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Monitoring and modeling of Quartz Crystal Microbalance sensors in a four-point probe configuration with a superconducting ammeter

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ABSTRACT

The Quartz Crystal Microbalance is an extremely sensitive instrument for detecting surface and thin-film changes, with sensitivities in the nanogram regime. Primary characterization is often achieved by monitoring changes in the fundamental resonant frequency of the sensor, which limits the ability to model the data collected from multi-component systems. Recent advances have allowed for the frequency and dissipation of QCM sensors to be monitored at the fundamental frequency and higher overtones, dramatically increasing the utility of this instrument for complex systems. In this short communication, we wish to describe a proof-of-concept, four-point probe system for measuring absolute voltage drops and currents at 5 MHz, including a superconducting sensor serving as an ammeter, along with multiphysics simulations providing comparable results. This data allows for direct comparison to predictions from linear piezoelectric models.

1. Introduction

Quartz Crystal Microbalances are exquisitely sensitive instruments for interrogating thin-films and their dynamic behavior [1,2]. Precise measurement of the resonant frequency of the quartz crystal sensor and any changes allows the calculation of a mass and/or film thickness. A change in resonant frequency may be caused by the addition or removal of a mass layer causing an effective change in resonator thickness and the resonant acoustic wavelength [1]. Two of the more simplified functions describing this relationship, the second introduced by Sauerbrey, can be seen in Eqs. (1) and (2).

$$\frac{\Delta f}{f} = -\frac{\Delta t}{t} \quad (1)$$

$$\Delta f = -\frac{2f_o^2 \Delta m}{A\sqrt{\rho_q \mu_q}} \quad (2)$$

Eq. (1) shows that the change in resonant frequency (f) can be represented simply a function of change in oscillator thickness (t) due to the interrelationship between the acoustic wavelength and resonant frequency. Eq. (2), first discussed by Sauerbrey relates the frequency shift from the oscillator's fundamental resonant frequency (f_0) to change in mass (Δm) at a sensor surface with active area (A). The key parameters describing the oscillator are f_0, density (ρ_q) and shear modulus (μ_q), where the *q* subscript denotes quartz. This second equation is generally more useful as it makes it possible to determine changes in surface mass per unit area, but it is only valid for extremely thin films with mechanical properties matching quartz. In practice, this equation may be implemented with sufficient accuracy to films <5% of the quartz's original mass, provided the film is sufficiently rigid [2,3].

Basic QCM instrumentation operates with the quartz crystal sensor as the resonant component in an oscillator circuit operating at frequency f_0 [4–6]. The *relative* frequency shift, Δf, with respect to base resonant frequency, f_0, is the primary data taken by QCM instruments [1,2]. When used to monitor the deposition of metal and semi-metal films, it is capable of monitoring such thin-film deposition processes at the angstrom level. For viscoelastic systems, the *dissipation*, D, may be calculated in currently available instrumentation, which quantifies viscous losses. When modeling a viscoelastic layer, the material's shear modulus is a mathematically complex quantity, with both real and imaginary components, where the imaginary component represents the material's viscosity [3,4,7]. The viscosity of a liquid sample environment will also cause a frequency shift, and these overlapping effects can signficantly complicate data analysis [8].

Assessing and understanding dissipation has been recognized by many researchers as a fundamental key to understanding the QCM, and the work of Rodahl et al. broke open new territory assessing the resonant frequency and dissipation, both at the fundamental frequency and higher overtones, multiplying the quantity of collected experimental data [9,10]. For greater

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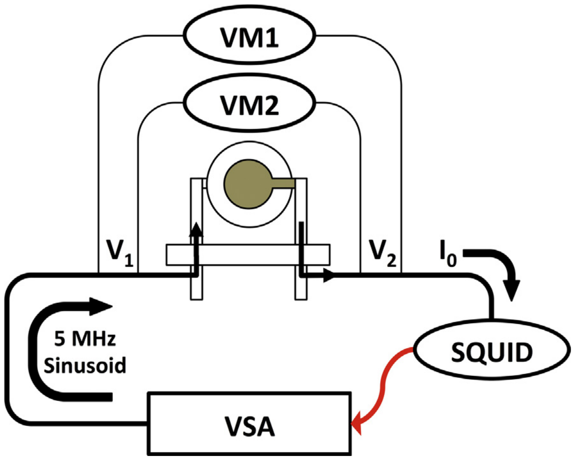

Fig. 1. Illustration of test setup used for oscillator and QCM SQUID measurements. $\mathbf{V_1}$ and $\mathbf{V_2}$ indicate voltage measurements, $\mathbf{I_0}$ indicates current flowing through the loop. **VM1** and **VM2** are the dual voltmeters, and the red arrow indicates the feedback control signal output of the SQUID electronics.

precision, quartz crystal resonators may be characterized by impedance analysis, examining radio-frequency signals passing through the sensor [3], to measure frequency response, dissipation and bandwidth [4,11]. This radio frequency signal is often supplied by equipment such as a vector signal analyzer (VSA), providing fine signal control [4,5,11].

