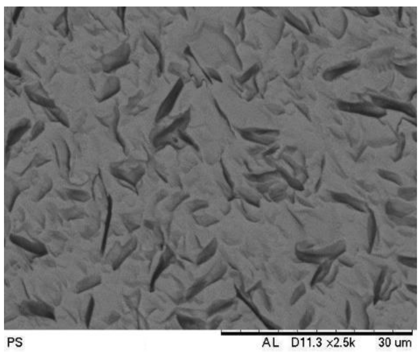

Figure 2: Morfologhy Of The QCM/Ps Using SEM

SEM results of the QCM/Ps surface after adding the polystyrene layer showed in Figure 2. The structure of the QCM/Ps has wavy with dark and light sections. The black part shows a cavity or space in the layer. The darker the color formed the cavity. The space in the layer representation porosity because centrifugal force creates the polystyrene layer to spread and coated the film. The surface becomes fractured because of the deformation by strain. The polystyrene layer deposited on QCM has flat, rough, and porous.

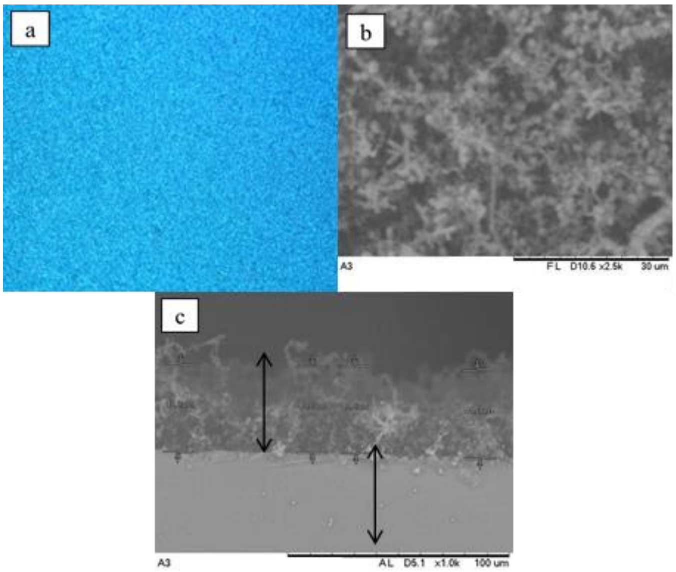

Figure 3: Morphology Of QCM/Ps/ZnPc (a) Using Optic Microscopy (b) Using SEM (c) Cross Section Using SEM With The Fiber Part is Znpc Layer The Solid Part is Polystyrene

The morphology of QCM/Ps after deposition ZnPc characterized using optical microscopy, and SEM showed in figure 3. Figure 3a shows a layer of QCM/Ps with ZnPc deposition has a blue surface with a distributed ZnPc particle. The color indicates that there are ZnPc particles deposited on the QCM/Ps surface. The ZnPc particles spread homogeneously on the substrate, designed that the ZnPc layer deposited on the sensor surface with a homogeneous layer. The distribution of ZnPc is homogeny because the previous layer on the QCM/Ps surface has a rough structure with large porosity. The deposition of ZnPc molecules trapped in the pore because of the large porosity. The next ZnPc molecules will spread to the surface that has not filled. The resulting surface structure is smoother than the previous layer by smaller pore size.

