Analysis of Quartz Crystal Microbalance Sensor Array with Circular Flow Chamber

K. Jaruwongrungsee[1,2,*], **T. Maturos**[1], **P. Sritongkum**[1],
A. Wisitsora-at[1], Guest members, **M. Sangworasil**[2], and **A. Tuantranont**[1], Members

ABSTRACT

In this paper, quartz crystal microbalance (QCM) sensor array integrated with circular poly(dimethylsiloxane) (PDMS) chambers is developed for flow injection based bio-sensing. An array of QCM sensors was fabricated on a single quartz substrate by Cr/Au sputtering through shadow masks and integrated with PDMS chambers, made by PDMS based microfluidic fabrication technology. Gold electrodes of QCM sensors were functionalized with carboxylic group and flow injection analysis was conducted for protein G binding. The resonance frequencies for four sensors were continuously monitored during protein G injection in a constant flow of PBS buffer solution. It was found that there was a significant variation in resonance frequency shift responses of identical QCM sensors in the circular QCM chamber. The cause of such undesired variation was then analyzed by fluid dynamic simulation. The simulation results reveal that the flow in a circular-shaped QCM chamber is primarily turbulent. In addition, the degree of turbulence is increased with flow rate. Thus, sensors at various locations see different sample dispersions causing their sensing behaviors to be significantly different.

Keywords: Quartz crystal microbalance; QCM

1. INTRODUCTION

Quartz crystal microbalance (QCM), an ultrasensitive mass sensor based on piezoelectric effect, is one of the most powerful methods for chemical and biological sensing. QCM has a wide range of applications in many fields such as thin-film measurement, chemical analysis [1], gas sensor [2], humidity sensor [3-4], and biosensor [5]. When the electric power is applied to a pair of electrodes, sandwiched between quartz crystal, mechanical force is generated via piezoelectric effect. With this effect, quartz crystal will resonate at its natural frequency by positive feedback through oscillator circuit. The oscillation frequency depends on many factors including quartz thickness, quartz density, type of cut, ambient conditions (temperature, pressure, humidity, etc) and most importantly deposited mass.

For the reason that oscillated frequency can be changed as a function of mass, quartz crystal has been used as a kind of mass sensor. AT-cut, the most popular cut of quartz crystal, was chosen on account of its frequency stability around room temperature. In 1959, Sauerbrey derived the equation of frequency shift of the quartz resonator in gas phase [6]:

$$\Delta f = -\frac{2f_o^2}{\sqrt{\rho_q \mu_Q}} \frac{\Delta M}{A} \tag{1}$$

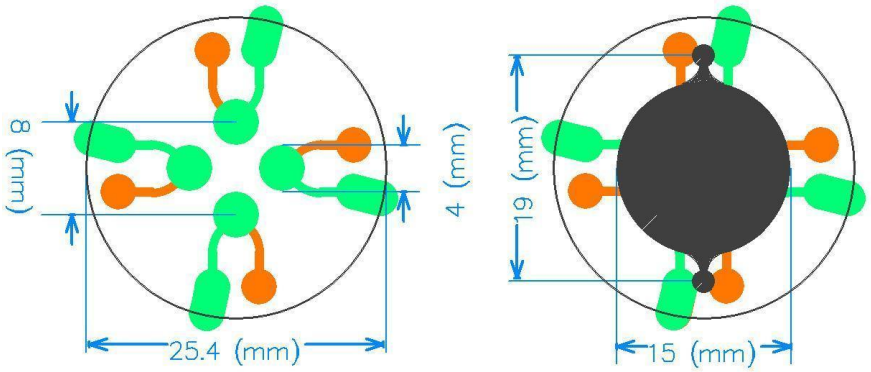
where: Δf is the frequency shift of the resonator, f0 is the fundamental frequency, ρ_q is the density of quartz (2.648 g/cm^3), μ_q is the shear modulus of quartz (2.947×1011 g/cm×s^2), ΔM is the mass deposited on the surface of electrode and A is piezoelectrically active area $(2/(\rho_q \mu_q)^{1/2}$ can be expressed as a constant, k, which is equal to 2.26×10^{-7}). This equation can describe only the added mass rigidly deposited on the electrode surface. For the attached liquid molecules, the frequency shift can be described by equation of Kanazawa and Gorgon [7], which use to find the frequency shift based on the liquid properties of the liquid on electrode surface:

$$\Delta f = -f_o^{\frac{3}{2}} \sqrt{\frac{\rho_L \eta_L}{\pi \rho_q \mu_q}} \tag{2}$$

where: ρ_L and η_L are the density and absolute viscosity of the liquid, respectively.

