

Femtogram mass resolution in a liquid environment using a low loss vacuum-gapped quartz crystal resonator

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The well-known dependence of Q on liquid damping effect has been significantly reduced through an acoustic energy loss isolation layer and a sensing diaphragm supported by microposts, which reduce the direct contact area at the interface between the resonator and surrounding liquid.

The quartz crystal resonator (QCR) has been widely used in bio-applications of mass sensing by resonant frequency shifts due to mass change on it. While QCRs have witnessed great improvements in mass sensing capability, their performance in liquid leaves much to be desired since many conventional QCRs suffer extreme Q reduction in liquid due to viscoelastic properties of the surrounding fluid. The use of the QCR for mass sensing in gaseous environments has been well established since the initial discovery of the relationship between shifts in resonance frequency and uniform mass accumulation of a thin film onto the crystal surface.¹ Further studies extended this relationship to films thicker than 2% of the total crystal mass.² The notion of stable oscillation behavior in liquid was inconceivable, until it was proved in 1980.³ Later research⁴ on liquid loaded QCRs revealed the connection between the liquid density–viscosity product and the associated shift in resonance frequency. These findings initiated further studies on the use of QCRs as sensors in liquid environments. However, the application of QCRs to mass sensing in liquid is very limited due to the extreme reduction of quality factor (Q) and mass sensitivity in viscoelastic media. Although quartz resonators have been utilized as sensors in viscous and conductive liquids,⁵ limited solutions by use of an additional oscillator tank circuit and capacitor were required to compensate Q reduction and frequency instability. In a liquid environment, the significant reduction in Q results from leakage of acoustic wave energy into the viscous media. Here, we present an effective way to realize a remarkably improved mass sensing resolution in liquid by preserving a high Q comparable to that in a gaseous environment. This has been accomplished through the inclusion of a thin acoustic-loss isolation layer. Furthermore, effective mass loading has been achieved through the microposts (Fig. 1), which help minimize the acoustic wave energy loss to the surrounding viscoelastic medium.

When QCR devices operate in gaseous environments, the acoustic wave energy remains confined within the crystal due to the large acoustic impedance mismatch with the surroundings. However, once introduced into a liquid environment, much of the acoustic wave energy is dissipated into the liquid. For a high Q resonance, and hence small mass resolution, the acoustic energy in a QCR must be well trapped in the piezoelectric crystal, but when one or both sides of

a QCR contacts liquid, the shear acoustic-wave energy is no longer well confined in the piezoelectric crystal.

The vacuum-gapped resonator in liquid is modeled as shown in Fig. 2 by a constant clamped capacitance C_0 in parallel with an acoustic (motional) arm Z_m that consists of motional capacitance C_m , motional inductance L_m , and motional resistance R_m . The inductive elements L_2 and L_3 are included to account for the mass loading effect due to liquid and mass respectively and represent the kinetic energy of the attached mass and entrained liquid. The loss components are R_m and R_2 , where R_m represents the loss in the piezoelectric layer and R_2 represents the loss due to radiation of a damped shear wave into the liquid. The device Q is inversely proportional to the resistance in the motional arm of the resonator. Assuming the quartz is ideal ($R_m \approx 0$), the main contribution to Q loss is the resistance associated with liquid damping (R_2). Therefore, any mechanism for effective mass sensing in liquid with high Q must necessarily minimize R_2 damping.

To increase the immunity to liquid damping, our design was focused on a device without much Q reduction associated with R_m and R_2 . It employs an acoustic loss isolation layer and a separate sensing diaphragm, which can significantly reduce Q reduction attributed to R_2 . The vacuum separation is achieved by using microposts between the QCR and the diaphragm, which contacts the liquid, allowing only a relatively small percentage of energy leakage through the post area.