As shown in Fig. 1, the novel four-point probe described in this report makes *absolute* measurements of current ($\mathbf{I_0}$, via the SQUID system) and voltages ($\mathbf{V_1}$ and $\mathbf{V_2}$, via dual voltmeters VM1 and VM2) for a VSA generated 5 MHz sinusoid passing through the quartz crystal sensor. These measurements, described next, are directly comparable to finite element simulation results providing a contrasting approach for comparison to standard techniques [4].

To accurately measure voltages across the QCM sensor at the relatively low power of a QCM system (often only a few μW), a Boonton dual channel voltmeter and HP vector voltmeter were used for redundancy and accuracy purposes, both with high impedance voltage probes. It is worth noting that the measurement techniques of both devices are different, with the Boonton rectifying the RF signal into direct current before voltage measurement, while the vector voltmeter operates uses a sampling, phase-locked, voltage measurement [12].

The constraint of making direct high sensitivity current measurements at radio frequencies [13,14], led to the novel implementation of SQUID (Superconducting QUantum Interference Device) technology [15]. SQUIDs are exquisitely sensitive to changing magnetic fields passing through the SQUID [16], and in the configuration used here (a flux-locked loop), current passing through the input sensing loop generates a miniscule magnetic field that sensed by the SQUID. Sophisticated feedback circuitry maintains the SQUID a zero flux state by energizing secondary feedback coils, and the feedback signal mirrors the current passing through the input loop [17]. Critically, the superconducting nature of the SQUID allows for unimpeded current flow through the measuring device, an ideal ammeter for integration into a four-point probe. Feedback ammeters using high frequency operational amplifiers should allow the use of SQUID hardware to be bypassed for replication purposes [18,19].

2. Methods and materials

A HP89441A Vector Signal Analyzer (VSA) was used for signal generation, frequency counting and frequency response analysis (FRA). Voltmeters, a Boonton Model 9200B and Agilent 8508a vector voltmeter, both with Type N 50 Ω T-adapters (Boonton part 952003, HP part 11536A), were operated as shown in Fig. 2, where VM1 is the Boonton instrument, while VM2 is the Hewlett-Packard system. A DC SQUID utilizing high frequency output current feedback (OCF) feedback, was custom manufactured by Magnicon to measure RF current (Berlin, Germany: XXF-1 SQUID electronics, SEL1 FLL electronics, CSE-1 Extension board, CAR-1 carrier, NC-1 niobium shield, CC-1 cryocable). The signal passing on the 50 Ω system into the SQUID is terminated on a 50 Ω resistance, with a fraction of the signal passing into the SQUID via the input sensing loop's 10 kΩ resistor. For more information on these SQUIDs, readers should refer to Drung et al. [15] 50 Ω type-N coaxial cables connect the quartz crystal sensor mounted on a Model 2397 Pomona electronics enclosure. QCM sensors were fabricated and mounted by International Crystal Manufacturing Co. (Catalog number: 151247-5, Blank Diameter: 0.538″, Surface Finish: Polished, Electrode Diameter: 0.267″, Electrode Material: 100 Å Cr, 1000 Å Au) The VSA and voltmeters were connected to and operated from a central PC workstation via HP10833A GPIB cables using custom-written and Magnicon-supplied LabVIEW control software. For calibration of the SQUID system, the VSA was powered to specific levels to give the calibration curve at 5 MHz, as found in the Supplementary information. Finite Element Analysis (FEA) models based on the physical quartz crystal sensor and environmental isolation were constructed in COMSOL (Version 4.4 including the MEMS package), with additional details given in the Supplementary Information.

3. Results

3.1. Frequency response analysis

For basic frequency response analysis a 0 dBm, 5 MHz sine wave was generated by the VSA, passed through uncoated QCM sensor, back into the VSA for power measurement. Table 1 shows experimental voltage and currents calculated at resonance (f_0) based on signal power, alongside comparison data generated from the 3-D model of the physical QCM in the COMSOL software package. The simulation shows nominally higher current with a nearly fourfold lower voltage drop ($\mathbf{V_1}-\mathbf{V_2}$), though the simplified virtual model here should strictly be viewed as a reference point for considering potential losses in occurring in the auxiliary circuitry attendant to the physical measurements.

Basic resistance calculations follow the standard Butterworth-van Dyke (BvD) model for the resonant behavior of the quartz crystal resonator. Here a mechanical-electrical analogy places the electrical capacitance of the quartz dielectric in parallel with the quartz's mechanical or "motional" inductance, capacitance and resistance in series [1,4]. At resonance, the quartz crystal sensor's impedance is solely the motional resistance, reducing the height and increasing the width of the resonant peaks seen in Fig. 2. Motional resistance at resonance was calculated using Ohm's law for the physical system. With respect to the COMSOL simulations, with an ideal motional resistance (or dissipation) of 0 Ω there would be an infinite current passing through the quartz crystal sensor with no voltage drop, so a one parts-per-thousand dissipative term was added in (see Supplementary Information). Further elaboration of these observations follows in Discussion.

3.2. Four-point probe analysis

The SQUID was calibrated without the QCM sensor in the transmission line to assure a linear response function for the SQUID over an operational range of 100 μV to 100 mVrms at 5 MHz. The linear