

# High Temperature SAW Gas Sensor on Langasite

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## ABSTRACT

Novel Surface Acoustic Wave (SAW) devices using the new langasite (LGS) family of crystals have been designed, fabricated, and tested for high temperature (up to 750°C) gas sensor applications. The devices were fabricated using platinum (Pt) and palladium (Pd) thin film technology and were mounted in a high temperature sealed stainless steel chamber for gas testing. The high temperature SAW sensors have been exposed to temperatures from 250°C to 750°C and cycled more than ten times in that temperature range over periods from two to six weeks. Gas sensing of C<sub>2</sub>H<sub>4</sub> in N<sub>2</sub> and H<sub>2</sub> in N<sub>2</sub> with baselines of O<sub>2</sub> and N<sub>2</sub> on the LGS SAW devices has been performed from 250°C to 550°C and is reported for the first time in this paper.

## 1. INTRODUCTION

SAW technology allows for the design of very sensitive gas and liquid sensors [1]. Benefits of SAW technology include small size, wide dynamic range, low cost when produced in large quantities, and light weight. The langasite (LGS) family of crystals is a recent piezoelectric material that offers the following attractive characteristics: temperature compensated orientations, up to six times higher piezoelectric coupling than quartz, and about 25% lower phase velocities than quartz [2]. Since this material can operate up to its melting point at 1470°C, without showing phase transitions, such as the  $\alpha\beta$  transition in quartz at 573°C [2-3]; LGS is being explored for high temperature acoustic wave applications [3-5].

As a result of this last property, bulk acoustic wave (BAW) nanobalance gas sensors [3] and surface acoustic wave (SAW) temperature sensors [4] have been developed using LGS crystals.

The design and fabrication of has sensors to operate in hostile environments is required for the aerospace, space exploration, and safety industries [6]. A particular application for the aerospace industry deals with increasing combustion efficiency, which immediately results in reducing travel costs and the pollution caused by incomplete burning of jet fuel. To meet such needs, it is desirable to develop sensors capable of operating at high temperatures for prolonged time with the ability to detect hydrocarbons, CO, CO<sub>2</sub>, NO<sub>x</sub>, and H<sub>2</sub> [6].

In previous work [5] the authors verified the capability of LGS crystals to operate up to 750°C for a period of at

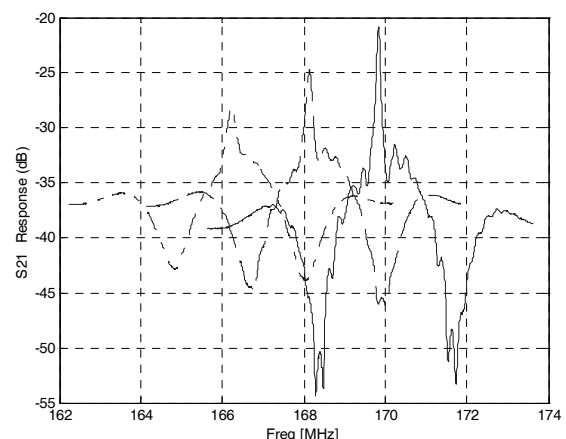
least 3 weeks. A modest seven dB increase in the magnitude of the transmission coefficient, |S<sub>21</sub>|, and a reduction in the quality factor, Q, from 2123 to 554 was reported when the SAW resonator device was taken from room temperature to 750°C (Fig. 1). With these results LGS qualified for potential high temperature SAW gas sensor applications.

In this work high temperature SAW gas sensors using LGS crystals at temperatures ranging from 250 to 450°C are reported. Original films for two-port SAW resonators were employed in the detection of ethylene (C<sub>2</sub>H<sub>4</sub>) in nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) in N<sub>2</sub>. Platinum (Pt) and platinum/tungsten trioxide (Pt/WO<sub>3</sub>) films were used to detect ethylene (C<sub>2</sub>H<sub>4</sub>) in N<sub>2</sub>. Platinum delay lines with palladium (Pd) sensing films and all Pd two-port SAW resonators were fabricated and tested for the detection of H<sub>2</sub> in N<sub>2</sub>. A high temperature gas chamber was designed and fabricated, along with a high temperature gas delivery system to introduce oxygen (O<sub>2</sub>), N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> gases into the gas chamber.

