ARTICLE
JOURNAL OF UNIVERSITY OF BABYLON
For Pure and Applied Sciences (JUBPAS)
Vol.30; No.2.| 2022

Novel Trend in Development of QCM System Based on Analysis of Adsorption Kinetics

Ali Al-Jawdah[1]

1Babylon University, Collage of Sciences, Iraq.

*Corresponding author email: aalimadlol@yahoo.com; mobile: 07807272365

Received:	19/ 2 /2022	Accepted:	30 /3 /2022	Published:	30 /6 /2022

ABSTRACT

In this work, modern approach was demonstrated which is improving the performance of gas sensors that utilize the quartz crystal microbalance technique. The gas sensors based on quartz crystal microbalance (QCM) are one of the common methods using for gas sensor applications. Although, these QCM sensors posses high sensitivities, its ability to discriminate the target gas still need to develop. It does not have the ability to identify or distinguish the type of gas. The idea of this work depends on investigating and invest the kinetics of the diffusion and adsorption thermodynamics gas molecules to identify gas species. So, the relationship between the parameter of the dynamic adsorption and chemisorption thermodynamic parameter were employed to know the concentration and type of the gases. The sensor was coated Polydimethylsiloxane (PDMS) ultrathin films are prepared via spin coating system, and micro incision via lithographic methods has been created on the PDMS film. In order to enhance the selectivity of the sensor. The outcome data prove the methology was working and considerable. Nevertheless, there are insufficiency. The gas molecules distinction was made possible by analysis the response signal. In particular, observing and taking into account the difference and change in the time constant. Where note a difference in the time constant due to present of the micro-pattern layer.

Key words:: Sensors, Quartz crystal, Polyemers, Thin film, SPR system.

INTRODUCTION

Recently, monitoring of pollution from gases has been a relevant topic in a lot of applications such as environmental science, chemical industry, and safety considerations. In this context, developmental the sensing devices and platforms, particularly in terms of sensitivity, selectivity and performance are on the demand for future and current applications. Moreover, most of gas sensors today are still far to provide optimum performance, which is required for industrial and environmental requirements. In recent years, the progression of nanomaterial and microelectric fields has enabled opening new directions for the development of these sensors. Therefore, researchers starts employ these techniques to improve sensors [1-2].

Quartz Crystal Microbalance (QCM) Quartz Crystal Microbalance (QCM) is considered one of the most promising technique, it is an extremely sensitive mass balance, has the ability to detect nanogram to microgram level changes.

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com

مجلة جامعة بابل للعلوم الصرفة والتطبيقية مجلة جامعة بابل للعلوم الصرفة والتطبيقية مجلة جامعة بابل للعلوم الصرفة والتطبيقية

The working principle of a QCM is based on the piezoelectric phenomenon that was discovered in 1880. Which can be summed up as; when a certain crystal such made of quartz or topaz is exposed to mechanical stress an electric potential difference is generated on both sides of it that is proportional to the amount of applied stress, and opposite, a mechanical deformation generated when voltage is applied to these crystalline materials. Later discovered that if voltage is applied on crystal sandwich between two metal electrodes, the crystal starts oscillates in specific frequency. The frequency of the generated vibration will have a specific value depend on the structure and thickness of the crystal, and given by[3]:

$$f = \frac{c_q}{2d} \quad (1)$$

Where f is the frequency, d is the thickness of the crystal, and c_q sound speed.

Equation 1 shows an increasing the thickness of the crystal as a result of the deposition of any material on the crystal surface will be reflected in a decrease in resonance frequency. Since this has been discovered, which resulted in finding a relationship between the mass increase and the change in resonance frequency, It has been realized that it can be QCM employed as a mass detector.The practically inferred relationship between the change in mass and the resonance frequency is called the Sauerbrey equation[3-4]:

$$\Delta f = -\frac{2f_0^2}{\sqrt{\rho_Q \mu_Q}}\frac{\Delta m}{A} \quad (2)$$

Where Δf the shift in resonant frequency ρ_Q Crystal density, μ_Q Shear stress of quartz, f_o Fundamental frequency, Δm mass change amount. According to equation 2, can be defined the sensitivity of the system to mass detecting as [5-6]:

$$S_m = \frac{\Delta f}{\Delta m} \quad (3)$$

Beside the fundamental resonance frequency, the QCR generates frequency higher the resonance frequencies known as harmonics. These frequencies are generated in odd multiples of the fundamental resonant frequency because of the nodes of the wave inside the crystal. According to above the QCM detects the deposited mass changes,regardless kind of the material, so that it called a non-specific sensor.

