NSF Award No. 0319486

SBIR Phase I: Utility of Thin Film Deposition Sensors in High Temperature Environments

Activities

A) Background

Historically, the method of measuring and controlling the thickness of vacuum deposited thin films used in the fabrication of optical or microelectronic components has involved the use of oscillating quartz crystals, or quartz crystal microbalances (QCMís). These devices operate on the principle that the crystalís resonance frequency changes when a thin film deposits on its surface. Knowing the density of the film being deposited, one can calculate the resulting film thickness from this change in frequency. QCMís are extremely sensitive; coatings of only a few Angstroms can be routinely detected. As a result, they have become indispensable in the vacuum coating industry.

Unfortunately, due to its large frequency changes with temperature, quartz is limited to applications below 150 ∫C and must be water-cooled to insure accurate measurements. This has proven to be a great obstacle to the measurement of films deposited using high temperature processes such as CVD, or chemical vapor deposition. Chemical vapor deposition is used to produce thin films via the pyrolysis or breakdown of gas phase chemical species at elevated temperatures. It offers advantages over other deposition technologies including high speed, throughput and highly conformal coating.

The typical method of CVD involves heating an evacuated chamber to a temperature in the 300 to 900∫C range, and introducing a gas such as Silane (SiH_4) that breaks apart at these temperatures. The pyrolyzed gas leaves a thin film coating on the hot surfaces with the chamber. In such a manner, silicon dioxide, silicon nitride and other films with microelectronic or optical component interest can be readily deposited, at very high rates.

In order to measure the deposition rate and thickness in CVD systems, various optical techniques have been employed, with limited success. However, without the high sensitivity and real-time, in-situ rate measurement offered by QCMís, the fabrication of precision thin film coatings by CVD is severely limited. A high temperature version of quartz would improve process control immensely.

Recently, a new piezoelectric material with properties very similar to quartz but with an operating range substantially higher, has been introduced, single crystal gallium orthophosphate, or $GaPO_4$.[1] A crystallographic homeotype of quartz, $GaPO_4$ is structurally similar to the α-quartz used for film thickness monitor crystals, and has several remarkable properties. $GaPO_4$ exhibits twice the piezoelectric activity of quartz, can operate up to 970 ∫C and can be fashioned into crystal resonators that are essentially temperature insensitive over a range of several hundred degrees. As early as 1997, $GaPO_4$, was proposed for uncooled microbalances for the measurement of thin film formation at up to 900 ∫C.[2]

Subsequent work[3] reported the use of gallium phosphate microbalances at temperatures up to 720 ∫C for the monitoring of thin oil film deposition and its subsequent evaporation. The work also described a special type, ì one-shotî crystal holder that was designed to withstand the high temperatures and stresses encountered in these depostions.

After several discussions with the Peter Worsch, product development manager of AVL, the company that invented and owns the rights to GaPO4, we decided to test out this material as a high temperature CVD thickness monitor. Our goal was to target CVD oxide and nitride deposition processes widely used in the semiconductor industries. Since gallium phosphate is very expensive ($60-100 for a 7 mm crystal), and very fragile (a 6 MHz crystal is 0.009î thick and brittle) we chose this market since it was the least price sensitive when it came to process improvements.

B) Goals and Objectives

Our research plan was broken down into two phases:

1) Build a GaPO4 thin film monitor deposition system capable of production use at temperatures of 100 to 900∫ C. Its key features would include:

    a) A simple and reusable sensor mounting system
    b) A microprocessor based controller system based on currently available technology and containing all key electronic systems (driving circuits, measurement and control function)
    c) An optimized geometry and temperature range GaPO4 crystal suitable for use in the temperature range of choice.

2) Test the system performance developed in phase 1 by:

    a) Monitoring the thickness and rate of chemical vapor deposited thin films of silicon dioxide and silicon nitride.
    b) Compare the reported thickness from the GaPO4 sensor with those obtained by
        1) SEM (scanning electron microscopy)
        2) Surface Profilometry
        3) Gravimetry

In the preparation phase of our experimental plan, we had in depth discussions with AVL regarding the suitable types of GaPO4 available (angle of cut, contours, frequency and electrodes) and mounting systems. Mr. Worsch was extremely helpful in this regard, offering us all current GaPO4 publications he had as well as offering advice on holder design. It is interesting to note that early work on GaPO4 described the use of a ì radialî high temperature microbalance holder that eliminated stresses on the sensor induced by the high temperatures. These stresses can interfere with the functioning and reproducibility of the device. Unfortunately we learned that this holder wasnít available for testing.

