High Temperature Microbalances

Background

Traditional microbalance systems based on AT-cut quartz crystal sensors are restricted to thin-film monitoring below ≈300°C. The piezoelectric constant of quartz (SiO_2) drops sharply above 300°C and reaches zero at 573°C where a phase transition takes place[1]. Quartz crystal sensors must be water cooled for accurate thickness measurements under typical thin-film growth conditions. The temperature stability of the quartz crystal resonator can be enhanced, relative to traditional AT-cut crystals, by choosing a different angle of cut. However, the resulting temperature coefficient is still temperature dependent and thermal stability is only possible over narrow temperature ranges (i.e. 20°C range).

For high temperature (i.e. >300°C) thin-film monitoring applications, gallium orthophosphate (GaPO4) is the preferred piezoelectric material. The Y-11° cut of the $GaPO_4$ sensor is about 100 times less sensitive to temperature than conventional AT-cut quartz crystals above 400°C and can be machined into resonators that are essentially temperature independent up to 970°C![2] Such a wide temperature range makes $GaPO_4$ crystals compatible with most modern viscous flow CVD processes (including atomic layer deposition) which typically take place between 300 and 900°C[3]. $GaPO_4$ sensors have been proven compatible with standard QCM instrumentation, and found to be an excellent replacement for quartz at temperatures above 300°C and below 720°C.

Typical specifications for $GaPO_4$ sensors:

Frequency [MHz]	3 – 10
Diameter [mm]	7.4, 10 and 14
Contour	Plano or Plano convex (*)
Orientation	Based on operating temperature. The rotated Y-11° cut crystal has the flatest frequency-temperature response between 350 and 650°C.
Surface finishes	Lapped (3-10 micron) or polished.
Temp Coefficient	3Hz/°C @ 450°C Decreases linearly with temperature.(#)
Resistance	55Ohms for 6 MHz crystal, unloaded.
Cost	\$60-\$100/crystal , 7 mm diam.

(*) A 100mm radius for plano convex 6MHz crystals is well known to avoid spurious resonances.

(#) 650Hz/°C for quartz at 390°C.

Sauerbrey Equation

Sauerbrey was the first to recognize the potential usefulness of the Crystal Microbalance technology and demonstrate the extremely sensitive nature of these piezoelectric devices towards mass changes. The results of his work are embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal:

$\Delta f = - C_f \cdot \Delta m$ where, (equation 1)

Δf - the observed frequency change, in Hz,
Δm - the change in mass per unit area, in g/cm^2, and
C_f - the sensitivity factor for the crystal used (i.e. 56.6 Hz $\square g^{-1}\ cm^2$ for a 5MHz AT-cut quartz crystal at room temperature.)

The basic assumption is that the incremental change in mass from the foreign film is treated as though it were really an extension of the thickness of the underlying substrate material (i.e. quartz or $GaPO_4$). The foreign film is considered rigid and so thin that it does not experience any shear forces during vibration. As a result, the sensitivity factor, C_f, is a fundamental property of the crystal's material and does not consider any of the properties of the foreign film (i.e. it is only dependent on the bulk acousto-elastic properties of the crystal)

$C_f = 2 \cdot n \cdot f_o^2/(\rho_c \cdot \square_c)^{1/2}$ (equation 2)

where,
n - number of the harmonic at which the crystal is driven, typically n=1.
f_o - the resonant frequency of the fundamental mode of the crystal, in Hz,

	AT- cut Quartz	Y-11° cut $GaPO_4$
ρ_c – density ($g\ cm^{-3}$)	2.648	3.570
$\square_c$ - shear modulus ($g \cdot cm^{-1} \cdot s^{-2}$)	$2.947 \cdot 10^{11}$	2.147
$(\rho_c \cdot \square_c)^{1/2\,(}$ $x10^5$ g/ (cm^2s)	8.834	8.755

Notice that when using a conventional film thickness monitor , calibrated for AT-cut quartz, with a Y-11° cut GaPO4 sensor, the resulting thicknesses should be multiplied by $Z_{GaPO4}/Z_{quartz} = 0.991$.

Film thickness is often the parameter of interest in gas-phase thin-film depositions. If the mass coverage is believed to be uniform, the thickness of the film is easily calculated dividing the mass per unit area provided by Sauerbrey's equation by the material's density:

$T_f = \Delta m \ / \rho_f$ (equation 3)

where,

ρ_f - density of film material, in g/cm^3,
Δm - change in mass per unit area, in g/cm^2 (calculated from Sauerbrey's equation), and
T_f - Thickness of the film, in cm.

GaPO$_4$ Suppliers

AVL (now Piezocryst) of Graz Austria is currently the sole manufacturer of Y-11° cut GaPO4 in the world[4]. For aditional information please consult: http://www.piezocryst.com/

Special order crystal can also be ontained from Tangidyne Corporation: www.tangidyne.com.

Note that the crystal holder provided with the QCM200 system is not compatible with high temperature operation. A custom holder will be required to connect a GaPO$_4$ sensor to the QCM25 crystal oscillator.

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[1] J. W. Elam and M. J. Pellin, "GaPO4 Sensors for Gravimetric Monitoring during Atomic Layer Deposition at High Temperatures", Anal. Chem. 77 (2005) 3531-3535. Note: High Temperature crystals operated in an Atomic Layer Deposition process at temperqature around 450C.
[2] Thanner H., Krempl P. W., Wallnöfer W., Worsch P. M., "GaPO4 high temperature crystal microbalance with zero temperature coefficient", VACUUM 67 (2002) 687.
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Krispel F., Schleinzer G., Krempl P. W., Wallnöfer W., "Measurement of the piezoelectric and electrooptic constants of GaPO4 with a Michelson interferometer", Ferroelectrics, 202 (1997) 307
[3] Scott Grimshaw, NSF Award Abstract - #0319486, SBIR Phase I: Utility of Thin Film Deposition Sensors in High Temperature Environments, July 1, 2003DMI DIV OF DESIGN,MANUFAC & INDUSTRIAL INNOV ENG DIRECTORATE FOR ENGINEERING
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[4] http://www.piezocryst.com/index.php?area=database