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Miniature Quartz Crystal Microbalance for Contamination Measurement

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This paper presents solutions to the unique problems involved in designing quartz crystal microbalance contamination monitors for cryogenically cooled spacecraft optical systems. Among the problems discussed are the piezoelectric crystal mass sensitivity at temperatures below 20 K, electronic components and oscillator circuits compatible with this temperature range and operable with heat dissipation of less than 200 μW, and selection of the sensing crystal's crystallographic cut for optimum temperature coefficients at these ultralow temperatures. A microbalance configuration is presented which incorporates the solutions to these problems and is miniature, thus facilitating placement within the optical system.

Introduction

QUARTZ crystal microbalance (QCM) contamination monitors are sensing instruments utilizing a piezoelectric crystal's resonant frequency change with mass addition to measure condensible molecular flows on spacecraft due to outgassing, etc. The past decade has seen the use of QCM's on spacecraft both as analytical instruments to determine the source of contaminant flux and as sensing elements of control systems to maintain optical cleanliness.

The advent of cryogenically cooled optical systems has produced the need for more sophisticated contamination monitors. Requisite features include molecular monolayer discrimination capability, miniature size, electronic circuit components compatible with liquid helium temperatures, and electronic circuits with minimal power dissipation. These requirements present many unique design problems. Monolayer surface coverage resolution requires essentially zero crystal temperature coefficient. Minimized power dissipation both in the crystal and oscillator electronics is essential if refrigeration capacity is limited. Matched surface material may be important for first-layer bonding effects. Lastly, the QCM must be lightweight, miniature in size, and capable of meeting qualification level spacecraft launch environments.

Many of these design features have previously been incorporated in an existing QCM.[1] The development of a low-power dual oscillator-mixer which operates near 5 K, however, represents state-of-the-art design. A power dissipation of less than 200 μW was considered desirable from a refrigeration standpoint and realistically achievable using current electronic components.

This paper discusses the development of the low-power oscillator circuit and the various considerations involved in below 20 K QCM design.

Mass Sensitivity of Quartz Crystals at Low Cryogenic Temperatures

Basic to the design of a QCM intended for operation below 20 K is the knowledge of the mass sensitivity of the crystal at these temperatures.

The quartz crystal's frequency response to mass addition was treated by Sauerbrey[2] in 1957 using a mass substitution assumption and later more rigorously by Stockbridge[3] in 1966 using a perturbation analysis which verified the validity of Sauerbrey's derivation if mass is uniformly distributed over the crystal. Numerous experiments have been performed confirming the mass to frequency proportionality constant with crystals at or near 25°C. Experimental data at low cryogenic temperatures is meager but does exist and will be reviewed here in an effort to define mass sensitivity values for crystals operating near 4 K.

The frequency to mass relationship is

$$\frac{\mathrm{d}(-\Delta f)}{d(\Delta m/A)} = \frac{2f^2}{\rho_q v} = S \tag{1}$$

where f is the crystal resonant frequency, Δf the change in frequency due to a change in mass per unit area on the crystal $\Delta m/A$, ρ_q is the density of the quartz, and v is the shear wave velocity perpendicular to the crystal surface. The shear wave velocity of Eq. (1) depends upon the stress constants and ϕ, the cut angle of the crystal. The mechanical properties of quartz, due to its hexagonal structure, are characterized by six independent stress constants C_{ij} where $ij = 11$, 13, 14, 33, 44, and 66. The shear wave velocity v can be determined from

$$\rho_q v^2 = (C_{66} + 0.76311 \times 10^{10})\cos^2\phi + C_{44}\sin^2\phi + 2C_{14}\sin\phi\cos\phi \tag{2}$$

The constant 0.76311 × 10^{10} is in dynes/cm^2 and is an empirical constant added to account for piezoelectric stiffening.[4] The stress constants of quartz have been measured at room temperature by several investigators and at 77.37 K.[5] Using the values given in Ref. 5 at 298.17 K for an AT-cut (thickness shear vibration) 35 deg 15 min crystal, the shear wave relationship is

$$\rho_q v^2 = 29.4828 \times 10^{10}\ \text{dyne/cm}^2 \tag{3}$$

Using a quartz density of 2.65 g/cm^3, the unit area mass sensitivity S of a 10 MHz crystal becomes, from Eqs. (1) and (3),

$$S = 2.2627 \times 10^8\ \text{Hz/g/cm}^2 \tag{4}$$

The deviation of this sensitivity from the more common value of 2.259 × 10^8 Hz/g/cm^2 is explainable by the spread in stress constant values found in the literature. The former value is used here to remain consistent with the same source's stress constants at 77 K. The same AT-cut crystal at 77.37 K