C) Experimental Design

1) Gallium Phosphate Sensor Specification

Our initial task was to specify and obtain suitable gallium phosphate single crystal samples to begin our research on. As indicated earlier, AVL (now Piezocryst) of Graz Austria is currently the sole manufacturer of this material in the world. We were limited by their production schedule and fabrication capabilities. The parameters we had to work with are outlined in Table 1:

Table 1: Gallium Phosphate Design Matrix

Frequency	Diameter	Contour	Orientation	Surface Finish	Electrode
3 MHz to 10 MHz	7.4, 10 and 14 mm	Plano or Plano-convex	Based on Temperature Range	Lapped (3-10 micron) or polished	Gold or Platinum, flag style electrode

Given the time frame and the restrictions of our test system (we wanted to use commercially available crystal monitor equipment) our choices narrowed down quickly. This limited us to the following design parameters:

1) Frequency: 5 or 6MHz We chose 6 MHz since this is supported by our test monitor (an Inficon IC5) and is the industry standard for film sensitivity.

2) Diameter: Due to cost constraints, 7.4 mm crystals were the most reasonable (~$60 each). 14 mm, the quartz industry standard for thickness monitors, cost in the neighborhood of $125 each.

3) Contour: For a 6 MHz 7.4 mm diameter, a 100 mm radius of curvature, plano-convex design has proven to be relatively immune from spurious resonance modes and coupled vibrations.

4) Orientation: The rotated Y-cut, Y-11° crystal has the flattest frequency temperature performance for gallium phosphate crystals. This is stable from 350 to 650∫ C according to published data[3].

5) Electrode Design: We had the capabilities of making our own masking and depositing metal electrodes via electron beam evaporation. For low

temperature(<550∫ C) experiments, gold over titanium is stable but above that platinum over titanium is the material of choice.

6) Surface Finish: To keep cost manageable (polished contoured crystals are prohibitively expensive), we chose a 7-10 micron surface finish. This is equivalent to commercially available quartz crystals used for thin film monitoring.

We obtained and fabricated 20 pieces of Y-11° cut, 7.4 mm diameter, 6 MHz (nominal) 100mm radius plano-convex gallium phosphate single crystals with a 10-micron finish. After ultrasonic cleaning and mild acid etching, electrodes were applied through a shadow mask via electron beam evaporation using a Temescal BJD-1800 evaporator operating at a base pressure of <5 x 10E-6 Torr.

2) CVD Test Chamber

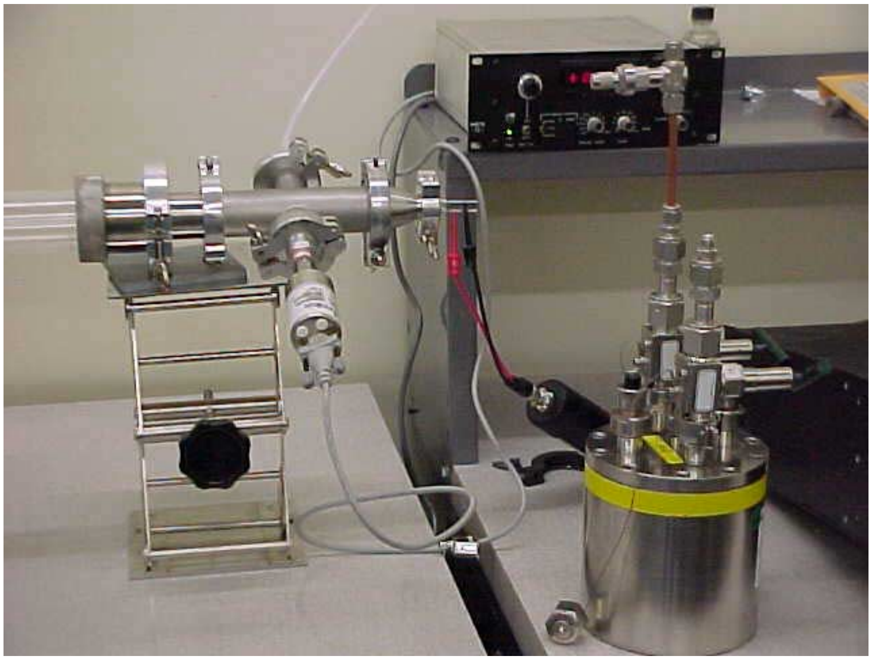
Our second task was to create a test bed system for the sensor to operate in. Since we wished to simulate a CVD environment, we needed to have a low vacuum (1-20 torr) high temperature chamber with appropriate connectivity to the test system electronics. We settled on a tube furnace arrangement, using a quartz tube with vacuum fittings for pumping, pressure and temperature measurement, gaseous precursor admission and electronic signal routing. Pictured in Figures 1 and 2 is the set-up which met all test criteria:

Figure 1: CVD Test System (Pumping End)

Furnace/Vacuum System Details:

1) Lindbergh Clamshell Tube Furnace, 20-1200∫ C Range
2) Eurotherm 818 Setpoint Temperature Controller
3) GE Quartz 2î OD Furnace Tube with KF-50 Vacuum Couplings
4) Tegam 840A Type K Thermocouple Thermometer (NIST traceable)
5) Edwards Rough Pump/JC Controls Thermcouple Gauge
6) MKS 250B Baratron Gauge/Pressure Controller

Figure 2: CVD Test System (Measurement End)



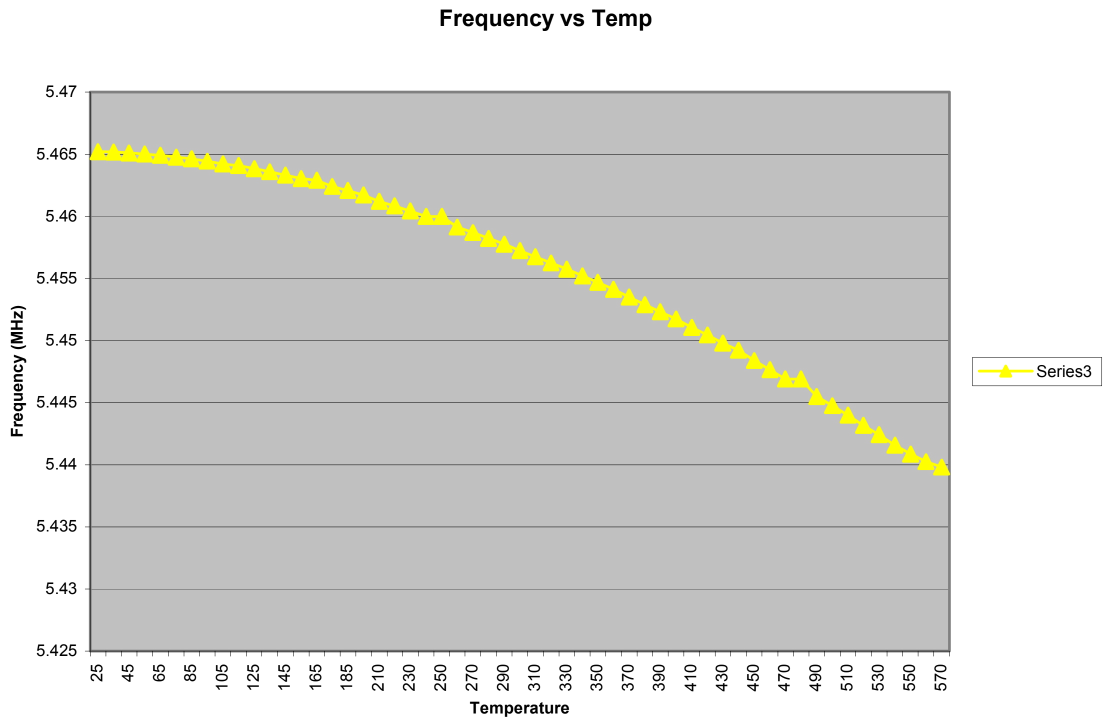
This system was capable of providing a low base pressure (<50 millitorr), controllable vapor flow (0-100 torr, using TEOS, a commonly used silicon dioxide CVD precursor as a source) and contained feedthroughs for thermocouples, vacuum connections, crystal electrical contacts and pressure measurement.

The electronics used to oscillate the crystal consisted of either an Inficon IC5 quartz crystal monitor and controller (commercially available microprocessor control with all functions integrated) or an Agilent E5100A Network Analyzer. The latter instrument allowed graphical display of the resonance trace as a function of frequency for more detailed information regarding the gallium phosphate electronic properties.