**Section 2** discusses the device specifications and fabrication, including gas selection. **Section 3** describes the test setup and gas delivery system. Experimental results are reported in **Section 4**. Conclusions, acknowledgements, and references are reported in **Sections 5, 6, and 7**, respectively.

## 2. DEVICE DESIGN AND FABRICATION

Fabrication of high temperature SAW devices requires the deposition of metallic thin film electrodes for the



**Figure 1: Measured |S<sub>21</sub>| for the LGS two port SAW resonator. Solid: 25°C Dashed: 500°C Dotted: 750°C**

interdigital transducers (IDTs) that can withstand prolonged exposure to high temperatures (up to 1000°C). Metallic sandwich films consisting of two or more different metals have been investigated in high power applications, which reach temperatures up to 200°C [7]. This temperature limitation in sandwich films is not suitable for the high temperature sensor applications reported here. For the SAW devices reported in this paper, Pt and Pd metals, with melting points of 1769°C and 1554.9°C respectively, were selected for the IDTs.

Two-port resonator structures were fabricated on LGS substrates, Euler angles [0°, 138.5°, 26.6°] with 80 fingers, 50 wavelength aperture, 500 short circuit reflector strips, 4 micron fingers, and a 1:1 mark to space ratio.

A Pt resonator was fabricated with a 40 Å zirconium (Zr) adhesion layer and a 500 Å Pt sensing layer. Both were electron-beam evaporated and processed by lift-off photolithography.

A WO<sub>3</sub>/Pt film was used for the detection of C<sub>2</sub>H<sub>4</sub>. Recent work indicated that WO<sub>3</sub> is appropriate for the detection of C<sub>2</sub>H<sub>4</sub> in a semi conducting metal oxide film sensor [8]. A two-port SAW resonator was fabricated with the 40 Å Zr and 500 Å Pt layer, with an additional 200 Å layer of WO<sub>3</sub> RF sputtered across the entire Pt two-port resonator including the non-metal surface.

A Pd film for the detection of H<sub>2</sub> was chosen because Pd can absorb up to 900 times its volume of H<sub>2</sub> [9,10]. A two-port Pd resonator was fabricated with a 200 Å layer of Zr and a 3000 Å layer of Pd for the detection of H<sub>2</sub>.

An open delay line structure was fabricated with 80 split finger pairs, 50-wavelength aperture, 310-wavelength delay (center to center), 4-micron fingers, and a 1:1 mark to space ratio. The delay line structure was fabricated with a 40 Å Zr and 500 Å Pt film. The delay line device had a Pd sensing film electron-beam evaporated into the delay path, of 200 Å Zr with 3000 Å Pd.

### 3. EXPERIMENTAL SETUP

A high temperature dual device gas test chamber was designed and fabricated at the University of Maine, as shown in Figure 2. This dual device chamber isolates two devices from each other with a ceramic paper airtight seal. This stainless chamber can withstand temperatures up to its melting point, 1440°C. Two 50-ohm coplanar waveguides were designed to mount in the test chamber to allow the easy replacement of SAW devices with minimal disturbance to the system setup. High temperature 50-ohm transmission lines from Meggitt Safety Systems, capable of withstanding temperatures up to 1000°C, were used to provide the RF access to the devices under test. A Thermolyne 6000 furnace (0-1200°C) was used for the high temperature gas sensor characterization.