To modify the system and make it specific sensor for certain molecules, coating layer deposit on the crystal surface in order to select and absorb targeted molecules. There are a variety of materials have been suitable for deposition on the surface of the crystal to employ it as a sensor to a specific target material. To some extent the deposited layer can be chosen to allocate the system towards a specific substance. However, it is still not easy to provide more details of the captured gas. Most of QCM which modified surface sensors show very good response for several types of gas at the same time. Therefore, still the the eclecticism is the weak point of this kind of sensor. Most of the previous papers is discussed the gas detection relaing on the quantity of adsorption, in other words, the highest variance of the peak in adsorbing mass. Which is widely utilized as a important parameter for display the performance of QCM system [7,8 and 9].

Moreover, the absorpting of molecules to the QCM system accompanied by the process of, which is a thermodynamic parameter, Therefore, various types molecule will show various kind of kinetic, also if they have same amount of concentration. So that, analysis and tracking of kinetic and thermodynamic behavior during the adsorption process would this be important method of gas discriminate [9-10].

In this work QCM chip has been modified by zinc hydroxystannate has been employed to measure three kinds of gas. Based on QCM sensor coated by ZSH film. When this QCM sensor exposed to these gases, it will give similar responses for all them, and impossible to know what the kind of the gas. So that, in this work ZSH was used to modify the QCM system and investigate the possibility of employing this new

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com

analysis approach (adsorption dynamic) to distinguish between the kinds of gas. In order to add the discrimination ability to these system.

Physical Structure

Quartz Crystal Microbalance system is consisting of two electrodes with a piezoelectric crystal among them Fig. (4). Normally silicon oxide crystal is used, so if alternating potential applied to these electrodes at the same value of the resonant frequency the crystal will be oscillate intensified, stably and result the high Q factor Fig. (1).

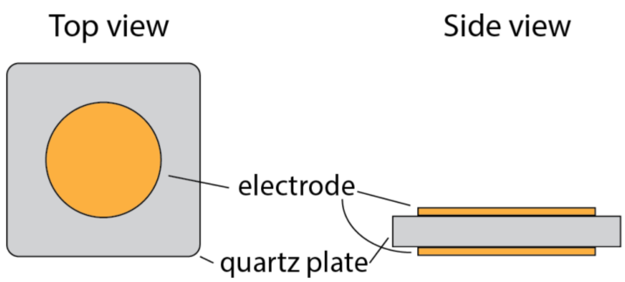

Figure 1. Basic structure of QCM.

The mode of vibration, and the characteristics of the QCM depends on the angle (relative to its axes) at that the crystal is cut. Typically, AT-cut (Figure 2) is the most common to make of the QCM crystal, and this mode of cutting is also widely available commercially available because it is used in electronic instruments. It is characterized by thermal stability at room temperature and suitable to work in the thickness-shear mode.

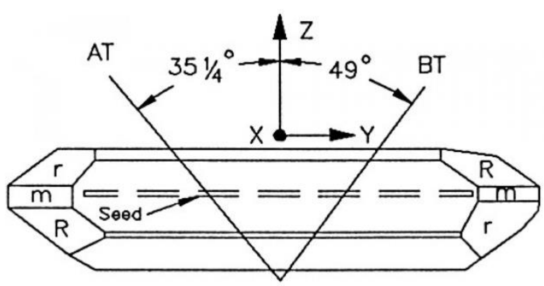

Figure 2. AT-cut Quartz crystal

In this operation mode, the displacement of the crystal will be perpendicular to the crystal thickness Figure 3. This will be done by crystal cutting at an angle of 35∘15′ to the crystal z-axis. The frequency–temperature curve Fig.3. Shows that there is an inflection point at 25 ∘C, that means this kind of crystal cutting has a low temperature coefficient at room temperature [11].

