Patterned Electrodes For Thickness Shear Mode Quartz Resonators To Achieve Uniform Mass Sensitivity Distribution

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Abstract — **Development of an electrode-modified thickness shear mode (TSM) quartz resonator that is responsive to nanogram mass loadings, while exhibiting a mass sensitivity profile that is independent of material placement on the sensor platform, is the aim of this study. The resulting nanogram balance would greatly enhance the field of mass measurement and become useful in applications like droplet gravimetry, the study of non-volatile residue (NVR) contamination in solvents. A ring electrode design predicted by an analytical theory for sensitivity distribution to achieve the desired uniform mass sensitivity distribution is presented in this work. Using a microvalve capable of depositing nanogram droplets of a polymer solution, and a linear stepping stage for radial positioning of these droplets across the sensor platform, measurements of the mass sensitivity distributions were conducted and presented. The measurements agree well with theory. Further improvements are possible and are identified to achieve better uniformity and to reduce the instability of resonant frequency of these devices.**

***Keywords* – TSM quartz resonator; non-volatile residue (NVR); mass sensitivity; nanobalance**

I. INTRODUCTION

Utilization of a thickness shear mode (TSM) quartz resonator as a mass characterization device for minute mass loadings, down to the nanogram level, is well established. Typically referred to as a quartz crystal microbalance (QCM), a TSM resonator consists of a quartz disk of varying thickness, depending upon the operating resonance frequency, with metallic planar electrodes deposited on both faces. Typical resonance frequencies are between 5 and 10 MHz [3], with the resulting mass sensitivities in the nanogram range. Deposition of mass, either in the form of a thin mass layer or point mass, on the device surface causes a reduction in the resonance frequency which is directly proportional to the minute mass deposited. However, an important limitation on the mass sensitivity of current TSM devices exists. Utilization of the Sauerbrey model to directly relate the frequency shift to mass loading requires that the mass be uniformly distributed across the surface plane of the TSM device. While the mass sensitivity distribution is quite non-uniform for typically utilized devices with circular electrodes, the Sauerbrey model agrees with experimental values within a percent or so, for uniformly distributed elastic films. The non-uniformity of mass sensitivity of current TSM devices is well documented, [2, 3], and is attributed to the reduction in quartz particle displacement amplitude extending from the center. At the device center, the propagating wave drives the quartz particles from all radial directions prompting maximum displacement and, consequently, mass sensitivity. However, moving away from the center, the displacement amplitude tapers off with radial position producing a Gaussian-like distribution in the mass sensitivity [3]. The purpose of this study is to eliminate the non-uniformity of mass sensitivity of commercially available devices through modification of the electrode design, the primary factor influencing the sensitivity profile [2]. A tangible TSM device exhibiting constant mass sensitivity across the active sensing area and high frequency stability will yield a viable robust nanobalance. The existence of a TSM-based nanobalance will enable its utilization in the determination of absolute mass, a shortcoming of current TSM devices, and eliminate the dependence on mechanical and analytical mass balances which are expensive, limited to microgram level mass sensitivity, and suffer considerably from mechanical vibrations. Processes involving gravimetric measurements such as the determination of non-volatile residue (NVR) contamination in high-purity solvents would benefit significantly with the advent of a nanobalance [1]. A current method to characterize NVR per volume of solvent involves a thermal gravimetric technique where a large quantity of solvent is evaporated and the remnant NVR weighed. This

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process is both expensive and time consuming. Available mathematical modeling of the radial mass sensitivity distributions for simple electrode designs, namely solid 'n-m' and ring configurations (Figure 1 depicts these two cases) is an efficient and valuable tool to predict designs producing a uniform mass sensitivity distribution. Presented below are the theoretical and experimentally measured mass sensitivity distributions for a ring electrode configuration having an inner and outer diameter of 4 and 10 mm, respectively, and a model driven Au/Cr electrode thickness predicted to produce a uniform mass sensitivity. Additionally, descriptions of the fabrication of the TSM devices and a novel experimental apparatus constructed to measure mass sensitivity are presented.

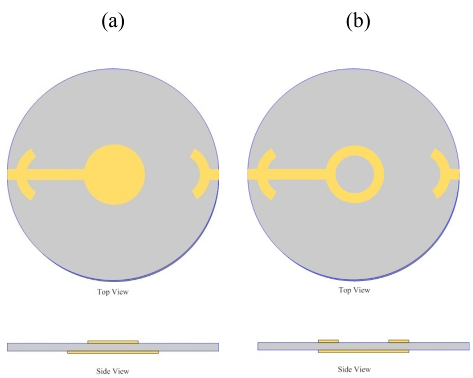

Figure 1. Simple electrode designs for a TSM quartz resonator: (a) solid "n-m" electrode configuration, and (b) single ring electrode configuration.