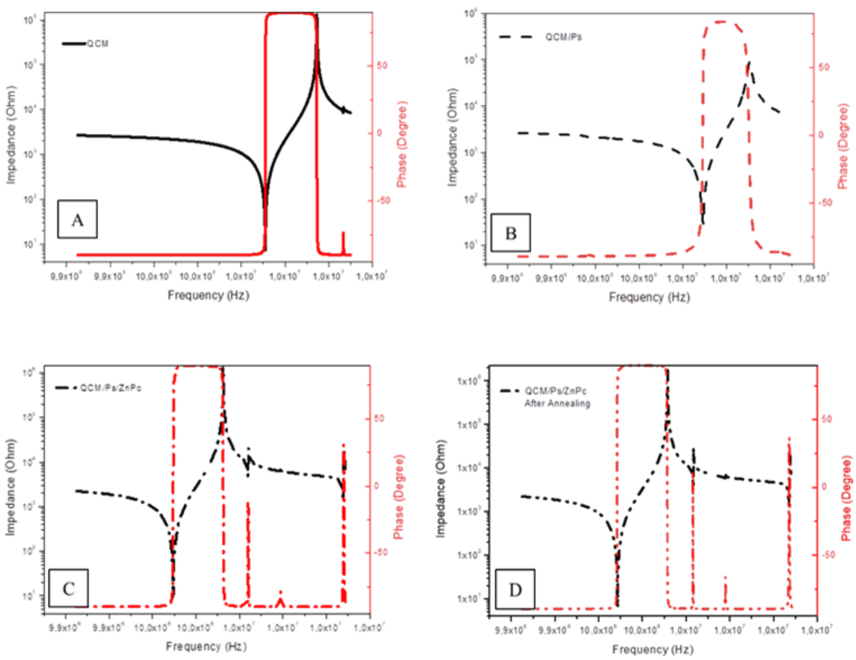

Figure 4: Impedance Curve of QCM Sensors Without Coating (A), Polystyrene Coating Using Spin Coating (B), Znpc Coating Using Vacuum Evaporation (C), and After Annealing Process (D)

Figures 3b and 3c show the morphological structure and cross-section of the QCM/Ps/ZnPc layer. The surface structure shows a fibrous layer with spherical ZnPc granules. The fibrous layer was formed from bonding ZnPc molecules to form fibers with spaces as pores in the substrate. The thickness of the fibrous layer in the cross-section was 40.8, 40, 40.5, and 41 µM. Indicate that the substrate was uniform and homogeneous. The deposition layer impedance was measured to determine the viscoelastic properties on sensors by knowing the frequency changes of the sensors.