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has a shear wave velocity relationship of

$$\rho_q v^2 = 29.4870 \times 10^{10} \text{ dyne cm}^2 \qquad (5)$$

but quartz density at 77 K is increased to 2.664 g/cm^3. Therefore,

$$S = 2.2566 \times 10^8 \text{ Hz/g/cm}^2 \qquad (6)$$

Thus the calculated change in crystal sensitivity using experimental stress constants of 298.17-77.37 K is only 0.27%.

$$S_{77.37\,\text{K}} = 0.9973\, S_{298.17\,\text{K}} \qquad (7)$$

In his studies of unsaturated helium films using a quartz microbalance, Yang[6] assumed the stress constants measured at 77 K would be essentially unchanged at lower, i.e., liquid helium, temperatures since changes are very small for most normal solids over this temperature range. This contention would seem to be valid since his quartz microbalance data are in excellent agreement with measurements on the absorption of argon, oxygen, helium, and nitrogen on aluminum foil using a mechanical microbalance. The conclusion would seem to be that mass sensitivity is only slightly affected by crystal temperature down to 4 K. Limited additional light is shed on the matter by the thin film thickness measurement work at 4 K using a quartz crystal and x-ray absorption by Barrett and Pasternak.[7] Various gases were deposited on the quartz crystal and on a beryllium target. The flow of gas was stopped at intervals and the film mass calculated by the measured absorption of an x-ray beam using experimental values of the absorption coefficient.

The sensitivity ratio obtained by averaging the measurements on various gases was

$$S_{5\,\text{K}} = 0.792\, S_{293\,\text{K}} \qquad (8)$$

Unfortunately, these data, as the authors warn, must be considered applicable only to their particular geometry since the crystal receives less mass than the target on which measurements were made. The crystal is unfairly penalized in Eq. (8) and the ratio is a higher value, but the actual magnitude is unknown.

A mass sensitivity calibration at 20 K was reported by Wallace[8] using $\phi = 30$ deg 45 min, 10 MHz crystals. A traceable incremental mass of nitrogen gas was introduced into a high-vacuum system wherein the crystal and its supports were the only cryopumping surfaces for the nitrogen. The measured sensitivity ratio was

$$S_{20\,\text{K}} = 2.237\, S_{293\,\text{K}} \qquad (9)$$

This result seemed surprisingly high even though a total of 27 calibration tests were conducted to obtain consistent results.

A later calibration of the same instrument was performed by Youngblood[9] using the constant pressure method of determining mass flow to the crystal. In this calibration,

$$S_{20\,\text{K}} = 2.769\, S_{293\,\text{K}} \qquad (10)$$

Obviously more experimental data are needed to resolve these differences. The degree of concern in the sensitivity spread should, however, be consistent with the impact these differences make in interpreting contaminant thickness calculations. Considering the fact that monolayers of many condensates of interest have mass densities of approximately 3×10^{-8} g/cm^2, the differences in frequency shifts predicted by the various sensitivities for 10 MHz crystals measuring a single monolayer at 20 K would be:

$\Delta f = 6.8$ Hz (stress constant prediction, Yang[6])
$\Delta f = 15.2$ Hz (mass increment, Wallace[8])
$\Delta f = 18.8$ Hz (constant pressure, Youngblood[9])

The mass sensitivity value spread thus results in only approximately 5 Å uncertainty in thickness for unit density single monolayer condensates at liquid helium temperatures. In many optical contamination situations, this magnitude of uncertainty may be acceptable.

Crystal Temperature Coefficient

Optical contamination measurements often are concerned with monolayer surface coverage. This measurement requires a crystal whose frequency ideally is independent of temperature change in the region of interest. This is usually accomplished by the use of two crystals with matched temperature coefficients (one exposed to mass deposition and the other protected from mass flux but in the same temperature environment) or by use of a doublet crystal (to be discussed later). Temperature coefficient matching over wide temperature ranges is made difficult by the fact that the single crystal fundamental resonant frequency may change as much as 20 KHz from room temperature to liquid helium temperature. The matching is simplified if crystal cuts are chosen which have minimal temperature coefficients over the primary operating range.