The fundamental frequency for this kind of crystal cutting is normally between 1 and 30 MHz. Moreover, QCM can also work at overtone mode. One of the best advantages of this QCM is the high of Q factor which can be up to ten [12].

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com

ARTICLE
JOURNAL OF UNIVERSITY OF BABYLON
For Pure and Applied Sciences (JUBPAS)
Vol.30; No.2.| 2022

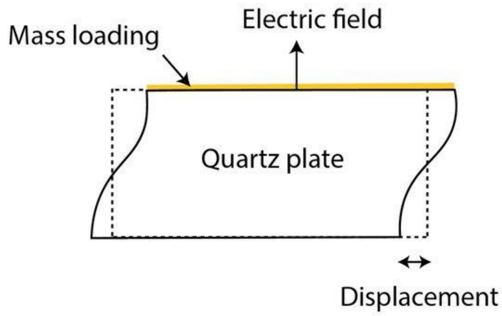

Figure 3. Thickness shear mode of QCM.

The fundamental frequency for this kind of crystal cutting is normally between 1 and 30 MHz. Moreover, QCM can also work at over tone mode. One of the best advantages of this QCM is the highest Q factor which can be up to ten [13]. The natural frequency of the QCM depended on the thickness of the quartz crystal and the cutting angle. The thickness-shear oscillation mode when the direction of displacement and quartz thickness in perpendicular state, in this case the maximum amplitude of the displacement will be at quartz plate surface Figure 3 [14].

RESULTS AND DISCUSSION

In this work, QSM system was installed (Figure 4), and prepared to measure three types of gas A, B and C. The structure and morphologies of the crystal were tested in the beginning using XRD and SEM. The XRD pattern shows most of the peaks look coincided perfectly with ZSH stander, and confirmed the structure is a as-synthesized with a typical “face centered cubic”. Moreover, intensity and peaks altitude indicate that ZSH was very crystallized.

The response of the modified sensor to different concentrations of A, B and C are shown in figure 4. The response curves were plotted as mass variation vs. time. The results confirm that the QCM modified sensor was very sensitive to all these three gases, and it is clear that the adsorbed mass increases with an increase of volume fraction for all these gases. The response curves show that the processes of desorption and adsorption had good reversibility, which means the ZSH is proper enough material to use in gas detection systems. Meanwhile, this adsorbing behavior demonstrates significant differences in the rate of mass adsorbing these (a, B and C) gases at the same concentration.

Particularly, gas A displayed the highest mass absorption rate, while the smallest rate has been observed for B gas. Most of the published works for other researchers shows similar data. However, they presented it to characterize the adopting process, from which can be acquired only limited information. In particular, the lack of selectivity, and hard to distinguish.

There is potential for exploitation and employment the thermodynamic characteristics and adsorption kinetics data to To enhance the distinction and selectivity features because these parameters are determind and controlled by both sensor materials and gas molecules. So, analysis of adsorption processes data can give more information.

The three gas adsorption processes in line with a “second-order model”. So, to adsorp processing obeys the “second order model”, should be conformed to this relationship:

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com

$$\frac{t}{Q_t} = \frac{1}{k} Q_{e,cal}^2 + \frac{1}{Q_{e,cal}} t \qquad (4)$$

where Qe,cal is the “equilibrium adsorption amount” which can be take it the calculations, k is the constant of adsorption rate.

