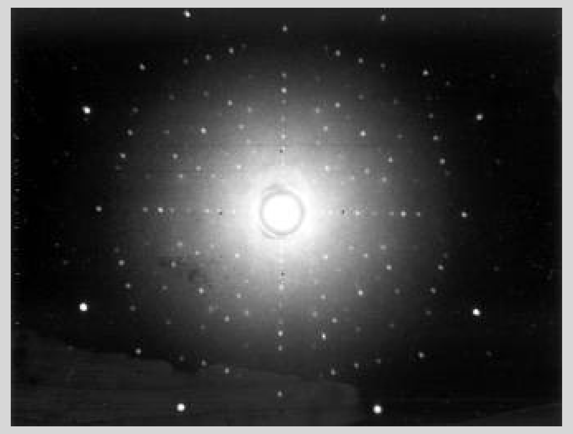


High Temperature Crystal Microbalances

For Thin Film Deposition Monitoring and Control

Scott Grimshaw , VB Sensors

VB Sensors, LLC

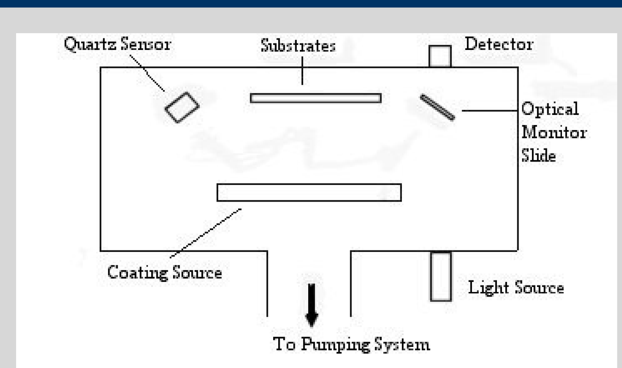
Introduction

The sensor of choice for vacuum thin film thickness monitoring is the quartz crystal microbalance (QCM). Since its introduction as a metrological tool in the early 1960's, the QCM has been an integral part of many vacuum coating systems, including MBE. The superior sensitivity of this tool, coupled with its high precision, has allowed users to build thin film structures on the atomic level.

Unfortunately, the instability of QCM's for the measurement of high stress films (including many oxides and metals), the inability to monitor elevated temperature processes (>100°C), and the effect of thermal shock on coating accuracy remain impediments in the research and production of new devices and materials.

New types of microbalance sensors, using novel crystallographic orientations of quartz, entirely new piezoelectric materials, and temperature adjustable sensor holders, are now available. These sensors address many of the QCM limitations and offer exciting new possibilities for thin film measurements.

Classical Microbalance Technology



The traditional QCM method uses a single crystal quartz disc, mounted in a water cooled stainless steel housing and positioned next to the object being coated.

The quartz is cut with a specific orientation to minimize temperature response ("AT-cut") and is electrically driven at its fundamental resonance frequency. This frequency is periodically sampled and the changes caused by film build-up ("mass accumulation") are converted to film thickness values using the Sauerbrey equation (or derivations):

$$t_f = -\Delta f\, K / 2 f_q^2 \rho_f$$

t_f = thickness of the film being monitored
Δf = frequency shift of the resonating crystal
f_q = starting frequency of crystal
ρ_f = density of the film being monitored
K = quartz material constants

Technology Limitations

•The resonance frequency can change due to *film stresses*, *temperature shift* and *mass accumulation*. It is often impossible to separate out the exact cause of the frequency shifts.

•It is difficult to measure very thin films (1-10 nm) because thermal effects (shock) can overwhelm mass accumulation effects.

• A practical upper temperature limit of ~100-150C exists because the frequency vs. temperature behavior of quartz becomes unfavorable.

• High stress films cause gross instability in the resonance frequency This rate "noise" can make exact measurements extremely difficult.

Minimizing the Effects of Thermal Shock

❖To eliminate radiation induced frequency changes, alternate orientations of quartz, or "cuts", are now being used, including the "IT" and "SC" versions.

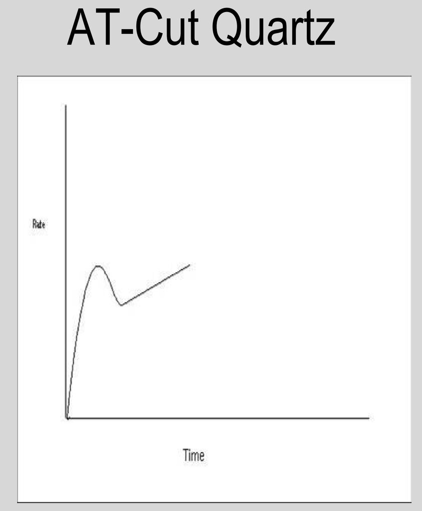
❖These new crystal types are referred to as "doubly rotated" cuts. The manufacture of these crystals involves a compound rotation of the quartz bar during its cutting into single discs.