3) Reusable Sensor Head

The third task, the construction of a simple and reusable sensor mounting system to insert into this furnace was more difficult. Our initial examinations started with a classical wire attached crystal holder, commonly used in the communications industry. This is a simple design, but ultimately suffers from the oxidation of Kovar (an iron-nickel-cobalt alloy) and the low temperature softening point of the glass used to make the hermetic seal base. For completeness, however, we mounted a gold-coated gallium phosphate crystal mechanically in such a holder and monitored the frequency via a Saunders 110HF crystal oscillator as we heated it from room temperature to >600∫ C. The frequency data is displayed below:

Figure 3: GaPO4 on Kovar Header



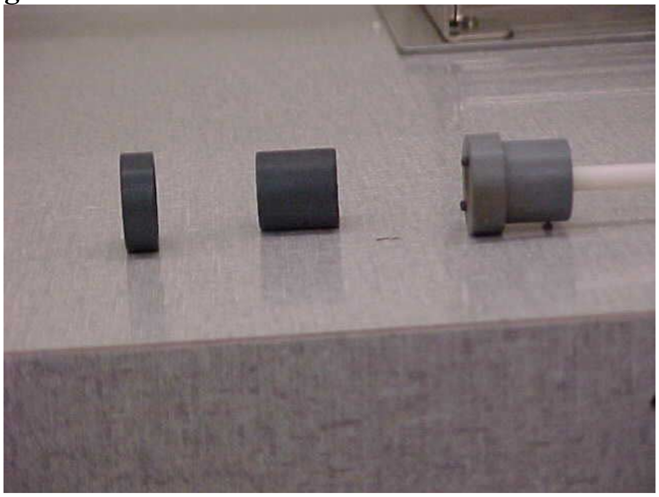
Above 570∫ C the crystal abruptly failed. Upon cooling and removal from the furnace, it was observed that the Kovar pins had moved in the base. The data was considered suspect due to the mechanical instability of the mounting system. A number of other designs were tried, including a Macor™ holder (pictured with platinum electrodes removed) and other glass ceramic types. These were discarded after testing due to mounting difficulties or unstable measurements. Some of the designs and an example of a before and after Kovar base crystal holder are pictured in Figure 4.

After repeated trials, a demountable head machined from aluminum silicate ceramic material (McMaster-Carr Supply Co) and featuring a threaded design with platinum electrodes gave the most stable performance. In addition, this system featured a 30 cm long alumina tube incorporating the platinum lead electrodes that were attached to a vacuum feedthrough. This allowed easy placement and removal of the sensor within the hot zone of the tube furnace. This latter feature became extremely valuable when furnace runs of 900∫ C required 2 and 3 hour cool down times for sensor removal.

Figure 4: Various High Temperature Crystal Head Designs

The final test fixture used through the balance of this work is pictured in Figure 5. Detailed AutoCad ™ drawings were also rendered.

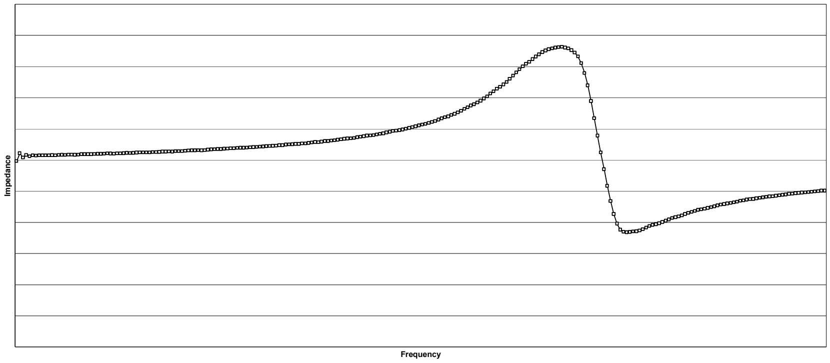
Figure 5: Demountable Sensor GaPO4 Sensor Head