Figure 3a gives the relation ($\left(\frac{t}{Q_t}\right) \backsim t$) for 3% of A, in which the fitting have a good linearity, this means the adsorption process of 3% O2 is a second-order. Therefore, the following equation can give the slope and intercept:

$$Q_{e,cal} = \frac{1}{a} \qquad (5)$$

$$k = \frac{1}{b} Q_{e,cal}^2 \qquad (6)$$

A and b is the value of the slope and intercept of the fitting equation. The term K represents the constant adsorption rate of the gas on the surface of the sensor. Herein, the equation of the mass absorb in molar and the absorption constant rate were used as attempt to provide selective ability. The behaviour of the adsorbed mass amount and k for these three gases in different concentrations are presented in Figure 3(b). All the dots in the four corresponding to a specific gas are linear. The plot shows all dots that belong each a specific gas are linear. The figure also displays that a gas with specific concentration and characteristics can be sitting in a certain position in the plane coordinates, which means different gases are located at different zone of the plane.

Therefore, if the analysed data of an unknown gas (which is one of these three gases) have been put in this plane coordinates, it will be possible to characterize its type and concentration. However, this method still limitations because of the overlap when the range of the concentration widening.

So that, another new analysis approach has been offered, that based on the data of adsorption thermodynamics. In this method the time to reach to 95 of the “maximum adsorption” TT, and “the maximum amount” of adsorption was used to identify the unknown gas as shown in figure 4.

EXPERIMENTAL

In a typical procedure, a commercial AT-cut 9 MHz QCM with Au electrodes was prepared by cleaning with ethanol for 20 min. Then rising in distilled water and desiccation in 25 C temperature using a nitrogen gas. On the other hand, For spin coating and manufacturing of PDMS thin films, The elastomer was dissolved in tetrahydrofuran (THF), then subject to shaking for 12 hours to make a “stock solution” of 15 % (w/w) Polydimethyl siloxane. From stock solution, polydimethyl siloxane solutions with concentrations in rang from 0.1 – 0.9 % (w/w) have been prepared, by diluting it with toluene and follow that by stirring for 12 hours.

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com

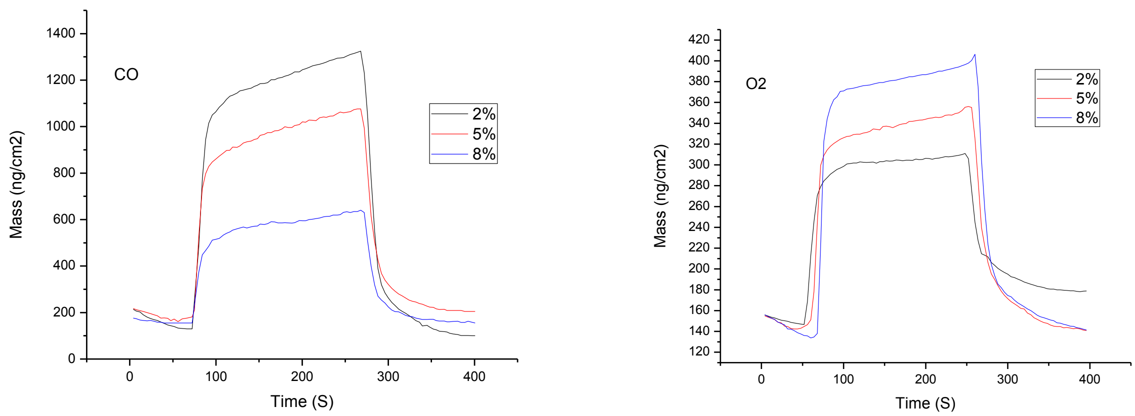

Figure 3. Response signals to different concentrations and gases

120 µl of PDMS solution has been used to deposit on a cleaned static substrate (Au electrode of the QCM), then subject to rotate at a spinning speed of 6000 revolutions per minute (rpm), then accelerated of 2500 rpms-1 for 60 s. The coated films were subsequently cured in a vacuum oven at 80 °C for 12 hours. Subsequently, the coated films were subjected to heat treatment in a vacuum oven at 80 °C for 12 hours. To make the micro pattern in the coated film, Patterned deposition of cellulose on PDMS surfaces by using of UV/ozone and lithographic method.