In the last few years, many researchers interested in QCM based sensor-array for advanced sensing applications, including electronic nose, electronic tongue and biosensor array. However, majority of reported QCM sensor arrays are still based on simple combination of single QCM sensors from different substrates [8-10]. The main problem of this scheme is the mismatch characteristics among QCM devices due to different piezoelectric properties, quartz-thickness, temperature, pressure, mass and material properties of electrode layers. To min-

* Corresponding author.
Manuscript received on January 29, 2009.,
[1]1Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center, Thailand
telephone: +662-564-6900 ext.2108, Fax: +662-564-6756
[2]Department of Electronics, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Thailand
E-mail addresses: kata.jaruwongrungsee@nectec.or.th (K.Jaruwongrungsee) adisorn.tuantranont@nectec.or.th (A. Tuantranont)



(a) (b)

Fig.1: *Schematic of QCM sensor array (a) electrode layout and (b) electrodes superimposed by PDMS*

imize the matching problem, QCM sensors in an array should be fabricated on the same quartz substrate under the same process parameters and conditions [11-12]. In addition, the effect of environmental conditions including temperature and humidity can be greatly reduced by employing one QCM in the matched array as the reference sensor so that the change in QCM characteristics due to ambient parameter can be effectively canceled. In this work, a QCM based biosensor array is integrated with poly(dimethylsiloxane) (PDMS) microfluidic platform for flow-injection based detection.

2. SENSOR FABRICATION

2.1 QCM Sensor Array Fabrication

An array of QCM sensors was fabricated on a single disc of 1-inch 5 MHz AT-cut quartz crystal substrate. The number of QCM sensors on a quartz substrate was designed as 4 and the patterns of electrode pair were laid out symmetrically within 1-inch circle as illustrated in Figure 1 (a). Since QCM electrodes were located on both sides of quartz disc, it is difficult to make electrical connection for testing. To circumvent this problem, the electrode layouts for both sides were made different. The back side patterns contain contact pads for both electrodes while the front side patterns have no contact pad but have connection line that run to the pad onto the other side of quartz disc through the circumference. The Cr/Au electrode was deposited on quartz substrate by sputtering through electroplated microshadow-mask. Microshadow-mask was fabricated by Ni electroplating on photoresist-patterned stainless-steel plate. The standard dry-film photolithography process was used to produce photoresist pattern of electrode designs on stainless steel plate. Uncovered area on stainless-steel plate was then coated by 40 m thick Ni film by electroplating process. Ni electroplating was conducted in Nickel sulphate plating solution for 4 hours. Nickel shadow masks were obtained by removing the photoresist by sodium hydroxide solution and detached the nickel film from stainless steel plate.

Before QCM electrode deposition, blank quartz disc substrates were cleaned in piranha solution (1:4 mixture of 50% H2O2 and 97% H2SO4) at 120 oC for 10 min. The shadow mask was then aligned and attached on a blank quartz disc by a permanent magnet. The chromium (Cr)/ gold (Au) layers were deposited on one side of quartz substrates by sputtering through the first set of electroplated microshadow-masks. The Cr and Au layers were successively sputtering under argon dc plasma. Before each sputtering run, the substrate was cleaned by 75W RF plasma for 5 min to improve adhesion to underlying material. The sputtering pressure, sputtering current and time for chromium were 3x10-3 mbar, 0.2 A and 2 min, respectively. Next, gold was sputtered under the same current and pressure for 10 min. The 50 nm-thick Cr and 300 nm-thick Au layers were obtained. The other Cr/Au layers were then sputtered on the other side of quartz disc through the second set of microshadow-masks. The second shadow masks were aligned to the first pattern via a cross marker at the center of the disc.

2.2 PDMS Micro Chamber Fabrication

Silicon wafer were cleaned in piranha solution at 120 oc for 10 min, carefully rinsed several time in deionized water and dried with gentle stream of air. After that silicon wafer were dehydrated at 150-200 oC for 10 min. SU-8 photoresist was spin-coated on silicon wafer using a spin coater (Laurell technologies corp. model WS-400A-6NPP), then soft baked to remove all the solvent in the layer. The photoresist coated wafers were exposed using MJB4 mask aligner (SUSS microtec) then post-baked in order to selectively cross-link the exposed portions of the film. The sample was left in the desiccators to cool down slowly at room temperature for more than 13 hours.