In the prototype design of the vacuum-gapped QCR (V-QCR), seven microposts (six in a hexagonal formation around a center post) were used to support the sensing diaphragm. The micro-posts cover

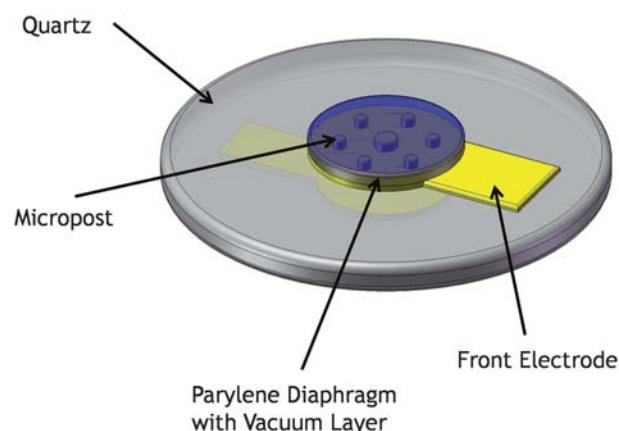


Fig. 1 Perspective schematic drawing of the vacuum-gapped quartz crystal resonator. A parylene diaphragm is supported by microposts and the vacuum separation provides an acoustic loss isolation layer. When the liquid is loaded onto the sensing diaphragm, the mass is transferred onto the resonator through the microposts.

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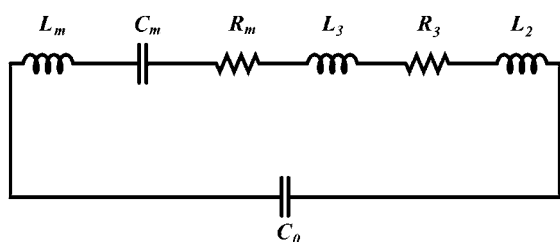


Fig. 2 Butterworth van-Dyke equivalent circuit model.

approximately 6.6% of the total active area; hence 6.6% of the acoustic waves are in direct contact with the liquid layer. Therefore, 6.6% of the energy can pass through the posts and be absorbed by the liquid. However, we must also consider the reflection of waves at the boundary due to the acoustic impedance mismatch between various layers. The top electrode (Au) is in contact with the top parylene layer through the micro-posts. The acoustic impedance of gold is 63.8 Mrayls and that of parylene is 2.8 Mrayls. Thus, the reflection coefficient Γ is given by:

$$\Gamma = \frac{Z_{\text{Au}} - Z_{\text{parylene}}}{Z_{\text{Au}} + Z_{\text{parylene}}} \quad (1)$$

Therefore the total incident to transmitted power ratio is given by $1 - |\Gamma|^2 = 0.16$. Considering the worst case scenario of the entire transmitted wave being absorbed by the liquid, the percent of energy leakage through the micro-posts is only 1.1%. Therefore, the vacuum gap reduces the loss of energy due to acoustic wave leakage by a large amount. Furthermore, the squeezed film damping effect encountered by the use of an air layer will not play an important role either due to the vacuum layer.

The QCR oscillation affects the oscillation of the sensing diaphragm through the microposts, but it is negligible since the resonant frequency of the QCR does not match the fundamental mode of the sensing diaphragm nor any of its dominant harmonics. Although the vacuum gap isolates the resonator from the effects of viscous damping, it does not inhibit the detection of mass on the surface of the sensing diaphragm. To verify this, finite element simulations were done to determine the von Mises stress profile due to the uniform loading of a small mass on the sensing diaphragm (Fig. 3). Results indicate that over 90% of the stress is concentrated in the area of the microposts, which supports the claim that the presence of mass on the

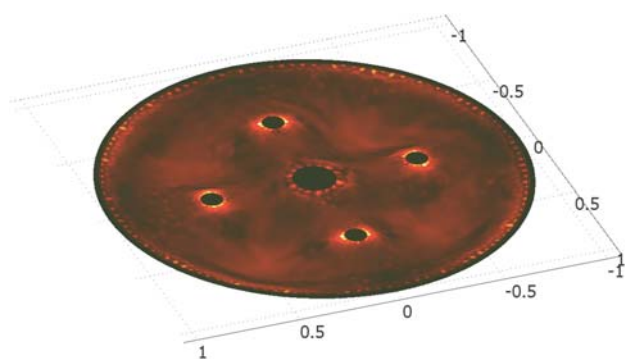


Fig. 3 Simulation result of von Mises stress and deformation plot due to loading of 5.4×10^{-9} g onto the sensing diaphragm. Mass distribution is concentrated on the areas of microposts as indicated by bright coloring.

sensing diaphragm is conveyed to the resonator *via* the microposts. In addition, although the oscillation of the QCR (MHz range) affects that of the diaphragm (kHz range) through the microposts, the effect is negligible since the resonant frequency of the QCR does not match the fundamental mode of the sensing diaphragm nor any of its overtones as illustrated in Fig. 4.

