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$GaPO_4$ HIGH TEMPERATURE CRYSTAL MICROBALANCE DEMONSTRATION UP TO 720°C

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Abstract

Quartz-homeotypic gallium (ortho-) phosphate, $GaPO_4$, is of special interest for resonator applications asking for temperature compensated cuts with higher electro-mechanical coupling than quartz and operational temperatures up to 970°C. The crystal microbalance technique, well known for quartz (QCM) which can be used only at moderate temperatures, can now be extended to much higher temperatures using $GaPO_4$ crystals, benefiting from all three advantages mentioned above. Two different experiments were done to demonstrate the advantages of a crystal microbalance based on $GaPO_4$. First, the $GaPO_4$ resonator was used for film thickness determination and compared with a commercial QCM. This experiment demonstrated that the measuring range can be extended by using $GaPO_4$ resonators instead of quartz. The second experiment demonstrates the possibility for thermogravimetric analysis up to 720°C by using a new concept for resonator mounting.

Keywords: BAW resonator, gallium(ortho)phosphate, $GaPO_4$, high temperature, microbalance, QCM, sensor mounting, thermogravimetry

Introduction

Because of its excellent thermal stability up to 970°C, a coupling coefficient twice as high as in quartz for the most favourable cuts and very low acoustic losses, $GaPO_4$ offers a large field of resonator applications, in particular at high temperatures [1]. During the last years, a lot of experimental and theoretical work in basic material property research has been done in both, BAW [2–3] and SAW [4–5] resonators. For thickness shear resonators, temperature compensated cuts near room temperature were found with a flatter frequency-temperature curve than in BT-cut quartz and other piezoelectric materials.

For singly rotated Y-cut $GaPO_4$ resonators, the inversion temperature (T_0) depends on the orientation of the crystal plate and the cut angle sensitivity of the inversion temperature is much lower than in quartz which opens the way for very high stability applications. The inversion temperature (T_0) of the resonant frequency increases by rotating the cut angle and the frequency temperature curve becomes flatter. Near 500°C the 2nd order temperature coefficient vanishes and the frequency temperature behaviour becomes cubic where the resonant frequency shifts only ±30 ppm in the temperature range from 350 to 650°C [2].

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$GaPO_4$ microbalance for film thickness monitoring

Film thickness monitoring

Quartz crystal microbalances (QCM) are commercially used for thin film thickness determination in particular for in-situ monitoring and control of the deposition rate in vacuum coating systems [6]. With a QCM, the thickness of metallic or dielectric films e.g. in the semiconductor and optical industry can be determined with a resolution less than 0.1 nm.

To show the principal function of a $GaPO_4$ crystal microbalance (GCM) for film thickness monitoring, gold was sputtered on both, a $GaPO_4$ thickness shear resonator 6.2 MHz (fundamental mode), temperature compensated near 50°C and on a 6 MHz AT-cut quartz standard microbalance simultaneously.

Fig. 1 $GaPO_4$ thickness shear resonator with gold electrodes (10 mm diameter)

Figure 1 shows a $GaPO_4$ thickness shear resonator with 10 mm diameter, plan convex design and with gold electrodes on both surfaces. The cutting angle is chosen near Y-15.5° [8] to achieve temperature compensation between room temperature and 100°C. The shifts in the resonant frequencies of both G(Q)CM, caused by the mass accumulation during the sputter process were measured, monitored and stored in frequency and film thickness units. Figure 2 shows the measured and calculated values for the GCM.