D) Results and Discussion

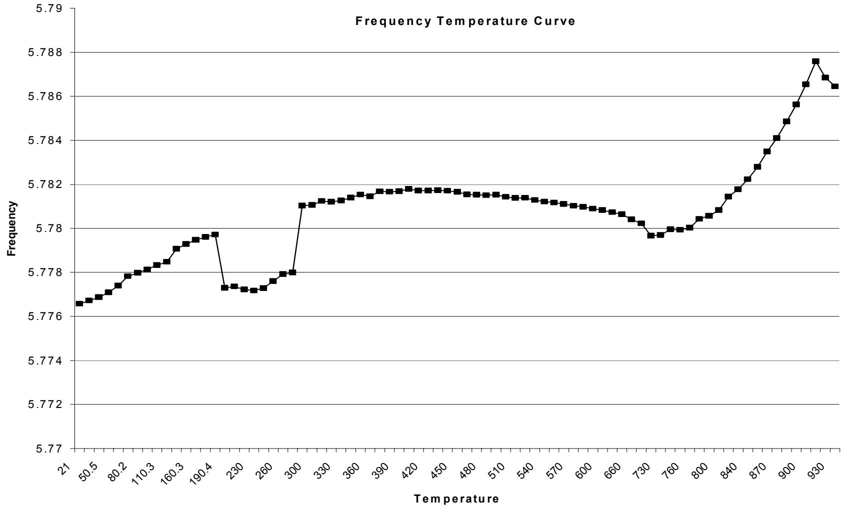
Within the evacuated and heated tube furnace, mounted gallium phosphate crystals were observed to oscillate from room temperature (21°C) up to 930°C. This oscillation was measured and monitored using the network analyzer, sweeping through a wide frequency range (5-6 MHz). As pictured in Figure 6, a classical resonance pattern was obtained. This resonance indicated the crystal was operating in the fundamental thickness shear mode; the characteristic vibration used in film thickness measurements. Above 930°C, all oscillation activity ceased and no resonance signal was discernible.

Figure 6: Resonance Spectrum of $GaPO_4$ at 50°C



A frequency versus temperature curve was then plotted over this range (Figure 7). Most notable was the appearance of a large shift in frequency at approximately 200°C and a corresponding recovery at 300°C. Given the abrupt nature of this shift, and by comparison with network analyzer sweeps, it appears that this is a result of the crystal movement within the crystal sensor housing. Remounting the crystal, as well as cooling and reheating, would produce the same result. After this recovery, the frequency shifted very little with temperature, in the range of 320°C to 660°C. This flat region agrees with the reported characteristics of the Y-11 angle of cut. At temperatures above 730°C the frequency rapidly increased with temperature.

Figure 7: Frequency-temperature Curve of a Y-11 cut GaPO4 Crystal



As the temperature was increased during the generation of this curve, periodically the appearance of multiple vibration modes was observed (Figure 8). Essentially, more than one type of vibration of the $GaPO_4$ crystal can take place and is manifested by coupled modes. This behavior is also common in quartz. This phenomenon complicates matters considerably for film thickness measurements since the frequency of the thickness-shear mode being monitored is momentarily disrupted, often displayed as a ì crystal failureî error on a commercial crystal monitor. These oscillation failures or coupled modes would appear and disappear at regular temperature intervals (changes of, for example, every 60 to 70°C). Occasionally there would be a frequency shift to a lower value after these coupled mode periods. Fortunately, this activity was short-lived and ceased within a few degrees of onset.