Finally sample was developed, cleaned with deionized water and isopropyl alcohol and gently dried with air. Spin speed, exposure time, baked time and developing time were optimized to achieve a smooth surface on mold. The SU-8 mold thickness was investigated by interferrometer (Polytec MSA400), the measured result show that the mold thickness is 214.9 μm.

Sylgard 184 Silicone Elastomer kit (Dow Corning), consisting of PDMS was prepared by mixing the precursors sylgard with a curing agent at a ratio of 10:1 by volume. The prepolymer mixture was degassed at 20-50 mTorr in ambient temperature desiccator with a mechanical vacuum pump for 10 min to remove any air bubbles in the mixture. PDMS mixtures were gradually poured onto the SU8 master mold to the height over the depth of designed chamber. Next, PDMS slab was cured at 80 oc for 3 hour. Finally, it was peeled-off from the mold. Figure 2 shows the photograph of fabricated QCM sensor array with PDMS chamber.

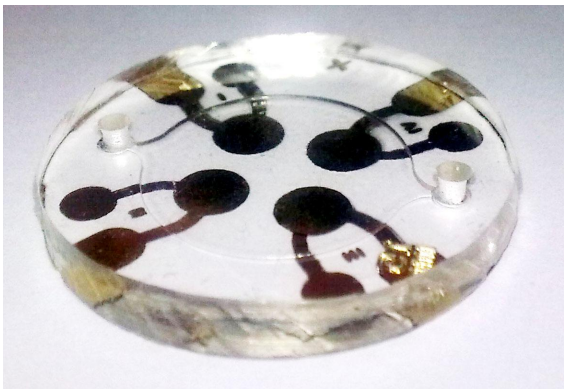


Fig.2: *QCM sensor array with PDMS chamber*

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

The sensor array was prepared for protein G binding. The surface of gold electrode was functionalized with carboxylated polyvinyl chloride (PVC-COOH) by self-assembly monolayer (SAM) technique. Flow injection measurement was conducted for protein G binding. The resonance frequencies for four sensors were continuously monitored during protein G injection in a constant flow of PBS buffer solution. It was found that there was a significant variation in resonance frequency shift responses of identical QCM sensors, as shown in table 1. In order to analyze this problem, computational fluid dynamics (CFD) simulation is used to design and simulate sample transport in flow injection QCM sensing system.

The 3D-simulation of fluid flow through QCM sensors was performed by ANSYS program. Figure 3 illustrates the finite element model of QCM chamber with circular design. The fluid dynamic simulation was carried out by imposing a constant sample flow rate condition throughout the chamber.

Table 1: *Measured frequency shift from the experiment*

Sensor Number	Measured Frequency Shift (Hz)
1	52
2	44
3	163
4	73

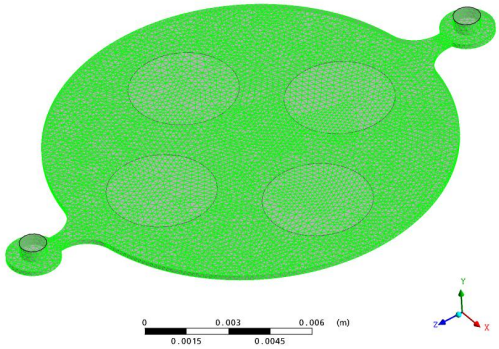
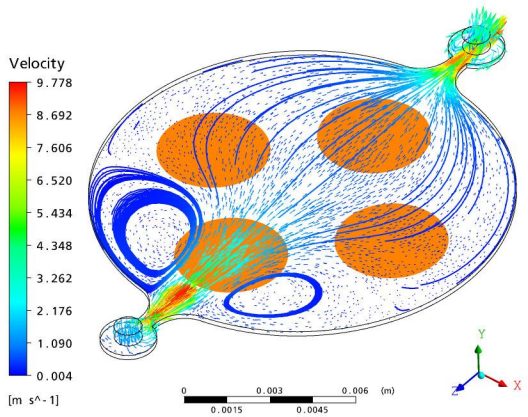