From the first-, second-, and third-order temperature coefficients of the elastic stiffnesses and compliances of quartz, the temperature dependence of all possible thickness modes can be calculated. A curve of the locus of the first-order zero temperature coefficient of frequency of thickness-shear modes has been calculated[10] and is shown in Fig. 1. Below liquid nitrogen temperature, the frequency-temperature characteristics have been investigated[11] for a wide range of crystallographic cuts and the data are presented in Fig. 2. There is a very desirable flattening of the curves below 20 K for crystals in the 39-40 deg range. A cut of 39 deg 40 min is seen to be a near optimum choice, considering both liquid nitrogen and liquid helium temperature operation.

Crystal Coatings

The intent of the QCM measurement is normally to describe mass deposition which is occurring on a nearby surface of interest, often an optical element or a thermal control element.

At the monolayer level, surface effects may be important in the condensation process and it may be desirable to have a surface on the resonating quartz monitor which duplicates the

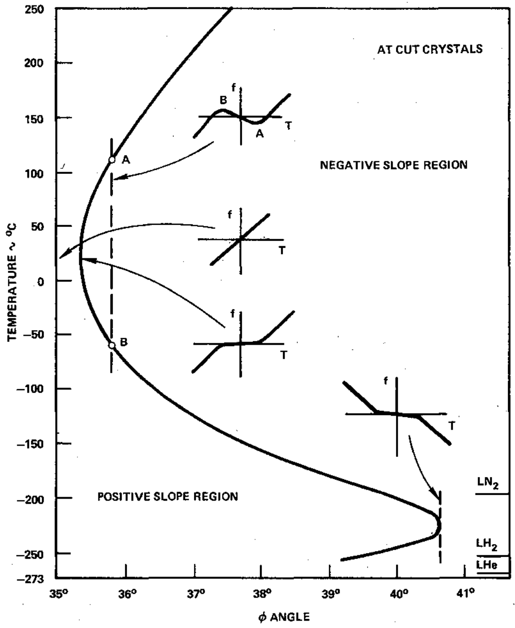

Fig. 1 Locus of first-order zero temperature coefficient of frequency for crystals in thickness-shear oscillation.

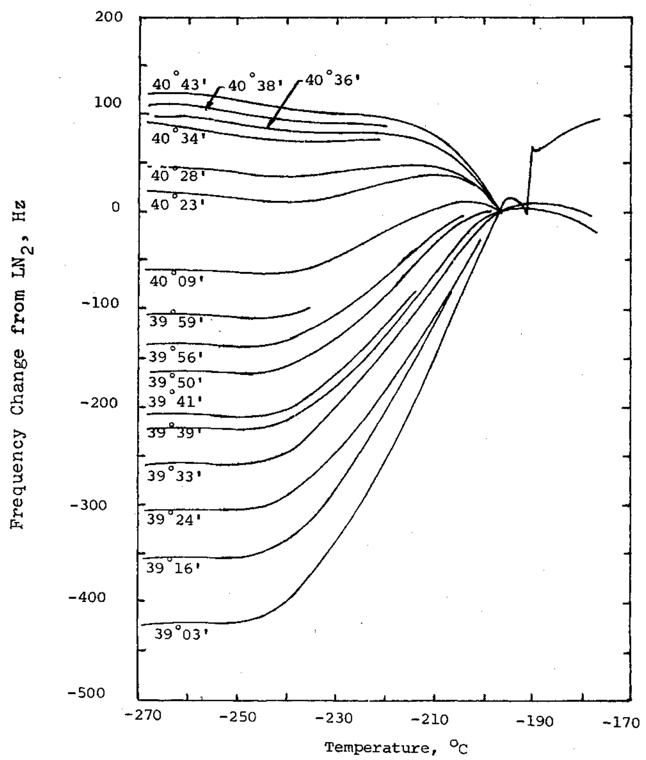

Fig. 2 Frequency-temperature characteristics, 5 MHz crystals (from Ref. 11).

surface of interest. Coatings such as magnesium fluoride, silicon dioxide, and aluminum oxide can be overcoated on the crystal's metal electrode in varying thicknesses depending upon the desired optical properties of the combined multiple thin films. Half-wavelength or quarter-wavelength layers can be used to minimize or enhance the effect of contaminant layers on the reflectance of the crystal or on thermal shock effects if varying solar thermal radiation is involved.