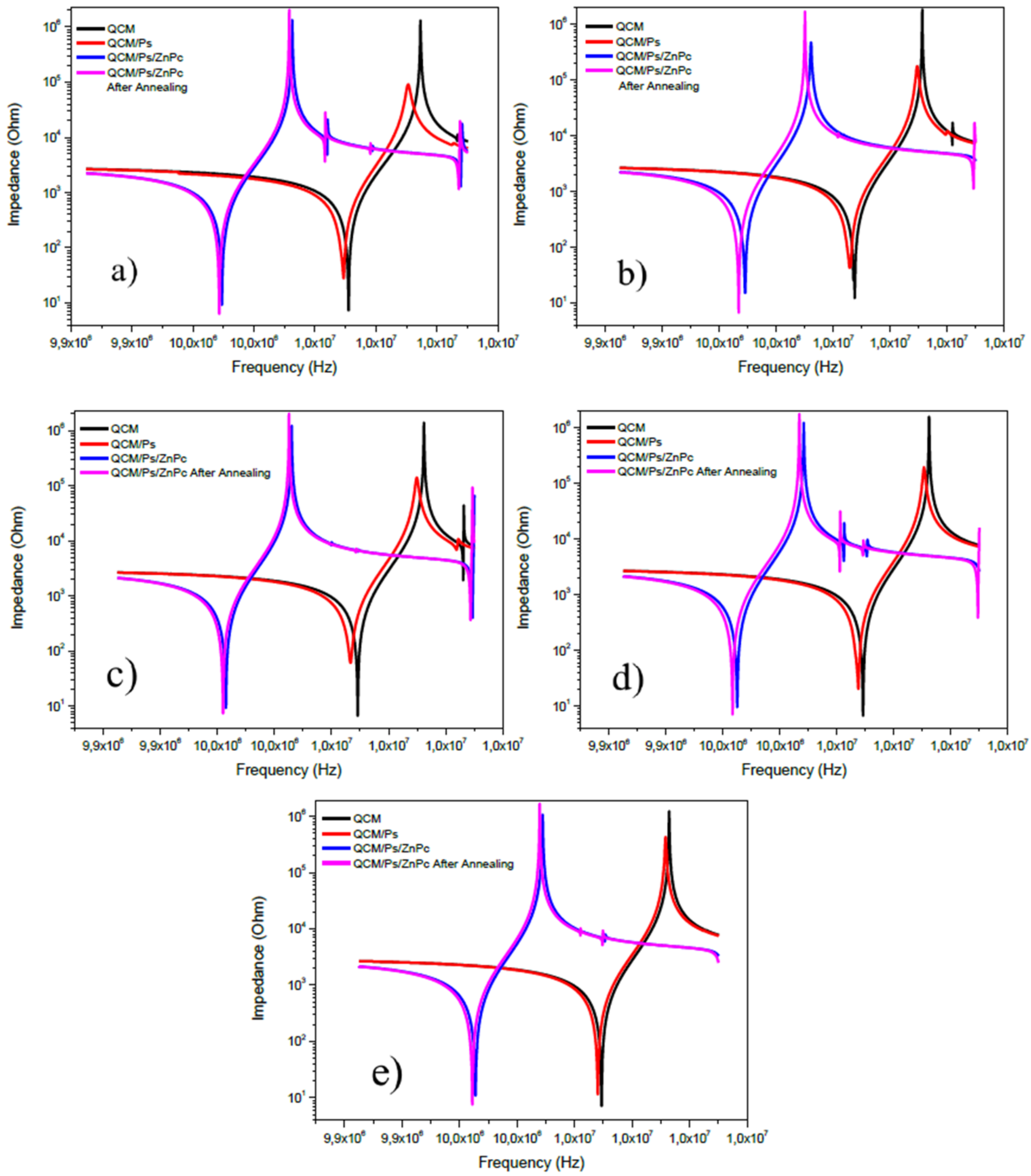

Figure 5: Frequency Changes in QCM Sensors with Variation of Deposition Time A) 1 Minutes 30 Seconds B) 1 Minutes 45 Seconds C) 2 Minutes D) 2 Minutes 20 Seconds E) 4 Minutes.

The frequency response graph created from the impedance value showed in Figure 4. The four graphs has similar shapes with the phase change at the minimum impedance and maximum impedance. The phase curve in QCM after polystyrene deposition has a different curve shape because of an increase in minimum impedance at the series resonant frequency that indicates the QCM sensor was damped. The graph of impedance to the frequency at the variation of deposition time of 1 minute 30 seconds, 1 minute 45 seconds, 2 minutes, 2 minute 20 seconds and 4 minutes shown in Figure 5. The frequency was shifted to the left when the layers adds to the sensor surface. The shift indicates a mass increase on the sensor surface after the addition of layers because of the frequency shift equivalent to the mass increase.

Table 1: Frequency changes in variations of deposition layers

Layers	Frequency Changes (Hz)				
	Deposition 1 (1 min 30 s)	**Deposition 2 (1 min 45 s)**	**Deposition 3 (2 min)**	**Deposition 4 (2 min 20 s)**	**Deposition 5 (4 min)**
QCM/Ps	1600	1800	2600	1700	1400
QCM/Ps/ZnPc	39900	36800	43600	42500	42500
QCM/Ps/ZnPc after annealing	850	2220	1030	1640	1100

Table 2: Minimum impedance values in variations of deposition layers

Layers	Minimum Impedance (Ω)				
	Deposition 1 (1 min 30 s)	**Deposition 2 (1 min 45 s)**	**Deposition 3 (2 min)**	**Deposition 4 (2 min 20 s)**	**Deposition 5 (4 min)**
QCM	7,159	6,635	6,645	12,176	7,358
QCM/Ps	11,4	20,216	60,833	42,656	27,995
QCM/Ps/ZnPc	10,883	9,508	9,224	15,133	9,238
QCM/Ps/ZnPc after annealing	7,358	7,03	7,364	6,667	6,378

The shift magnitude of the frequency shift in Table 1 shows that the increased thickness causes the frequency changes. The addition of ZnPc resulted in the series resonant frequency changes are 36.8000-43,600 Hz. The lengthy deposition time increases the mass of the ZnPc particles deposited so that the frequency changes. Table 2 shows the addition of layers provides a variation of the minimum impedance value with the highest minimum impedance at the deposition of polystyrene with a settling time of 2 minutes is 60.833 Ω. The increase in impedance detected from the upward shift in the impedance curve indicates damped sensors. The annealing process can improve QCM performance by decreasing the minimum impedance. The least minimum impedance concerned in the QCM/Ps/ZnPc layer after annealing with a deposition time of 4 minutes is 6.378 **Ω.**

The addition of layers to QCM modeled using the circuit shown in Figure 6. The mass increases because the addition of layers on QCM improves the energy dissipation during oscillation with increasing impedance value. Polystyrene has viscoelastic properties that dampen oscillation in the QCM sensor. The collapse oscillation of the QCM because the high damped affected the QCM surface to weak to identify biomolecules. The ZnPc deposition and the annealing eliminated the damping effect on the sensor because the film becomes active. The fibers organize to fill the gaps in the space that form the decrease impedance value. The decrease in minimum impedance value indicates a low damping effect means the QCM sensor does not encounter viscoelasticity.