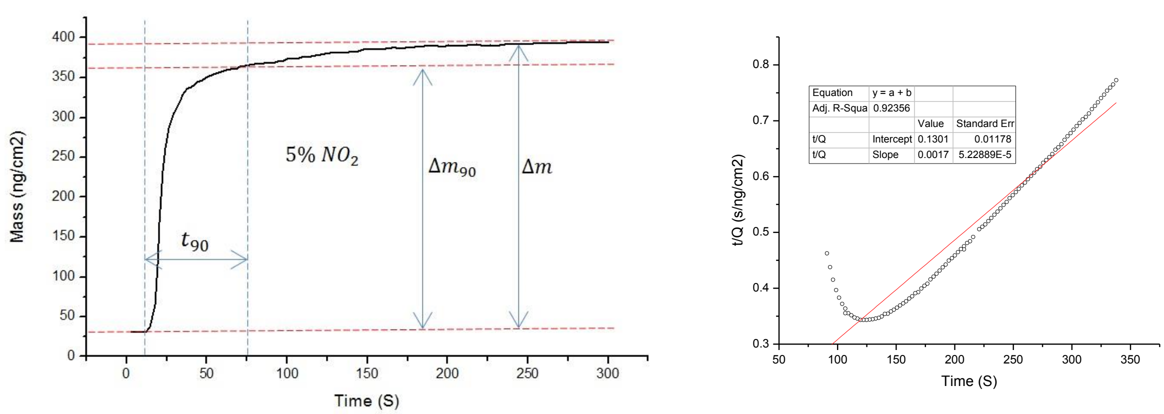

Figure 4. Response dynamics analysis

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com
مجلة جامعة بابل للعلوم الصرفة والتطبيقية

Conflict of interests.

There are non-conflicts of interest.

References

1.A. Kaushik, R. Kumar, S. K. Arya, M. Nair, B. D. Malhotra and S. Bhansali, Chem. Rev., 2015, 115(11), 4571.
2 . D. Compagnone, M. Faieta, D. Pizzoni, C. D. Natale, R. Paolesse, T. V. Caelenberg, B. Beheydt and P. Pittia, Sens. Actuators, B, 2015, 207, 1114–1120.
3. M. Procek, A. Stolarczyk, T. Pustelny and E. Maciak, Sensors, 2015, 15, 9563.
4. V. A. Minh, L. A. Tuan, T. Q. Huy, V. N. Hung and N. V. Quy, Appl. Surf. Sci., 2013, 265, 458.
5. N. A. Masdor, Z. Altintas and I. E. Tothill, Biosens.Bioelectron., 2016, 78, 328. Open Access Article. Published on 05 October 2017. Downloaded on 05/10/2017 13:49:30.
6 .S. ¨Ozt¨urka, A. K¨osemen, Z. A. K¨osemen, N. Kılınc, Z. Z. ¨Ozt¨urk and M. Penza, Sens. Actuators, B, 2016, 222, 280–289.
7. M. Yang and J. He, Sens. Actuators, B, 2016, 228, 486–490. 8 C. Chen, X. Zheng, J. Yang and M. Wei, Phys. Chem. Chem. Phys., 2014, 16, 20073–20078.
9. W. H. Feng, Z. X. Pei, Z. B. Fang, M. L. Huang, M. L. Lu, S. X. Weng, Z. Y. Zheng, J. Hu and P. Liu, J. Mater. Chem. A, 2014, 2, 7802–7811.
10. H. Zhang, P. Song, D. Han and H. Yan, Sens. Actuators, B, 2015, 209, 384.
11. H. Wang, X. X. Liu, J. Xie, M. Duan and J. L. Tang, J. Alloys Compd., 2016, 657, 691–696.
12. H. Wang, X. X. Liu, J. Xie, M. Duan and J. L. Tang, Chin. Chem. Lett., 2016, 27, 464–466.
13. R. Tseng, P. Wu, F. Wu and R. Juang, Chem. Eng. J., 2014, 237, 153–161.
14. Y. Liu, Colloids Surf., A, 2008, 320, 275–278.

ISSN: 2312-8135 | Print ISSN: 1992-0652
info@journalofbabylon.com | jub@itnet.uobabylon.edu.iq | www.journalofbabylon.com