Low-Temperature Oscillator

Locating the oscillator/mixer electronics in close proximity to the sensing and reference crystals has several distinct advantages: the sensing element becomes a single package, thus easier to locate within cryogenic systems with multilayer insulation, etc.; and high-frequency leads with inherent capacitance problems are minimized, the audio frequency mixer output of the QCM sensor being easily sent considerable distances.

Investigation of quartz oscillators at low cryogenic temperatures has been underway since 1956 but usually with the resonator cold and warm electronics. It was recognized at this early date that cryogenic temperature operation of the quartz crystal provided the advantages of increased Q factor, decreased aging and reduced electronic thermal noise.

In the case of semiconductors, it is a case of finding devices which maintain acceptable transconductance at low temperature. As described in Ref. 12, the current gain β of bipolar transistors is so severely decreased that they are probably unusable at liquid helium temperature. The use of n- or p-channel junction field effect transistors is also problematical since their transconductance is decreased by a factor of three at liquid helium temperature compared to room temperature.

MOSFET type transistors have been used, however at these low temperatures their use in low power oscillator circuit design is made difficult by the fact that manufacturer's current/voltage curves are only marginally useful. To achieve low power dissipation, the field effect transistor must be operated at the threshold of conduction which places them in a nonlinear operating region and a very inaccurate portion of the current/voltage curves. Considerable experimental breadboard work was thus required to achieve an optimized oscillator.

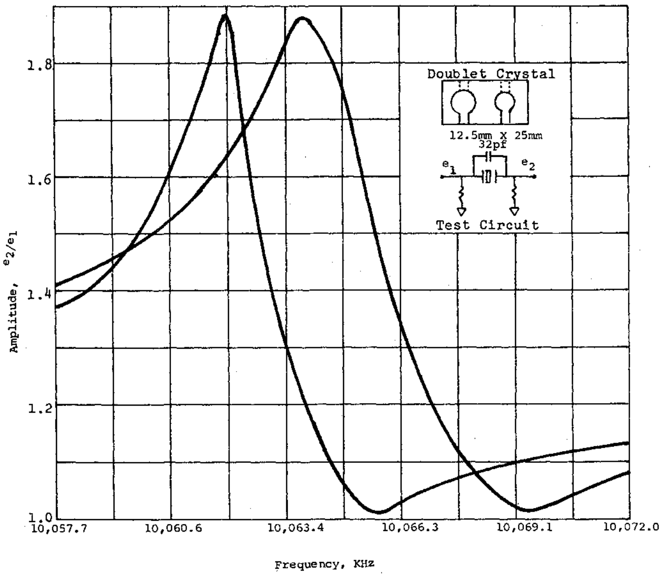

Fig. 3 Crystal voltage amplitude ratio curves for 10 MHz crystal with independent ground electrodes.

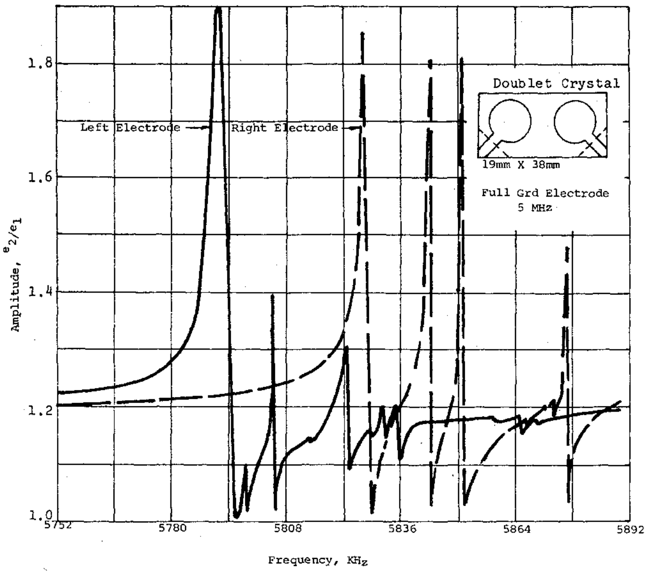

Fig. 4 Crystal voltage amplitude ratio curves for 5 MHz crystal with full ground electrode.