II. THEORY

Development of analytical mathematical models for predicting the mass sensitivity of TSM devices having simple electrode configurations has been extensive since Sauerbrey's initial study of the frequency shift due to mechanical loading on the device surface in the 1950s. Typically, these models are generated through either a resonant frequency analysis or three-dimensional perturbation modeling of the quartz particles. However, these techniques share a common assumption that the mass sensitivity is proportional to the square of the quartz particle displacement amplitude [2, 3]. In this study, we employ a model that is based upon a resonance analysis across the sensor platform [2].

As mentioned previously, the radial mass sensitivity profile of a TSM device is primarily influenced by the electrode design configuration. Utilizing the analytical model of Josse *et al.* [2] for both the simple "n-m" and ring electrode cases, we determined that the ring configuration is capable of producing a uniform mass sensitivity distribution due to the bimodal response in mass sensitivity across the sensor platform. Given this, only the model calculations for the mass sensitivity distributions of the ring electrode designs will be considered. Figure 2 shows the bimodal response of mass sensitivity for the ring electrode

Mechanical mass sensitivity for any TSM device as a function of quartz radius is governed by the particle displacement amplitude resulting from the shear horizontal wave propagating through the quartz substrate:

$$S_f = \frac{|\tilde{u}_1(r)|^2}{\int_0^{\infty} r|\tilde{u}_1(r)|^2 dr} C_f \qquad (2.1)$$

Determination of the particle displacement amplitude, $|u_1(r)|$, is dependent upon the electrode geometry, as well as the electrode mass loading factor, R, a comparison of the overall electrode areal mass, $\rho_e h_e$, to that of the quartz substrate, $\rho_q h_q$. The electrode mass loading factor is an important parameter setting both the magnitude of the mass sensitivity and the extent to which the profile tapers toward the center of the quartz surface for the ring electrode case. The particle displacements from the Josse *et al.* model are given by the following equation for ring electrodes [2]:

$$\tilde{u}_1(r) = \begin{cases} AI_0\left(k_y^p r\right) & 0 \le r \le a \\ BJ_0\left(k_y^e r\right) + CN_0\left(k_y^e r\right) & a \le r \le b \\ DK_0\left(k_y^u r\right) & b \le r \le \infty \end{cases} \qquad (2.2)$$

$$R = \frac{\rho_e h_e}{\rho_q h_q} \qquad (2.3)$$

The radial boundary variables *a* and *b* represent the inner and outer radii of the ring electrode, respectively. I_0, J_0, N_0, and K_0 are Bessel functions of the zeroth kind. The amplitude constants *A*, *B*, *C*, and *D* are obtained by solving a set of linear homogeneous equations, as described in Ref. [2].

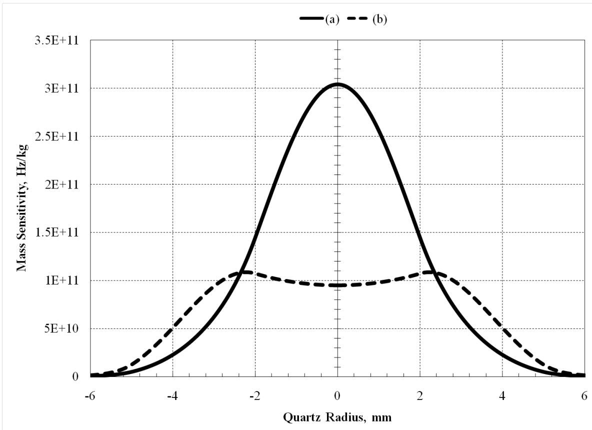

Figure 2. Theoretical mass sensitivity distributions for simple electroded TSM devices with R = 0.0036: (a) "n-m" electrode configuration with top and bottom diameters of 4 and 10 mm, respectively, and (b) ring electrode configuration with inner and outer diameters of 4 and 10 mm, respectively.

III. Experimental

A. TSM Device Fabrication

To produce the TSM devices, a simple photolithographic process and metal deposition was conducted. The blank quartz substrates utilized were polished 1 inch diameter AT-cut crystals with an operating frequency of 5 MHz. These blanks were placed in a spin-coater and a photoresist was deposited at 3500 rpm for 30 seconds. Once the photoresist was cured in a vacuum oven, it was exposed to viable electrode designs on a photomask using a UV lamp, baked again in the vacuum oven, and developed in developer solution. Metals were deposited in a thermal evaporator where the chromium adhesion and gold layers were deposited to the desired thickness.