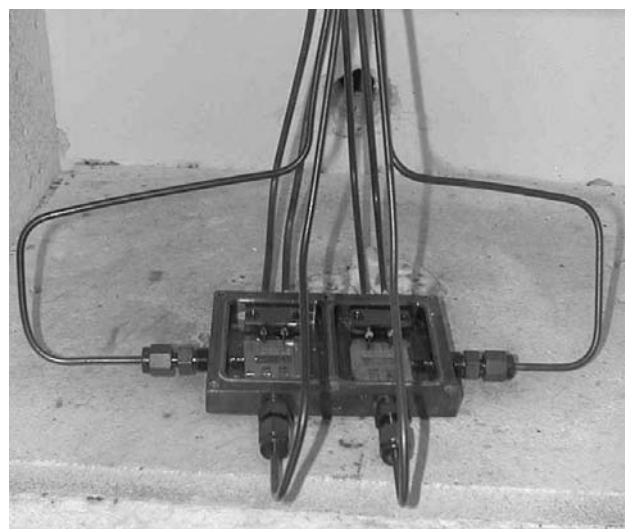


Figure 2: High Temperature Gas Chamber, lid removed

The gas delivery system includes two Tylan mass flow controllers and appropriate electronics to precisely control the gas flow to the test chamber. Stainless steel tubing was employed to deliver the gas from room temperature gas cylinders into the high temperature test chamber.

A tank of 10 ppm Ethylene/Nitrogen (C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub>), 1000 ppm Hydrogen/Nitrogen (H<sub>2</sub>/N<sub>2</sub>), high purity O<sub>2</sub>, and high purity N<sub>2</sub> was utilized throughout the testing phase for the sensors presented. The devices S-parameters characterization was done with the aid an HP 8753ES network analyzer and a PC was utilized to save the measurement data. The test set up is depicted in Fig. 3.

### 4. TEST RESULTS

The Pt resonator was exposed to O<sub>2</sub> for thirty minutes to oxidize the Pt film, followed by the exposure to C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> for fifteen minutes. In the temperature range

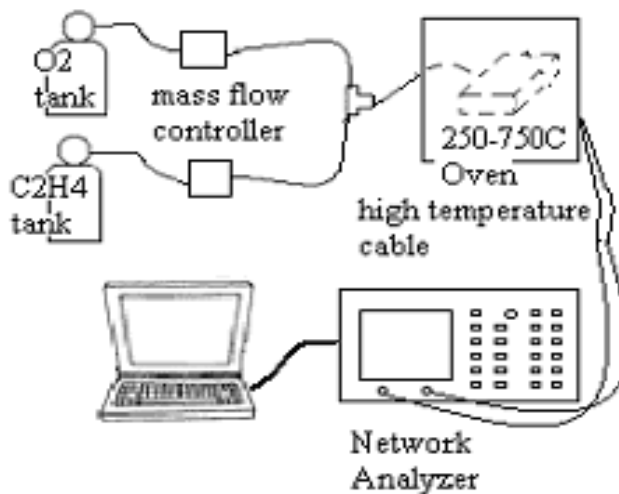


Figure 3: Gas delivery and Measurement test setup.

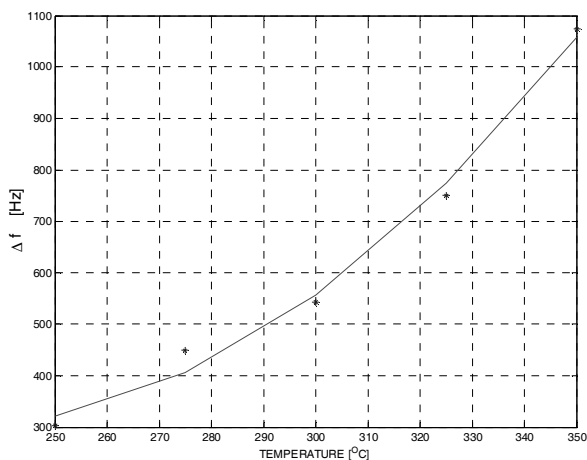
from 250°C to 350°C, the dominating physical phenomenon was the removal of surface-bound O<sub>2</sub> from the resonator by the reaction with C<sub>2</sub>H<sub>4</sub> to form CO<sub>2</sub> and H<sub>2</sub>O. Fig. 4 shows a positive frequency variation ( $\Delta f$ ) from 0.3 KHz (at 250°C) to 1.1 KHz (at 350°C), which was measured between the exposure to O<sub>2</sub> and the subsequent exposure to C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub>. The measurements were taken at constant temperature. The positive frequency variations in Fig. 4 consistently indicate the removal of mass from the Pt film on the surface of the Pt resonator.