Fig.3: *Meshed circular design of sensor chamber*

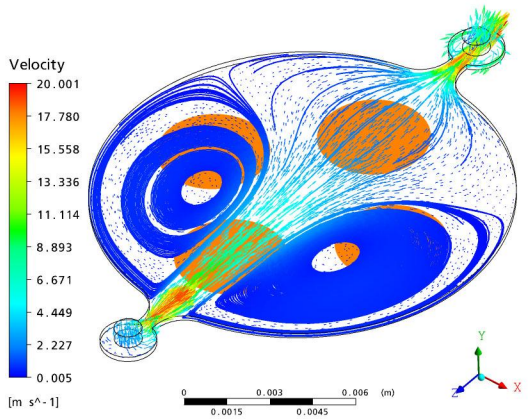
Figure 4 shows sample dispersion trajectories at various flow rates including 50 μl/min and 100 μl/min. Simulation results show that the flow in this circular-shaped QCM chamber design is primarily turbulent. In addition, the degree of turbulence is increased with flow rate. The sample dispersion especially on both far sides of chamber where sensor electrodes are located is nonlinear. The sensors at various locations see different sample dispersions causing their sensing behaviors to be significantly different. Thus, the simulation results can explain the observed signal variation among four QCM sensors in the circular PDMS chamber. In order to solve this problem, QCM chamber will be redesigned with different geometries and the results will be presented elsewhere.

4. CONCLUSIONS

In conclusion, quartz crystal microbalance (QCM) sensor array integrated with poly(dimethylsiloxane) (PDMS) chambers has been designed and fabricated for flow injection based bio-sensing. It was found that there was a significant variation in resonance frequency shift responses of identical QCM sensors in the circular QCM chamber. The cause of such



(a)



(b)

Fig.4: *The geometries of turbulent flow effect inside circular chamber in 3D simulations and velocity variation over the sensor surface at different flow rate (a) 50 µl/min, (b) 100 µl/min*

undesired variation was then analyzed by fluid dynamic simulation. Fluid dynamic simulation of QCM chamber shows that the sample flow in circular QCM chamber is turbulent. The results can explain the observed significant variation in sensing responses of identical QCM sensors. In the future, QCM chamber will be redesigned with different geometries to obtain laminar flow through all sensor electrodes so that every sensor experiences the same sample dispersion under a constant flow condition.

5. ACKNOWLEDGMENT

This project is funded by NECTEC's Sensor Platform Technology under QCM sensor for food safety project. The authors would like to acknowledge with gratitude to Dr. Chamras Promptmas at Mahidol University for information supporting. Moreover, we would like to thanks Asia Institute of Technology (AIT) for the use of simulation software and hardware.

References

[1] J. Rabe, S. Buttgenbach, J. Schroder, and P. Hauptmann, "Monolithic miniaturized quartz microbalance array and its application to chemical sensor systems for liquids," *IEEE Sensors Journal*, Vol. 3, pp. 361 - 368, August 2003.

[2] Masashi Kikuchi, Katsuya Omori, and Seimei Shiratori, "Quartz Crystal Microbalance (QCM) Sensor for Ammonia Gas using Clay/ Polyelectrolyte Layer-by-Layer Self-Assembly Film," *IEEE Sensors Proceedings 2004*, vol. 2, pp. 718-721, October 2004.

[3] K. Jaruwongrungsee, A. Wisitsoraat, T. Lomas and A. Tuantranont, "Humidity sensor utilizing multiwalled carbon nanotubes coated quartz crystal microbalance," *The 2nd IEEE Nanoelectronics Conference*, pp. 961-964, March 2008.

[4] H. Ito, S. Kakuma, R. Ohba, and K. Noda, "Development of a humidity sensor using quartz crystal microbalance," *SICE Annual Conference 2003*, pp. 1175-1178, August 2003.

[5] Robert B. Towery, Newton C. Fawcett, and Jeffrey A. Evans, "Determination of chloroplast DNA in a cultured soybean line using a QCM biosensor," *IEEE Sensors Journal*, Vol. 4, pp. 489 - 493, August 2004.

[6] G. Sauerbrey, "Use of vibrating quartz for thin weighing and microweighing," *Z. Phys.*, vol.155, p.260, 1959.

[7] K.K. Kanazawa and J.G. Gordon, "The oscillation frequency of a quartz resonator in contact with a liquid," Anal. Chim. Acta., vol. 175, p.99, 1985.

[8] A.Yuwono, and P. Schulze Lammers, "Performance Test of a Sensor Array - Based Odor Detection Instrument," *Agricultural Engineering International: the CIGR Journal of Scientific Research and Development*, May, 2004.