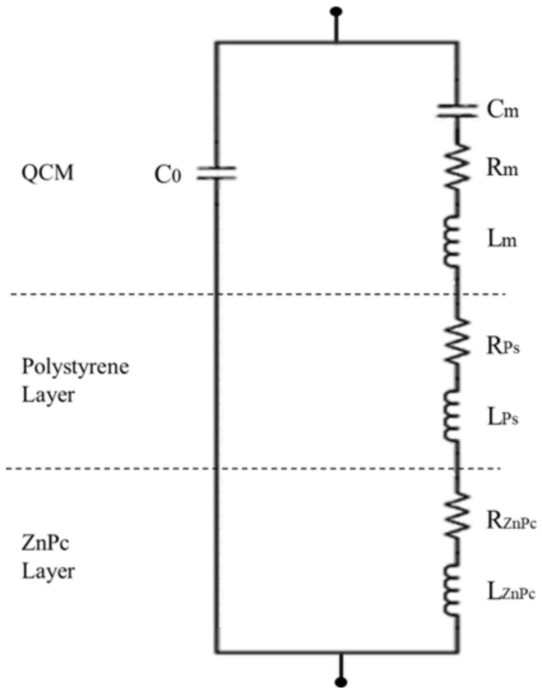

Figure 6: Circuits Models

4. Conclusion

QCM with Polystyrene deposition has a rough and porous morphology with a homogeneous coating. The addition of a polystyrene layer increases the minimum impedance by 60,833 Ω. The QCM/Ps layer deposited by ZnPc has a fibrous, small porous, and homogeneous morphology. The addition of the ZnPc layer shifts the highest series resonant frequency that indicates a mass increase. The performance of the QCM improved by the annealing sensor with reducing the damping effect that the QCM sensor does not respond to viscoelasticity and can use as a biosensor.

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References

Asai, N., Terasawa, H., Shimizu, T., Shingubara, S., & Ito, T. (2017). “Highly Sensitive Quartz Crystal Microbalance Based Biosensor using Au Dendrite Structure”. *Japanese Journal of Applied Physics*, *57*(2S2).

Didik, L. A., Rahmawati, E., Robiandi, F., Rahayu, S., & Santjojo, D. J. D. H. (2014). “Penentuan Ketebalan Lapisan Polistiren dan Zinc Phthalocyanine (ZnPc) dengan Modifikasi Persamaan Sauerbrey dan Scanning Electron Microscope (SEM)”. *Natural B*, 2(4), 331-335.

Didik, L. A. (2020). “Characteristics of QCM Coated Polystyrene and ZnPc Morphology Studied by AFM and SEM”. *In 2nd International Conference on Islam, Science and Technology (ICONIST 2019)* (pp. 134-137). Atlantis Press.

Fitriani, S. W., Masruroh, M., & Sakti, S. P. (2014). “Pengaruh Ketebalan Lapisan Zinc Phthaloacynine (Znpc) Di Atas Permukaan Polistiren/QCM Terhadap Sifat Viskoelastis Berdasarkan Nilai Impedansi”. *(Doctoral dissertation, Brawijaya University)*.

Guo, K., Jiang, B., Li, X., Wu, Y., Tian, S., Mi, C., ... & Zhao, M. (2021). “Impact on the Voltage Amplitude on Microquality Detection of QCM” in *IOP Conference Series: Earth and Environmental Science* (Vol. 651, No. 2, p. 022060). IOP Publishing.

Hori, K., Zhou, Y., Kanai, T., & Habuka, H. (2020). "Temperature Influence on Organic Molecular Interaction on Silicon Oxide Surface In Situ Measured Utilizing a Quartz Crystal Microbalance". *ECS Journal of Solid State Science and Technology*, *9*(10), 104007.

Hu, R., Zhang, K., Fan, G., Luo, Z., & Li, G. (2015). "Development of a High-sensitivity Plasticizer Sensor Based on A Quartz Crystal Microbalance Modified with A Nanostructured Nickel Hydroxide Film". *Measurement Science and Technology*, *26*(5), 055102.

Itoh, A., & Ichihashi, M. (2010). "Separate Measurement of the Density and Viscosity of A liquid using A Quartz Crystal Microbalance Based on Admittance Analysis (QCM-A)". *Measurement Science and Technology*, *22*(1), 015402.

Kanazawa, K., & Cho, N. J. (2009). "Quartz Crystal Microbalance as A Sensor to Characterize Macromolecular Assembly Dynamics". *Journal of Sensors*, *2009*.

Khusnah, N. F., Sakti, S. P., & Santjojo, D. J. D. H. (2018). "Oxygen Plasma Effect on QCM Sensor Coated Polystyrene Film". *MSE*, 367(1), 012030.