B. Mass Sensitivity Measurements

Various techniques to measure the mass sensitivity across the surface plane of a TSM resonator have been developed including x-ray diffraction to characterize quartz particle vibration, surface charge distribution measurement, and characterization of optical speckle patterning produced by coherent light incident across the quartz surface. However, all of these methods have significant limitations. Details are available in Ref. [3]. Another approach is an ink dot method where dots from a fine-tipped felt pen are placed at precise radial positions and the resulting frequency shifts are recorded. This technique is effective and efficient providing the mass of each dot deposited is reproducible which is very difficult to achieve. In our study, we developed a novel apparatus using a similar technique; however, eliminated the issue of reproducible mass upon each deposit. The apparatus consists of a microvalve capable of depositing nanogram droplets, a stainless-steel test cell with drilled channels for heated water circulation to ensure evaporation of the droplets, and linear and rotary micro-positioners for precise positioning of droplets. Figure 3 depicts the apparatus in detail.

Mass sensitivity measurements of the fabricated devices were conducted by depositing nanogram droplets of a 0.65 wt % hydroxypropylcellulose (HPC)/water solution using the microvalve at precise radial positions and the resulting frequency shifts recorded. Details of the experiment are given in Table 1.

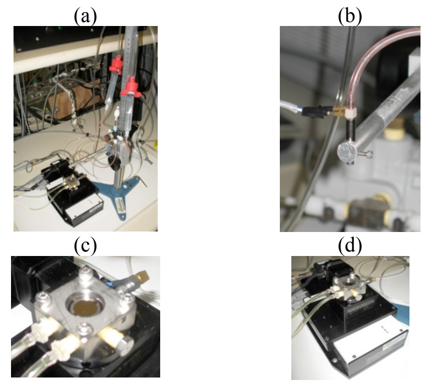

Figure 3. The experimental apparatus for measurement of the mass sensivity distributions of TSM devices: (a) entire apparatus, (b) TechElan microvalve, (c) stainless-steel test fixture, and (d) linear and rotary stage positioners.

TABLE I. Experimental Details

# of droplets per position	2
HPC mass deposited, ng	227 ±20 ng
Position step interval, mm	0.5

IV. Results and Discussion

Utilizing computations based upon the analytical modeling, it can be shown that the ring electrode structure exhibits greater promise to exhibit a uniform mass sensitivity profile than the typical solid 'n-m' electrode TSM device given the bimodal response. Figure 4 presents the experimental mass sensitivity measurements for both the standard solid 'n-m' Maxtek TSM resonator and the ring electrode with R = 0.0334 having inner and outer diameters of 4 and 10 mm, respectively. In comparing Figures 2 and 4, the experimental results agree well with theory and, as stated above, the experimental mass sensitivity profile for the 4-10 mm ring structure approaches a uniform sensitivity distribution toward the active center of the device.

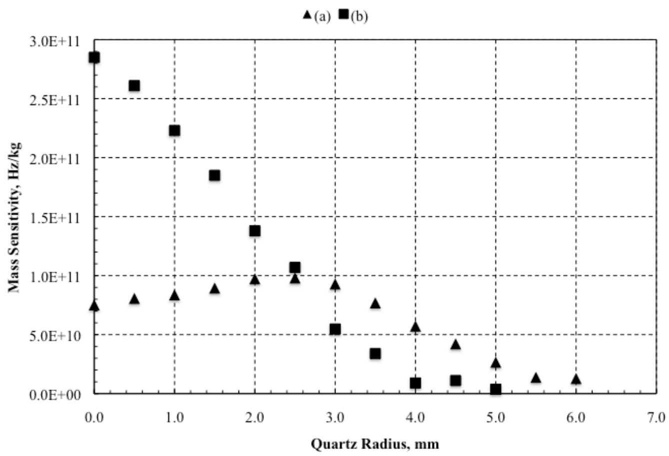

Figure 4. Experimental mass sensitivity distributions: (a) single ring electrode TSM device having inner and outer diameters of 4 and 10 mm, respectively, with R = 0.0334, (b) Maxtek solid 'n-m' electrode device.

V. CONCLUSIONS

In this study, a ring electrode design that produces a uniform mass sensitivity distribution across a TSM device is presented. A new technique and apparatus to measure this mass sensitivity distribution is also presented. Fabricated devices utilizing model predictions were tested using this apparatus, and good agreement between theory and experiment is found. A viable TSM device that can be utilized to construct a nanobalance is the result of this work; however, improvements are possible, both in terms of improved stability of the device resonance frequency and more uniform sensitivity distribution over a larger device surface. Such designs require extensions of the analytical model utilized in this work, or finite element simulations. These studies are underway.

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