To produce the vacuum gap, photoresist was utilized as a sacrificial layer. A parylene layer was subsequently deposited over the sacrificial layer. Reactive ion etching (RIE) was utilized to etch a hole in the parylene layer, through which the sacrificial layer was released using acetone. Another parylene coating was applied to seal the hole under vacuum. The separation layer is at best a low vacuum in the range of several tens of mTorr and in the worst case simply an air gap, which still would not greatly affect the performance of the device.

The device was mounted in a test setup and tested with an HP 8753D network analyzer. The reflection coefficients (S_{11}) were extracted with a Labview program which calculated the series resonant frequency directly from the incoming data. The Q in air and liquid are 226 180 and 196 350 respectively (Fig. 5). This corresponds to an only 13.2% reduction compared to the Q in air. The V-QCR in water is also compared to a normal QCR in water and exhibits superior performance with minimal damping as shown in Fig. 5.

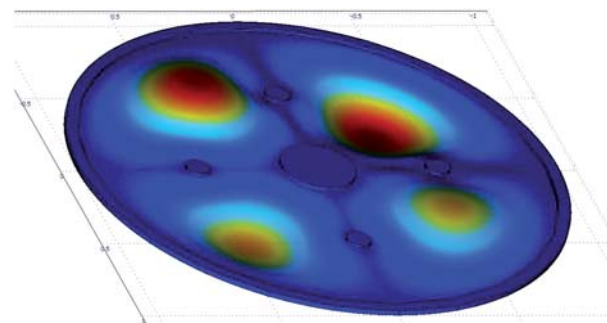


Fig. 4 Modal displacement analysis of diaphragm with five micropost areas shows the fundamental frequency of 52.547 kHz, which is far less than the resonant frequency of the resonator.

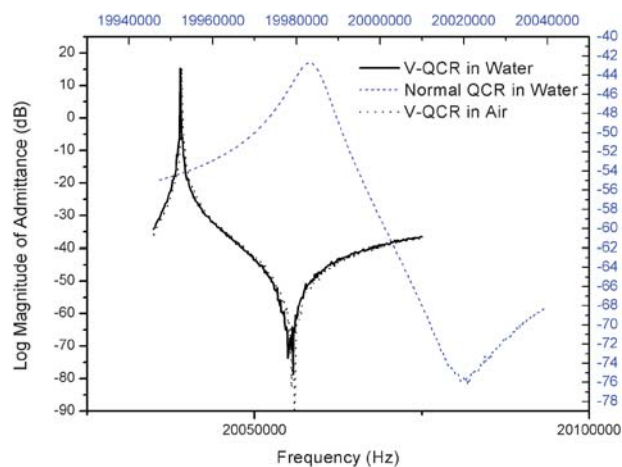


Fig. 5 Comparison of V-QCR in water to a normal QCR in water. The QCR without vacuum gap and microposts experiences substantial dissipation of acoustic energy into the liquid.

Table 1 Summary of V-QCR response to various loadings on sensing diaphragm

Loading material	Mass/ μg	Frequency shift/kHz
Water ^a	—	0.25
Chromium ^b	6.78	6.13
Chromium etchant	—	0.15

^a Water loading was carried out separately from chromium loading.

^b The given frequency shift does not include the shift due to the chromium etchant. The effect of liquid loading can be determined for each device and then used to compensate mass loading results.

The maximum attainable Q of a BAW resonator in vacuum is given as⁶ $Q_{\text{max}}f = 1.6 \times 10^{12}$ Hz, which was extended to include the effects of liquid damping⁷ assuming ideal quartz ($R_{\text{m}} \approx 0$):

$$Q_{\text{max}}\sqrt{\rho\eta}f_s \approx 7.8 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1} \quad (2)$$

where $\rho\eta$ is the density viscosity product of the contacting liquid. This gives a maximum Q in water of 1850. Comparing the experimentally determined Q in water with its associated Q_{max} , it is evident that the inclusion of the vacuum layer has overcome the barrier imposed by traditional QCRs on maximum Q .

