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A High-Q Quartz Crystal Microbalance with Mass Sensitivity up to 10^{17} Hz/kg *

Qiao Chen(陈桥), Xian-He Huang(黄显核)**, Wei Pan(潘威), Yao Yao(姚尧)
School of Automation Engineering, University of Electronic Science and Technology of China, Chengdu 611731

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A high-Q quartz crystal microbalance (QCM) sensor with a fundamental resonance frequency of 210 MHz is developed based on inverted mesa technology. The mass sensitivity reaches 5.332×10^{17} *Hz/kg at the center of the electrode, which is 5–7 orders of magnitude higher than the commonly used 5 MHz or 10 MHz QCMs (their mass sensitivity is* 10^{10}–10^{12} *Hz/kg). This mass sensitivity is confirmed by an experiment of plating 1-ng rigid aluminium films on the surface of the QCM sensor. By comparing the changes in QCM equivalent parameters before and after coating the aluminum films, it is found that the QCM sensor maintains the high-Q characteristics of the quartz crystal while the mass sensitivity is significantly improved. Therefore, this QCM sensor may be used as a promising analytical tool for applications requiring high sensitivity detection.*

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Quartz crystal microbalance (QCM) consists of a thin vibrating AT-cut quartz wafer sandwiched between two metal electrodes (always, Au), which is used to measure real-time ultra-small masses in various fields (including chemical fields,[1–3] biomedical fields,[4–6] food fields,[7–9] and other fields[10–13]), due to unprecedented simple structure, high sensitivity, low cost, and operational capability in both gas and liquid phases.[14–17]

Mass sensitivity is a vital parameter in quantitative analysis of QCM applications, and was given by the Sauerbrey equation describing the mass–frequency relationship on the surface of the QCM,[18]

$$\Delta f = -\frac{2f_0^2}{A(\rho_q \mu_q)^{1/2}} \cdot \Delta m = -C_{\rm QCM} \cdot \Delta m, \qquad (1)$$

with

$$C_{\rm QCM} = \frac{2f_0^2}{A(\rho_q \mu_q)^{1/2}},$$

where Δm and Δf are the mass change and frequency shift, respectively; $C_{\rm QCM}$ is the mass sensitivity; f_0 is the operating frequency of the QCM; A is the effective area of the QCM; ρ_q and μ_q are the density and shear modulus of the piezoelectric quartz crystal, respectively.

Equation (1) shows that $C_{\rm QCM}$ is proportional to the square of operating frequency (f_0^2), and inversely proportional to the effective area. Thus, the mass sensitivity $C_{\rm QCM}$ can be significantly increased by increasing the operating frequency and reducing the effective area of the QCM. However, it is worth noting that the operating frequency of the QCM is proportional to the thickness of quartz crystal blank t: $f_0 = c/(2t)$, where c is the velocity at which waves travel through the crystal. In other words, although the QCM with a higher fundamental frequency has a higher mass sensitivity, it is more susceptible to cracking, which is the difficulty of using QCMs with ultra-high frequency in practical applications.

The commonly used fundamental frequencies of QCMs were mostly 5 or 10 MHz in practical applications.[19–22] Ultrasensitive QCM sensors with the resonant frequencies from 39 to 110 MHz for measurements in the liquid phase were presented by Uttenthaler *et al.*[23] March *et al.* found that the 100 MHz HFF-QCM carbaryl immunosensor could show the highest sensitivity, after comparing the performance of several immunosensors between the fundamental frequencies of 50 to 100 MHz with carbaryl insecticide as a model analyte.[24] Fernandez *et al.* introduced the design, characterization, and validation of a QCM sensor with a high fundamental frequency of 150 MHz for bio-sensing applications.[25] Ogi *et al.* developed a highly sensitive 170 MHz QCM biosensor and its mass sensitivity is up to 15 pg/(cm^2·Hz).[22] Lubczyk *et al.* designed a quartz crystal microbalance (200 MHz) system for detection of TATP (tri-acetone triperoxide).[26]

In this Letter, a QCM sensor with a fundamental resonance frequency of 210 MHz is developed based on inverted mesa technology. The purpose of the inverted mesa technique is to thicken the edges of the quartz crystal to ensure that the middle can be very thin. The inverted-mesa structure has the advantage of reducing the thickness of the quartz wafer to increase the fundamental frequency while ensuring that the mechanical strength of the wafer is not reduced.