Liang, D., Zhang, J., Govindaiah, M. T., Tanguy, L., Ernst, A., Zengerle, R., & Koltay, P. (2014). "Liquid Volume Measurement Method for The Picoliter to Nanoliter Volume Range Based on Quartz Crystal Microbalance Technology". *Measurement Science and Technology*, *25*(9), 095302.

Masruroh., Djoko, D. J. D. H., Didik, L. A., Rachmawati, E., Robiandi, F., Padaga, M., & Sakti, S. P. (2015). "Modification of Polystyrene Morphology and Its influence to the Coated Zinc Phthalocyanine Layer and Frequency Change in QCM sensor". *In Materials Science Forum* (Vol. 827, pp. 257-261). Trans Tech Publications Ltd.

Mista, C., Zalazar, M., Peñalva, A., Martina, M., & Reta, J. M. (2016). "Open Source Quartz Crystal Microbalance with Dissipation Monitoring" in *Journal of Physics: Conference Series* (Vol. 705, No. 1, p. 012008). IOP Publishing.

Novianti, Z. A., Saraswati, D. A., & Astuti, S. D. (2013). "Implementasi Jaringan Saraf Tiruan Sbagai Alat Bantu Deteksi Infeksi Saluran Kemih Melalui Citra Bakteri Pada Urin". *(Doctoral dissertation, Universitas Airlangga)*.

Nurramdaniyah, N., Padega, M., Santjojo, D. H., Sakti, S. P., & Masruroh, M. (2017). "Study of Stearic Acid Layer (SA) Microstructure on Surface Quartz Crystal Microbalance (QCM) Sensors". *Natural B, Journal of Health and Enviromental Sciences*, 4(2), 105-110.

Pan, W., Huang, X. H., Chen, Q., Fan, Z. C., & Xu, Y. (2019). "Analysis and Verification of the Relationship Between the Maximum Mass Sensitivity of Quartz Crystal Microbalance and Electrode Parameters". *Chinese Physics Letters*, *36*(7), 070701.

Parlak, Z., Biet, C., & Zauscher, S. (2013). "Decoupling Mass Adsorption from Fluid Viscosity and Density in Quartz Crystal Microbalance Measurements using Normalized Conductance Modeling". *Measurement Science and Technology*, *24*(8), 085301.

Rahman, N. A. A. A., Ma'Radzi, A. H., & Zakaria, A. (2018). "Determination Of Non-Invasive Lung Cancer Biomarker By Quartz Crystal Microbalance Coated With Pegylated Lipopolymer" in *IOP Conference Series: Materials Science And Engineering* (Vol. 458, No. 1, P. 012020). IOP Publishing.

Robiandi, F., Didik, L. A., Rahmawati, E., Rahayu, S., Masruroh, M., Sakti, S. P., & Santjojo, D. H. (2014). "Effect Of Deposition Rate On Morphology Of Zinc Phthalocyanine Layer (Znpc) On Polystyrene Surface/QCM With Vacuum Evaporation Process". *Natural B, Journal Of Health And Environmental Sciences*, 2(4), 336-342.

Santjojo, D. J., Widyarti, S., & Robiandi, F. (2015). "Functionality of ZnPc Thin Film Deposited on Polystyrene Interlayer for Immobilization of Biomolecules in QCM Based Biosensor". *In Materials Science Forum* (Vol. 827, pp. 266-270). Trans Tech Publications Ltd.

Stambaugh, C., Shakeel, H., Litorja, M., & Pomeroy, J. M. (2020). “Linking Mass Measured by the Quartz Crystal Microbalance to the SI”. *Metrologia*, *57*(2), 025002.

Sutantri, R. E., Wulansari, I. H., Santjojo, D. D. H., & Masruroh, M. (2014). “Studi Pengaruh Laju Pemanasan Terhadap Morfologi Pada Penumbuhan Lapisan ZnPc Di Atas Quartz Crystal Microbalance (QCM) Dengan Metode Evaporasi”. *(Doctoral dissertation, Brawijaya University)*.

Vashist, S. K., & Vashist, P. (2011). “Recent Advances in Quartz Crystal Microbalance Based Sensors”. *Journal of Sensors, 2011*.

Wu, B., & Raghavan, S. (2019). “Removal of BTA Adsorbed on Cu: A Feasibility Study Using the Quartz Crystal Microbalance with Dissipation (QCMD) Technique”. *ECS Journal of Solid State Science and Technology*, *8*(5).