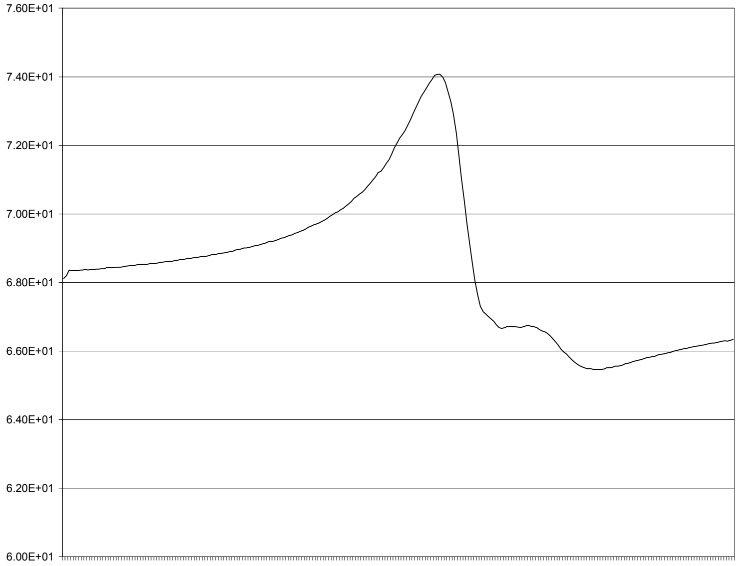


Figure 8: Coupled Resonance Mode of GaPO4 at 120° C

Once a stable oscillating condition was established, the next phase was to operate the $GaPO_4$ with a commercial film thickness monitor. The network analyzer was replaced with an Inficon ™ IC5 6 MHz quartz crystal controller. The IC5 utilizes phase locking technology and will automatically track the crystal resonance frequency. Implicit in the operation of the IC5, however, is the requirement of an electrical circuit condition termed the zero phase angle. This condition occurs at the resonance frequency maximum and minimum peaks and is a necessary for a crystal oscillation to be sustained. Such a condition is not needed for driving the crystal through passive frequency sweeping as is done with a network analyzer.

A Y-11 cut platinum electrode gallium phosphate crystal was mounted in the aluminum silicate sensor head and placed in the tube furnace. Its initial frequency was 5.769 558 MHz with an impedance of 56.4 Ohms (as measured with the network analyzer). This falls within the operable parameters of a quartz crystal typically used in a monitor (normal range is 5-6 MHz with 10 to 100 Ohms impedance). The crystal oscillated as evidenced by a crystal rate reading of 0+/-0.2 Angstroms per second. This indicates a stable crystal with no deposition occurring. The furnace was pumped down to 50 millitorr and furnace heating initiated. As the temperature ramped to the set point of 650°C (the temperature at which the CVD deposition of TEOS can occur), oscillation continued smoothly until 550 C, where the IC5 began to intermittently indicate crystal failure. This occurs in all commercial monitors when the oscillator circuit no longer locks onto the zero phase condition of the crystal, or where the impedance of the crystal rises beyond the drivable range. With continued heating, the crystal began to recover slightly and appeared stable until the temperature within the tube reached 601.5 °C. At this point the IC5 indicated the crystal was no longer oscillating and flashed a steady failure message.

The crystal was hooked back up to the network analyzer and a strong resonance was observed. This indicated the crystal was still electronically active. However, a phase angle measurement taken with the analyzer indicated there was no zero phase condition at either resonance frequency maximum or minimum. Frequency sweeps of crystals with a zero phase condition and non-zero phase condition are presented in Figures 9 and 10. Without a zero-phase point, the IC5 could not be used to track the crystal frequency. Repeated heating and cooling produced the same result, with the failure of the IC5 typically occurring at 550-600°C.