An additional restraint in the oscillator design was the requirement to ground the sensing electrode electrically. Charged particles, ionized gas, etc., striking the crystal could produce voltage spikes disastrous to the electronics as well as producing a charged, nonrepresentative surface for incoming contaminant.

A "Clapp" oscillator was finally developed using an insulated gate, field effect transistor. The mixer employs a dual-gate n-channel depletion-mode IGFET. The circuit operates on a +5 V supply, delivers a 1.5 V signal at the mixer output, and uses 300 μW at room temperature which drops to 200 μW below liquid nitrogen temperature. At reduced supply voltage, the circuit has operated at 95 μW at low temperature. Power dissipation in the crystal is less than 5 μW.

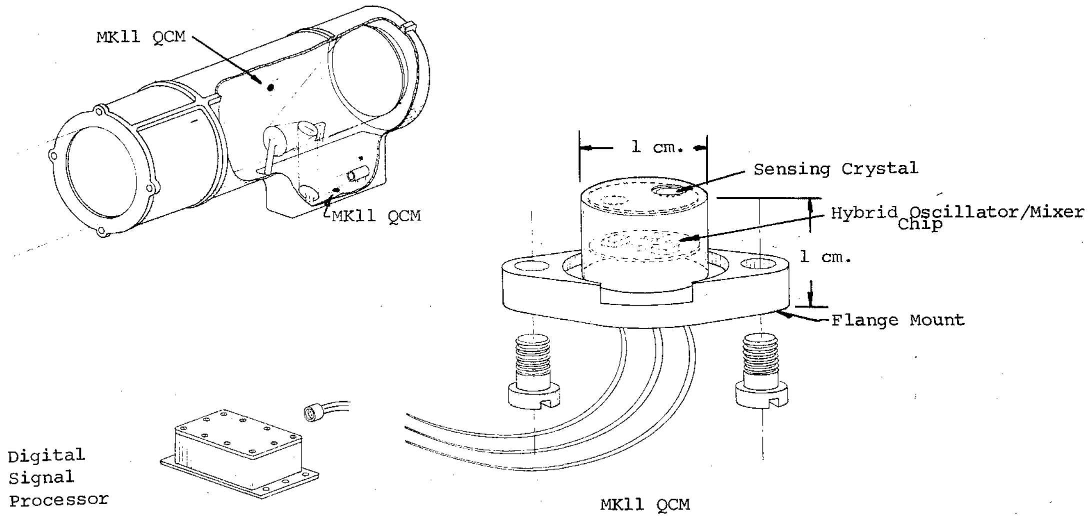

Fig. 5 MK11 low-temperature low-power QCM configuration with typical mount locations in an optical system.

Doublet Crystals

The use of a doublet crystal, i.e., a quartz plate with two areas resonating independently, does reduce the problem of temperature coefficient matching as mentioned earlier in this report. The sensing and reference electrodes are located side-by-side on the same quartz blank minimizing temperature gradients. Phillips, et al.,[13] found frequency shifts of only 30 and 200 Hz for 35 deg 10 min and 39 deg 49 min cut crystals respectively when the crystal temperature was changed from 298 to 133 K. Care must be taken however in the crystal design to avoid "cross-talk" between the two resonating areas. This effect can normally be reduced by making the sensing electrode more massive than the referenced electrode. However, as important to the stability of the oscillation is the avoidance of a common ground electrode deposited over the entire quartz plate. The activity curves of Figs. 3 and 4, measured by a vector voltmeter (HP 8405A) show spurious activity for the 5 MHz crystals with common ground similar to the crystal used by Phillips, et al., whereas the independently grounded 10 MHz crystal indicated completely independent oscillation.

QCM Sensor Configuration

A miniature QCM sensor incorporating the design features discussed in this paper is shown in Fig. 5, along with several suggested points of application in an optical system. The sensing crystal and hybrid electronics are mounted in a 1 cm diameter case which is 1 cm in length including the mounting flange. The crystals operate at 10 MHz with the hybrid mixer providing a beat frequency output. This QCM has undergone launch environment shock and vibration tests successfully.

Conclusions

A miniature QCM has been developed for use at liquid helium temperature which has a power dissipation of less than 200 μW. Selective coatings can be applied to the cryocut crystal to achieve required optical or surface properties. The crystal cut can be selected to achieve near zero temperature coefficient in the desired operating range.

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