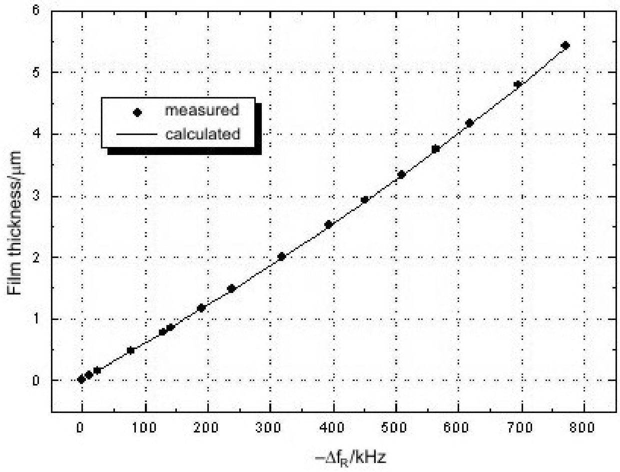

Fig. 2 Film thickness determination by using a $GaPO_4$ microbalance (GCM)

Figure 2 shows the excellent validity of the so-called '*Z*-match theory' [7] for thin film thickness monitoring by using a GCM, too. In addition, the very favourable temperature compensated behaviour of the resonant frequency suppresses the thermal influence caused by the sputter process. The use of commercially available deposition monitors in combination with $GaPO_4$ sensor elements is possible simply by modifying the acoustic impedance ratio *Z*, depending on the density and shear modulus of the piezoelectric sensor material and the deposited layer material.

Q-value in high vacuum

The initial sensitivity of a crystal microbalance is given by the resonant frequency of the 'unloaded' resonator. The fundamental mode resonant frequency of most commercially available quartz resonators for QCM applications is in the range of 6 to 10 MHz.

The maximum resolution of a microbalance measuring system (e.g. film thickness resolution) is limited by the used oscillator electronic and the *Q*-value of the piezoelectric resonator. While the resolution of the oscillator electronic remains essentially constant, the resonator becomes more damped with increased mass loading. For that reason, the resolution of the microbalance system decreases during the mass loading process (e.g. film-thickness monitoring). This limits the measuring range of the microbalance system.

The *Q*-value is defined by

$$Q=\frac{f_R}{\Delta f} \tag{1}$$

where f_R is the resonant frequency and Δf is the 3 dB bandwidth which can be determined from the resonance behaviour of the resonator.

Figure 3 shows the resonance curve of a $GaPO_4$ thickness shear resonator, which was measured with a HP network analyser. The resonator was mounted in a standard microbalance holder for measuring the resonance behaviour in high vacuum. The

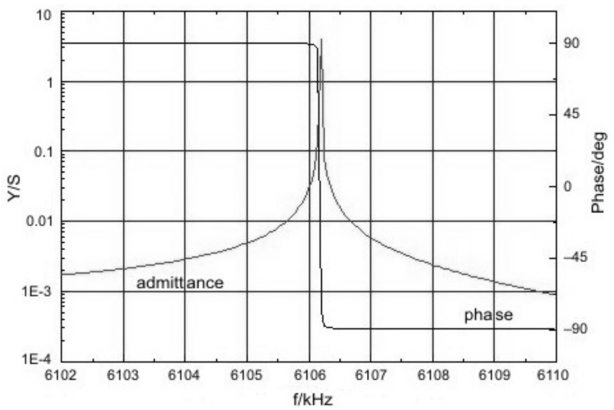

Fig. 3 Resonance behaviour of a $GaPO_4$ thickness shear resonator in high vacuum (fundamental mode)

center frequency around 6.1 MHz and a 3 dB bandwidth near 5 Hz lead to a *Q*-value of about 1.2 million by using Eq. (1).

The performance of a piezoelectric resonator, which is influenced by the resonant frequency (Qf_R=const.), the resonator design and limited by the crystal quality can be defined as

$$Qk^2=\text{const.} \quad (2)$$

where k is the coupling coefficient.

For a 14 mm diameter AT-cut quartz resonator with silver electrodes (6.0 MHz fundamental mode), measured in high vacuum, follows with Eq. (2):

$$0.944\cdot10^6(8.8\%)^2=7300 \quad (3)$$

and for the $GaPO_4$ resonator, measured under comparable conditions:

$$1.2\cdot10^6(15\%)^2=27000 \quad (4)$$

The comparison of Eqs (3) and (4) shows the very high performance of the $GaPO_4$ resonator and this indicates the excellent crystal quality, too.