❖The effect of this additional rotation dramatically reduces the response of the crystal resonance frequency to rapid heating.

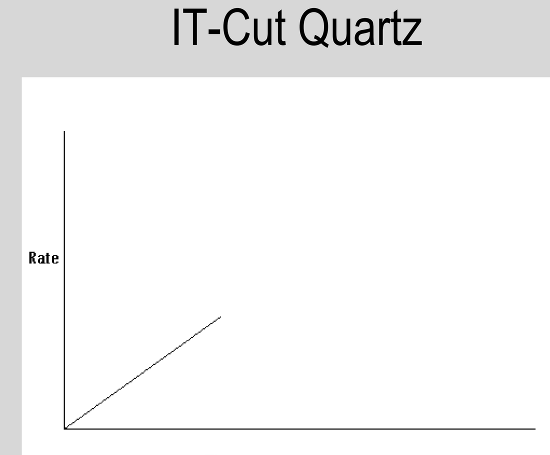
❖Upon exposure to a hot evaporation source, AT-cut crystals exhibit a frequency overshoot that can mask the deposition rate by up to 50%. For very thin films this leads to errors of 100% or more. This overshoot is eliminated with IT-cut crystals.

Crystal Response to Initial Exposure to Coating Source

AT-Cut Quartz

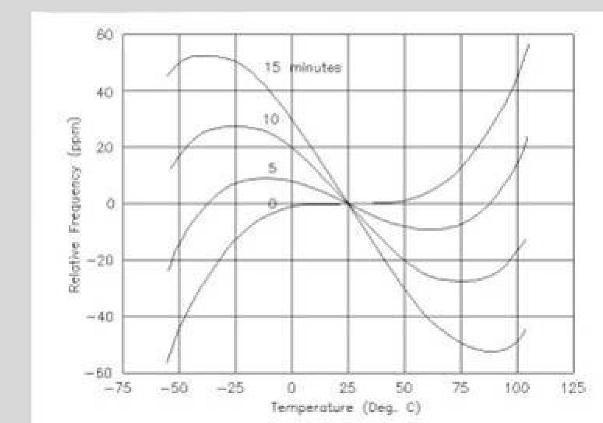


IT-Cut Quartz



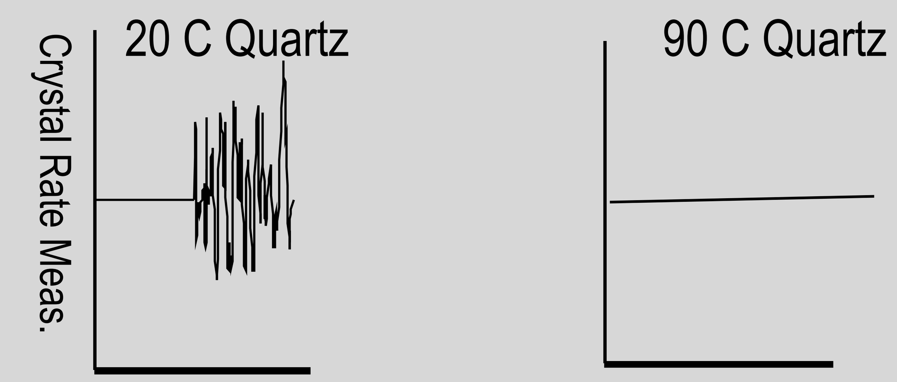
Minimizing the Effects of Film Stress

The conventional thinking holds that an AT-cut quartz crystal must be water cooled to ~20° C in order to minimize the change of frequency with temperature according to its F vs. T curve:



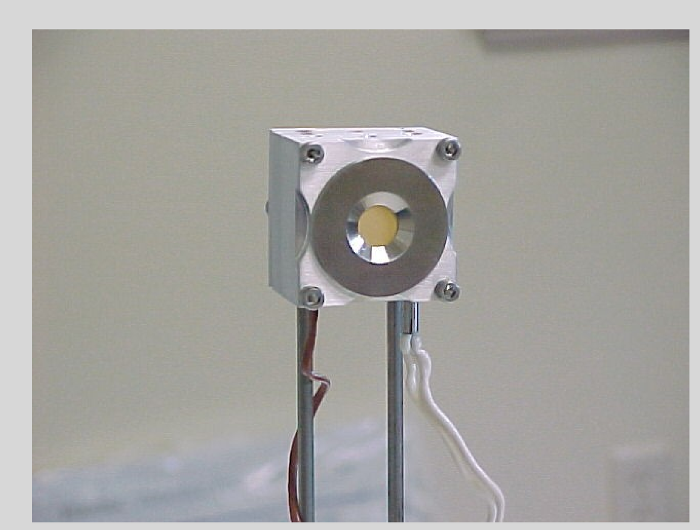
In practice, experiments have shown that a comparatively cold surface of 20°C also *increases rate instability by* inducing stress in the growing film, far exceeding temperature effects.

A dramatic reduction in stress exhibited by oxide films growing on quartz can be demonstrated by *heating* the crystal to 90°C (using a water cooled sensor).



Rate Vs. Time: Cooled Vs. Heated QCM

(silicon dioxide evaporated by an electron beam source)



250°C QCM with Integral Heater and Temperature Measurement

Maximizing Temperature Range

➢QCM's are limited to use at temperatures below 150 °C. Above that, the extreme slope of the frequency vs. temperature curve makes stable frequency measurement difficult.

➢A new class of crystal resonators has been developed, without this limitation. Of these materials, single crystal gallium orthophosphate (GaPO4) is becoming the best known and most readily available

Gallium OrthoPhosphate: A High Temperature Quartz Replacement

✓$GaPO_4$ is a new material based on the crystallography of quartz with gallium and phosphorous substituting for silicon in the crystal lattice.

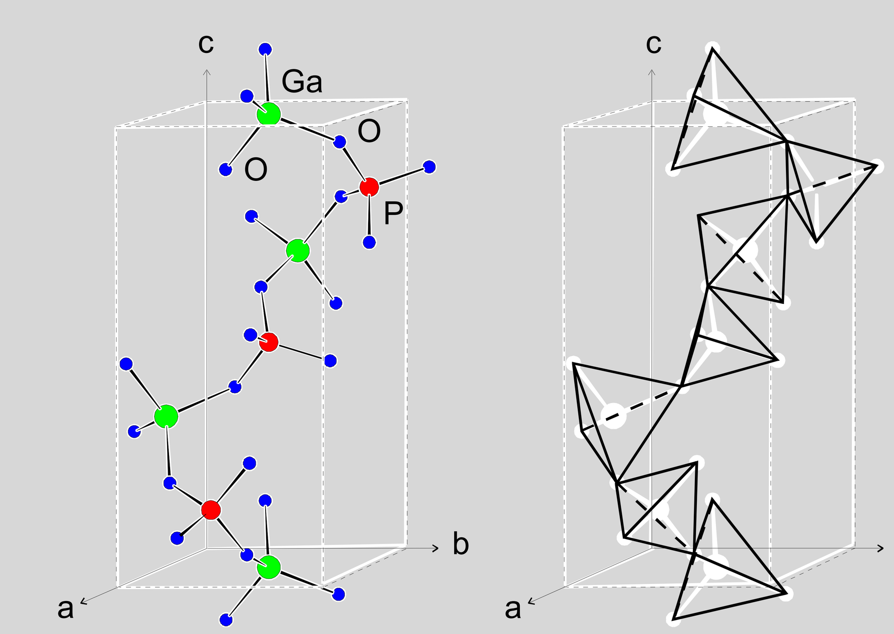
✓It exhibits nearly identical piezoelectric performance to quartz in all applications but also has an extended operating range (up to ~900° C).

✓It exhibits twice the piezoelectric sensitivity of quartz, leading to greater signal strength and potentially longer life.

✓$GaPO_4$ has been fashioned into a mass (film thickness) sensor that can be "tuned" to optimum operation from room temperature to 930°C.

✓It has been used as a chemical vapor deposition sensor and can be heated to re-evaporate films off its surface, potentially a "self cleaning" MBE sensor.

✓Will allow the microbalance to be heated to the same temperature as the substrate being coated, and for some materials, the actual temperature of thin film evaporation, e.g. aluminum, organics, etc.



Gallium Phosphate Structure (Quartz Homologue)

Contact information

Scott Grimshaw
VB Sensors
PO Box 202
Marcellus, NY 13108
(315) 673-2024
Mobile: (315) 263-0340
Sgrimshaw@tangidyne.com