[9] Pengchao Si, John Mortensen, Alexei Komolov, Jens Denborg, and Preben Juul Moller, "Polymer coated quartz crystal microbalance sensors for detection of volatile organic compounds in gas mixtures," *Analytica Chimica Acta*, Vol. 597, pp. 223-230, 2007.

[10] I.A. Koshets, Z.I. Kazantseva, and Yu.M. Shirshov, "Polymer films as sensitive coatings for quartz crystal microbalance sensors array," *Semiconductor Physics, Quantum Electronics & Optoelectronics*, Vol. 6, pp. 505-507, 2003.

[11] A. Palaniappan, Xiaodi Su, Francis and E.H. Tay, "Quartz sensor array using mesoporous silica hybrids for gas sensing applications," *Proc. 2005 IEEE Sensors*, pp. 1312-1315, 2005.

[12] K. Jaruwongrungsee, T. Maturos, A. Wisitsoraat, C. Karuwan, T. Lomas, A. Tuantranont, "Fabrication and Characterization of QCM Gas Sensor Array on Single Quartz Disc," *The 4th Asia Pacific Conference on Transducers and Micro/Nano Technologies (APCOT'08)*, pp. 168, June 2008.

Kata Jaruwongrungsee received the B.Eng. and M.Eng. degree in electronics engineering from King Mongkut's Institute of Technology Ladkrabang (KMITL), Thailand, in 2003 and 2005 respectively. Since 2006, he has been with the Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center (NECTEC), Thailand, as an assistant researcher. Presently, he is also doing his Ph.D. on electronics engineering at KMITL. His research is mainly focused on QCM based gas sensors and biosensors.

Thitima Maturos received the B.S. degree in physics from Thammasat University, Pathumthani, Thailand in 2002 and the M.S. degree in Physics from Mahidol University, Bangkok, Thailand in 2006. Since 2006 she has been with Nanoelectronics and MEMS Laboratory, National Electronics and Computer Technology Center (NECTEC), Thailand, where she is now assistant researcher. Her research interests include microfabrication, cell manipulation and Lab-on-a-chip.

Pornpimol Sritongkum received her Ph.D. in electroanalytical chemistry from Cranfield University (United Kingdom) in 2002. Her current research is focused on the surface modification of QCM- and electrochemical biosensors and on the development of development of novel diagnostic devices.

Anurat Wisitsora-at received his Ph.D., M.S. degrees from Vanderbilt University, TN, U.S.A., and B. Eng degree in electrical engineering from Chulalongkorn University, Bangkok, Thailand in 2002, 1997, and 1993, respectively. His research interests include microelectronic fabrication, semiconductor devices, electronic and optical thin film coating, sensors, and micro electromechanical systems (MEMS).

Manas Sangworasil was born in Bangkok, Thailand in 1951. He received the bachelor of engineering and Master o Engineering from King Mongkut's Institute of Technology at Ladkrabang, Bangkok, Thailand in 1973 and 1977 respectively, and the D. Eng (Electronics) from Tokai University, Japan, in 1990. Following his graduate studies, he worked almost 28 years at Electronic Department, Faculty of Engineering, King Mongkut's Institute of Technology at Ladkrabang, Bangkok where he is currently an associate professor. His research interest are in the area of image process with emphasis on Image Reconstruction, 3D modeling, Image Classification and Image Filtering.

Adisorn Tuantranont received the B.S. degree in electrical engineering from King Mongkut's Institute of Technology Ladkrabang, Thailand, in 1995, and the M.S. and Ph.D. degrees in electrical engineering (laser and optics) from the University of Colorado at Boulder in 2001. Since 2001, he has been the director of the Nanoelectronics and MEMS Laboratory, National Electronic and Computer Technology Center (NECTEC), Pathumthani, Thailand. He also serves on the founding committee of the National Nanotechnology Center (NANOTEC), the first nanotechnology center in Thailand, under the Ministry of Sciences and Technology. His research interests are in the area of microelectro-mechanical systems (MEMS), optical communication, laser physics, microfabrication, electro-optics, optoelectronics packaging, nanoelectronics, and lab-on-a-chip technology. He has authored more than 60 international papers and journals and holds five patents. Dr. Tuantranont received the Young Technologist Award in 2004 from the Foundation for the Promotion of Science and Technology under the patronage of H. M. the King.