Motional resistance R_1

Another definition of the *Q*-value of a piezoelectric resonator is given by

$$Q=\frac{1}{2\pi f_R R_1 C_1} \quad (5)$$

where R_1 is the motional resistance and C_1 dynamic capacity.

The dynamic capacity C_1 is mainly determined by the properties of the used piezoelectric material, the thickness of the resonator plate and the diameter of the electrode. For that reason, C_1 remains essentially constant during thin film deposition onto the resonator surface.

The motional resistance R_1 represents the acoustic losses in the resonator. For that reason, R_1 increases with increasing mass loading. Figure 4 shows the measured values of R_1 of the GCM and the QCM during thin film deposition.

In Fig. 4 one can see, that the motional resistances R_1 for the $GaPO_4^-$ and the quartz resonator started at nearly the same value. But during the film deposition, R_1 of the quartz resonator increased much more as the R_1 of the $GaPO_4$ resonator. This indicated clearly a larger possible measuring range for the $GaPO_4$ resonator for microbalance applications as it is possible with the AT-cut quartz resonator. The physical reason for this very attractive behaviour is given by the higher coupling coefficient k of the $GaPO_4$ resonator which is twice as high as the coupling coefficient of the commonly used AT-cut quartz resonator.

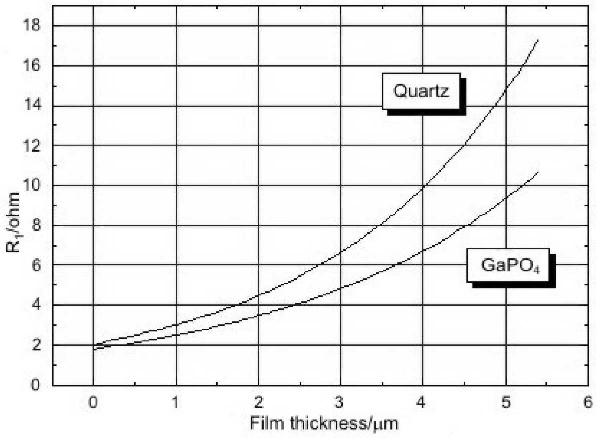

Fig. 4 Motional resistance of a $GaPO_4$ and a quartz thickness shear resonator during thin film deposition

High temperature microbalance application

High temperature crystal holder

The maximum specified temperature limit of the most commercially available microbalance holder is near 120°C. In addition there are some bakeable microbalance holders on the market with a maximum temperature limit at 400°C.

Several reasons which limit the maximum operating temperatures have been found:

- thermal influenced mechanical expansions cause mechanical stress in the sensor element
- thermal variations of the mechanical contact forces
- thermal variations of the electrical contact resistances

For that reason, a new concept of resonator mounting for very high temperature microbalance applications has been developed. The new microbalance holder, shown in Fig. 5, is based on a single ceramic plate. The basic principle of this sensor holder is to apply only radial mounting- and electrical contacting-forces on the lateral surface of the sensor element (Patent pending). For this reason, the electrodes of the resonator plate have to be extended to the lateral surface.

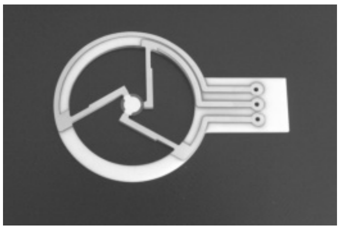

Fig. 5 New 'radial' forced high temperature microbalance holder

High temperature microbalance demonstration

To show the high-temperature performance of the GCM, lube oil was applied on one resonator surface and after this, the crystal was heated up to 720°C. Figure 6 shows the measuring procedure schematically.