In practical applications, the mass sensitivity is not a specific value like $C_{\rm QCM}$ but a function whose distribution is a Gaussian shape.[27,28] The mass sensitivity of QCMs depends on the particle displacement amplitude function and the distance from the given point to the center of the electrode. The mass sensitivity distribution of QCM is defined as follows:[29–31]

$$S_f(r,\theta) = \frac{|A(r,\theta)|^2}{2\pi \int_0^\infty r|A(r,\theta)|^2 dr} \cdot C_f, \qquad (2)$$

where $S_f(r,\theta)$ is the mass sensitivity function in units of Hz/kg, C_f is Sauerbrey's sensitivity constant,

*Supported by the National Natural Science Foundation of China under Grant No 61871098.
**Corresponding author. Email: xianhehuang@uestc.edu.cn
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$A(r,\theta)$ is the particle displacement amplitude function, and r is the distance from the point to the center. The particle displacement amplitude is not dependent on the angular direction θ in QCM devices.[29,32]

The particle displacement amplitude function $A(r)$ is the solution to the following Bessel equation[33]

$$r^2\frac{\partial^2 A}{\partial r^2}+r\frac{\partial A}{\partial r}+\frac{k_i^2 r^2}{N}A=0, \tag{3}$$

where N depends on the material constants of the quartz crystal, and $k_i^2=(\omega^2-\omega_i^2)/c^2$ with i=E, U (E and U represent the fully electroded region and non-electroded region, respectively); $c=\sqrt{\mu_q/\rho_q}$, ω_i is the cut-off frequency of fully electroded region ($\omega_{\rm E}$) and non-electroded region ($\omega_{\rm U}$), respectively.

According to Eq. (2), the theoretic mass sensitivity distribution of the AT-cut, plano-plano QCM with a fundamental resonance frequency of 210 MHz shown in Fig. 1. The diameter and thickness of gold electrode (m-m type) are 0.28 mm and 500 Å, respectively.

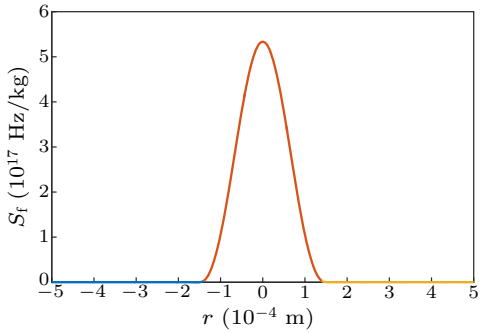

Fig. 1. The mass sensitivity distribution of QCM with a fundamental resonance frequency of 210 MHz. The diameter and thickness of gold electrodes (m-m type) are 0.28 mm and 500 Å, respectively.

However, it is difficult to directly detect the mass sensitivity of QCM. Most results of QCM's mass sensitivity reported so far are usually relative or normalized values.[32,34] Our previous work presented the equivalent mass sensitivity model which considers both the Gaussian distribution characteristic of mass sensitivity and the influence of electrodes on the mass sensitivity.[27] Moreover, we propose a method of coating rigid thin films on the surface of QCMs to indirectly measure the mass sensitivity of QCM. Then, the theoretical frequency shift can be calculated by

$$\begin{aligned}\Delta f&=-C^*_{\rm QCM}\cdot\Delta m,\\ C^*_{\rm QCM}&=\frac{1}{\pi r_d^2}\int_0^{r_d}2\pi r S_f(r)dr,\end{aligned} \tag{4}$$

where r_d is the radius of the specified circular region where mass load is attached on, and $C^*_{\rm QCM}$ is the equivalent mass sensitivity.[27]

To verify the mass sensitivity of 210-MHz QCMs, the experiment of plating 1-ng rigid aluminium films on the surface of QCM was performed in a class 10000 ultraclean room of Wintron Electronic Co. Ltd. The temperature was maintained at 23 °C. Ten 210-MHz quartz crystals were purchased from Wintron Electronic Co., Ltd. All quartz blanks were processed with the quartz wet etching process: (1) forming a protective film, a photosensitive sheet on a quartz wafer, (2) exposing and developing an electrode shape, (3) etching the quartz crystal into an "inverted steps shape". Finally, quartz crystal was shaped like inverted steps with a thinner middle and a thicker edge, and its size is shown in Fig. 2.

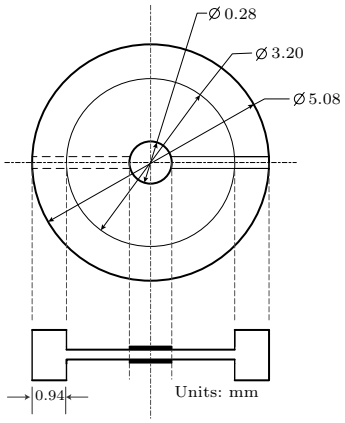

Fig. 2. Details of quartz wafer of QCM with a fundamental resonance frequency of 210 MHz based on the inverted mesa technique. Here $\phi_1=0.28$ mm and $\phi_2=3.20$ mm are the diameters of the electrode and the etched area, respectively; $\phi_3=5.08$ mm is the diameter of the crystal plate. Accordingly, the length of the unetched circular ring could be calculated to be 0.94 mm.