Due to the loading of water on the diaphragm, a 0.25 kHz decrease in series resonant frequency was observed. To determine the mass sensitivity of the device in liquid, a 300 nm layer of chromium (mass of 6.78 μg) was evaporation-deposited onto the parylene sensing diaphragm and a 0.15 kHz shift in resonant frequency was measured upon exposing the mass layer to the chromium etchant. Due to the complete removal of the chromium surface mass layer, a clear upward shift in series resonant frequency of 6.13 kHz occurred (with respect to an already downward shifted frequency resulting from addition of chromium mass and etchant). The shift was detected in coincidence with the etching of chromium due to the presence of the liquid etchant on the sensing diaphragm (no drying was required to detect frequency shift due to Q preservation). The frequency shift corresponds to a mass sensitivity of 6 $\text{cm}^2 \text{ g}^{-1}$ and demonstrates the ability of the V-QCR to perform mass sensing in liquid while maintaining high Q . A summary of the various frequency shifts due to mass and liquid loading are summarized in Table 1.

The Sauerbrey equation predicts a sensitivity of $2.26 \times 10^{-6} f_s$ ($\text{cm}^2 \text{ g}^{-1}$), which is 45.2 $\text{cm}^2 \text{ g}^{-1}$ for our device. The disparity between experimental sensitivity and that given by Sauerbrey is due to the incorporation of the sensing diaphragm. Since the device includes multiple layers beyond the electrodes, the Sauerbrey approximation no longer holds. For a multilayer device, the sensitivity is given as:

$$s = \frac{1}{\sum_i \rho_i h_i} \quad (3)$$

where ρ_i and h_i are the density and thickness of the i^{th} layer respectively. The geometry of the sensing diaphragm precludes the use of eqn (3) for quantitative purposes, yet it still provides a qualitative insight. From eqn (3), the inclusion of the sensing diaphragm has the effect of reducing sensitivity. Therefore, the height of the microposts and the thickness of parylene diaphragm should be made as thin as possible to minimize reduction in sensitivity due to parylene.

However, the extent to which the vacuum layer (determined by the height of the microposts) can be thinned is restricted by fabrication limitations (stiction, removal of sacrificial layer) and the parylene diaphragm thinness is limited by structural integrity considerations. Future work on the V-QCR will optimize the diaphragm geometry to maximize sensitivity.

Given the Q and sensitivity of the resonator, the minimum detectable mass change is dictated by the combined phase noise of the resonator and read-out mechanism. In the time domain, the Allan deviation $\sigma_y(\tau)$ is used as a standard measure of frequency instability over an averaging time τ , and is equivalent to the minimum detectable fractional frequency deviation due to noise.⁸

An empirical relationship between $\sigma_y(\tau)$ and the resonator Q was given⁶ as $\sigma_y(\tau)_{\text{min}} = 1 \times (10^{-7}/Q)$. Combining these with eqn (2) gives $6 \times 10^{-21} f_s$ as the best theoretical frequency resolution of a quartz oscillator in vacuum, assuming the maximum attainable Q . Thus, the ultra high Q value of the V-QCR in water gives a minimum frequency resolution of 0.51 parts per trillion (ppt). This corresponds to a mass resolution of 90 fg cm^{-2} , which is several orders of magnitude higher than the one in the recent report.⁹ Such a high mass resolution is achievable due to the preservation of an ultra high Q in liquid *via* the vacuum-gap isolation layer.

In summary, this paper demonstrates improved mass sensing capability of a quartz crystal resonator in liquid by employing an acoustic loss isolation layer, microposts and a sensing diaphragm. The sensing diaphragm serves to isolate the liquid damping effect from the high frequency resonance of the quartz. The microposts have very effectively provided a pathway through which the mass adhered to the sensing diaphragm may be sensed by the QCR in liquid without losing much sensitivity. The vacuum-gapped QCR (V-QCR) has successfully demonstrated the preservation of Q in a liquid environment ($Q = 196\,350$), with an only 13.2% reduction in Q compared to that in air. This is an unprecedented Q value for a resonator operating in a liquid environment, yielding a minimum detectable surface mass density of 90 fg cm^{-2} . The effect by maintaining a high Q in liquid has potential applicability to a variety of other acoustic devices. This work was supported by National Science Foundation CAREER Award #ECS-0846960.

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