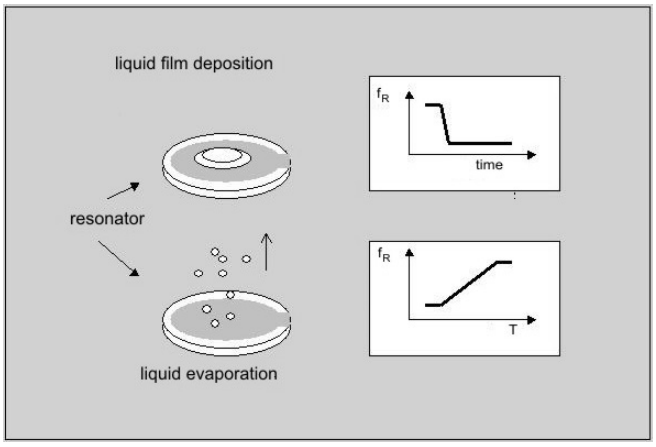

Fig. 6 Measuring procedure for high temperature microbalance demonstration based on $GaPO_4$ resonators

For this measurement, a single rotated Y-11° cut [8] $GaPO_4$ resonator with 7.4 mm diameter and a resonant frequency near 6.2 MHz (fundamental mode) was used. The frequency temperature behaviour of this resonator is very flat in the temperature range between 350 and 650°C as reported in [2].

The resonator was mounted in the new high temperature microbalance holder which is shown in Fig. 5. Then lube oil was applied on one resonator surface. During this procedure, the resonant frequency was measured and is shown in Fig. 7.

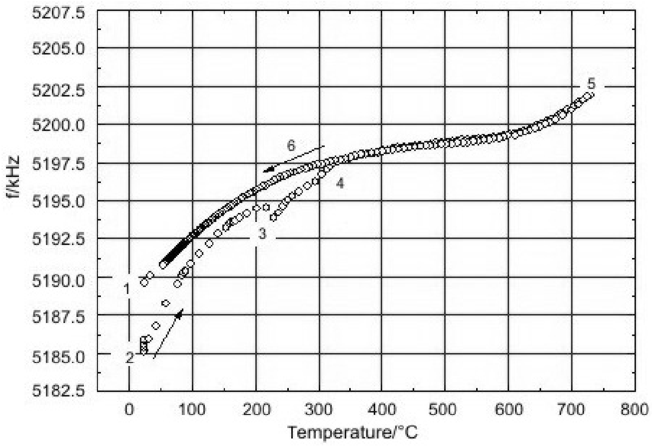

Fig. 7 Thermogravimetry and crystal cleaning by heat up to 720°C

Description of Fig. 7: The shift in the resonant frequency Δf_R caused by the added liquid film was approximately 4.2 kHz (1)→(2). Then the resonator was heated up and the resonant frequency increased rapidly because of the thermal influenced decrease of the viscosity and density of the liquid. Near 200°C, the properties of the liquid film changed and became viscoelastic (3), which lowered the resonant frequency. With further increased temperature, the liquid film evaporated from the resonator surface and near 350°C the resonant frequency approached the 'unloaded' frequency temperature behaviour of the resonator (4). During the following heating procedure, up to 720°C (5), the resonant frequency approximated more and more the 'unload' behaviour. Finally the heater was switched off and the resonant frequency decreased like the well-known cubic behaviour (6) which indicated a completely cleaned resonator surface.

Conclusions

The experiments demonstrated the very favourable function of $GaPO_4$ resonators for microbalance applications in particular at very high temperatures.

The mass accumulation, e.g. during thin film deposition, caused a much lower damping in $GaPO_4$ than in quartz AT-resonators. Therefore, with $GaPO_4$ resonators the maximum measuring range can be extended and the resolution can be increased respectively for both thin film deposition monitors and (high-) viscose liquid measurement applications.

Also the performance of the new high temperature microbalance holder has been demonstrated up to 720°C successfully. This opens the way to combine the high sensitive microbalance method with thermogravimetric analysis in an extended temperature range.

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