The experimental setup is shown in Fig. 3. A total of 10 quartz crystals were plated with gold electrodes in diameter of 0.28 mm and thickness of 500 Å. The shapes of the gold electrodes are identical (m-m electrode). Their resonant frequencies were measured and recorded to be f_1 by an S&A 250B-1 network analyzer. The S&A 250B-1 network analyzer (Saunders & Associates, LLC. Phoenix, AZ, USA) is a professional crystal test equipment that can quickly detect various parameters of crystals, such as frequency, power, and equivalent parameters. Then, thin aluminium films with diameter of 0.28 mm and thickness of 60 Å were plated on the gold electrodes (about 1 ng). After the second plating, their resonant frequencies were measured and recorded as f_2 by the S&A 250B-1 network analyzer.

In the plating process, we used the S&A 5600 base plating system (Saunders & Associates, LLC; Phoenix, AZ), while the coating thickness was set by the equipment's program.

From Fig. 2, the maximum mass sensitivity of 210 MHz QCM is 5.332×10^{17} Hz/kg at the center of the electrode. According to Eq. (4), the equivalent mass sensitivity $C^*_{\rm QCM}$ within the electrode region is 1.617×10^{17} Hz/kg, which is 5–7 orders of magnitude higher than the commonly used 5 or 10 MHz QCMs (for example, 11 MHz QCMs, 2.1×10^{12} Hz/kg[32]).

Our experimental results are listed in Table 1. $\Delta f=f_1-f_2$ is the frequency shift caused by the mass of thin aluminum film which was been plated in the second plating process. Δf_a and δ are the aver-

age value and the standard deviation of Δf, respectively. Δm is the mass change (about 1 ng) caused during the second plating process; f_s is the theoretic frequency shift caused by Δm according Eq. (4), E_s is the relative error between f_s and Δf_a.

As shown in Table 1, the standard deviation δ (4633.0 Hz) is very small compared to Δf_a (191553 Hz), indicating the high stability of the test system and therefore showing that the experimental data are valid. The theoretical values agree well with the experimental data, confirming the ultra-high mass sensitivity (1.617×10^{17} Hz/kg) of 210 MHz QCM.

Table 1. Experimental results.

Δf (Hz)	1#	2#	3#	4#	5#
	185290	186580	191830	188260	193560
	6#	7#	8#	9#	10#
	190600	194260	188880	195660	200610
Δf_a (Hz)	191553				
δ (Hz)	4633.00				
Δm (g)	1×10^{-9}				
$C^*_{\rm QCM}$ (Hz/kg)	1.617×10^{17}				
f_s (Hz)	161700				
E_s	15.58%				

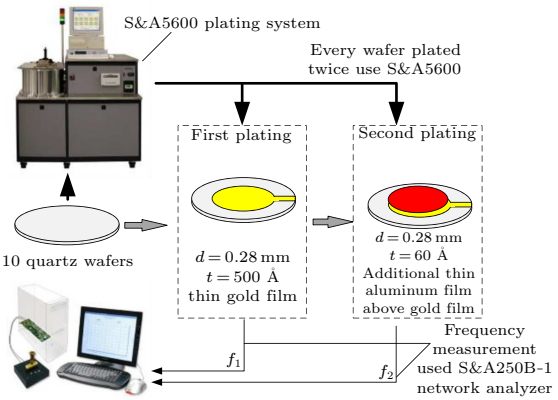

Fig. 3. Schematic diagram of the experimental setup.

Table 2. Typical QCM parameters before and after coating the aluminum film taking 1# as an example.

	$R\,(\Omega)$	C_1 (fF)	Q
Before	31.82	1.51	15781
After	32.44	1.50	15597

The relative error E_s (15.58%) was attributed to the plating process. The aluminum film thickness was set to stop at 60 Å by the plating program. However, superfluous aluminum film was still plated on the surface of QCM in the shutdown process. In other words, the aluminum film thickness must be thicker than 60 Å. According to our experience, the actual film thickness may be about 5–10 Å thicker than the set value, which results in the final true film thickness up to 65–70 Å and the f_s arrives at 175175–188650 Hz. Accordingly, the relative error E_s is 9.3%–1.5%.

The equivalent parameters of QCM were tested by the S&A 250B-1 network analyzer to observe the stability of 210-MHz QCM, and the results are listed in Table 2.

From Table 2, we can find that the high-Q characteristics of the quartz crystal are maintained in comparison of the quality factor Q of 210-MHz QCM before and after plating the aluminum film.

In summary, a high-Q QCM with a fundamental resonance frequency of 210 MHz is developed based on mesa technology. The mass sensitivity reaches 5.332×10^{17} Hz/kg at the center of the electrode, which is 5–7 orders of magnitude higher than the commonly used 5 or 10 MHz QCMs (the mass sensitivity is 10^{10}–10^{12} Hz/kg). This mass sensitivity is verified by an experiment of plating a 1-ng rigid aluminium film on the surface of the QCM sensor. The QCM sensor keeps the high-Q characteristics of the quartz crystal, while it significantly increases the mass sensitivity. The QCM sensor may be used as a promising analytical tool for applications requiring high sensitivity detection.

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