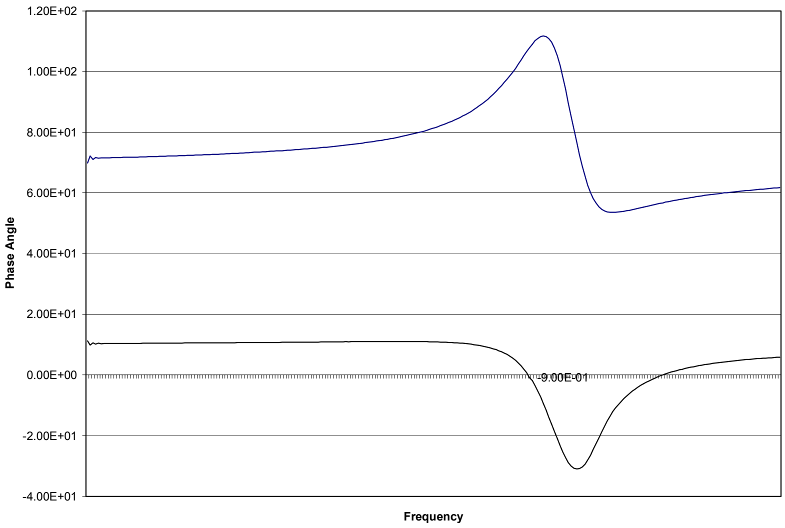


Figure 9: Zero-Phase Angle Crystal Resonance Condition, 260°C

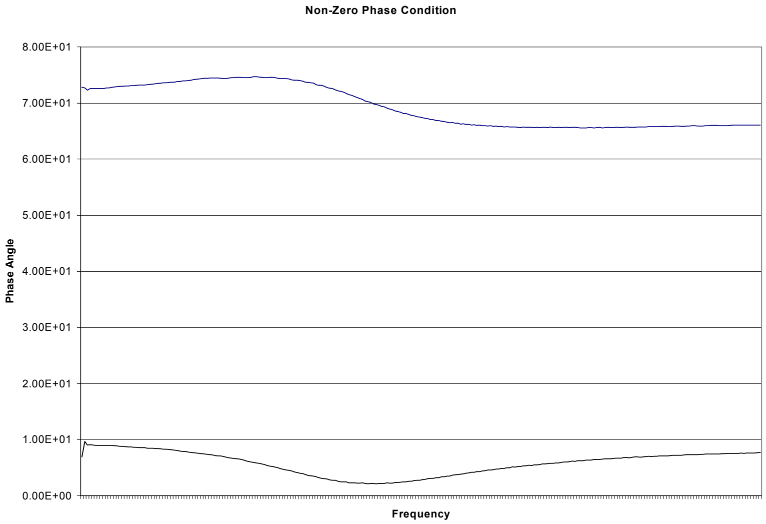


Figure 10: Non-Zero Phase Angle Condition, 610°C

An attempt was made to monitor the resonance frequency with the network analyzer, since it does not require this zero-phase condition to operate. Frequency maxima and minima can automatically be captured by the analyzer software, and used for the basis of a film thickness calculation. The connections from the IC-5 were shifted to the network analyzer and heating was continued up to 655°C. A resonance frequency minimum of 5.776 820 MHz was noted. At this point a flow of TEOS, sufficient to raise the chamber pressure to 5 Torr, was initiated. This was held constant for 30 minutes. The resonance frequency was tracked with the network analyzer and values were recorded at 5-minute intervals. The shifts observed were erratic and fell within the measurement uncertainty of the analyzer (+/-100 Hz, at a slow sweep and 1KHz IF bandwidth). During this time, the quartz CVD tube became cloudy with a white haze typical of silicon dioxide formed from the breakdown of TEOS. A clear shift in frequency of the crystal before and after the TEOS introduction was not observed.

It should be noted that silicon dioxide, in the bulk phase, has a density near 2 g/cm3. On a 6 MHz crystal, 1 Angstrom of deposited material causes a negative frequency shift of approximately 2 Hz, calculated from Sauerbreyís film thickness equation. Therefore, a deposition of as little as 10 Angstroms per minute of silicon dioxide would register a frequency shift of 600 HZ in 30 minutes, well above the error of the network analyzer measurement. This was not measured.

The temperature was elevated to 681°C and the TEOS pressure increased to 10 torr to increase the rate of reaction and determine if a faster deposition rate would register on the crystal. The gallium phosphate crystal frequency immediately jumped to a higher value of 5.777024 MHz and remained stable. After 30 minutes of this pressure and temperature regime, no frequency shift was measured and the experiment discontinued.

This process was repeated 24 hours later, but with the temperature set to 757°C and the TEOS vapor pressure increased to 20 torr. After 30 minutes this led to the same result. Upon removing the sensor head, a white haze was observed on the $GaPO_4$ crystal indicating that some pyrolysis had occurred. Apparently silicon dioxide was forming on the sensor, but the noise level of the frequency reading obscured the measurement.

A frequency- temperature run, monitoring specifically the zero-phase angle behavior was undertaken. Scans were recorded approximately every 10 degrees up to 700°C. In reproducible runs it was observed that in the vicinity of 570 to 620°C, the zero phase condition would vanish. Cooling the system below these temperatures would restore it. If a crystal monitor were attached to the crystal when the zero phase condition was satisfied (and the crystal resistance was under 100 Ohms), the crystal would oscillate. Under all conditions however, the network analyzer detected a resonance. The electronics of commercial crystal monitors, however, do not have the capabilities to measure this.

Further work must be undertaken to develop a film thickness monitor that uses passive frequency measurement techniques to detect the resonance point of an oscillating crystal. This would eliminate the tracking problems caused by active crystal oscillator systems currently in use. Nevertheless, at temperatures less than 600°C, gallium phosphate is exceptionally stable and can be used with existing instruments. Gallium phosphate crystals that are temperature controlled could be excellent candidates for monitoring thin film deposition processes that exceed the range of quartz and do not require water-cooling. There are lower temperature CVD processes that could be monitored with gallium phosphate, but they generally involve highly toxic precursors. Since we were not equipped to safely handle these materials, they were not studied in this work.

References:

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