In an attempt to increase the sensitivity of the high temperature LGS sensor to C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub>, the investigation into a sensing WO<sub>3</sub> film was explored. The WO<sub>3</sub>/Pt resonator was exposed to O<sub>2</sub> for thirty minutes, followed by the exposure to C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> for twenty minutes, in the temperature range from 300°C to 450°C. Negative frequency variations ( $\Delta f$ ) from 0.8 KHz (at 450°C) to 1.5 KHz (at 350°C) were measured between the exposure to O<sub>2</sub> and the subsequent exposure to C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub>, Table 1.

**Table 1. Measured frequency variations ( $\Delta f$ ) with exposure to C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> on a Pt/WO<sub>3</sub> gas sensor.**

Temperature [°C]	300	350	400	450
$\Delta f$ [KHz]	1	1.5	1.2	0.8

Investigation into the sensing of H<sub>2</sub> with a Pd film was conducted. The Pt delay line device discussed earlier with the Pd sensing film in the delay path was tested with the exposure of H<sub>2</sub>/N<sub>2</sub>. The Pd delay line was exposed to O<sub>2</sub> for forty minutes followed by the exposure to H<sub>2</sub>/N<sub>2</sub> for twenty-five minutes, in the temperature range from 250°C to 400°C. Figure 5 shows the response with the 200 Å Zr 3000 Å Pd sensing film. As can be seen in Fig. 5 there is a 500 Hz frequency shift to the exposure of H<sub>2</sub>/N<sub>2</sub>, with an O<sub>2</sub> baseline at 300°C. This film was also



**Figure 4:  $\Delta f$  vs. T [°C] plot indicating the removal of O<sub>2</sub> from Pt and formation of CO<sub>2</sub> and H<sub>2</sub>O.**

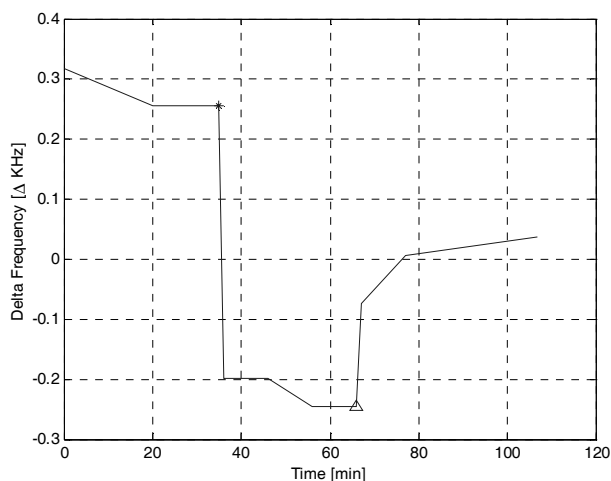
tested at 250°C with a frequency shift of 200 Hz measured and at 400°C with a shift of 4 KHz measured.

Figure 6 plots the results of H<sub>2</sub>/N<sub>2</sub> exposure to the Pd resonator with a N<sub>2</sub> baseline at 250°C. As can be seen, the exposure and recovery are consistent and repeatable, with the same magnitude of change of approximately 4 KHz.

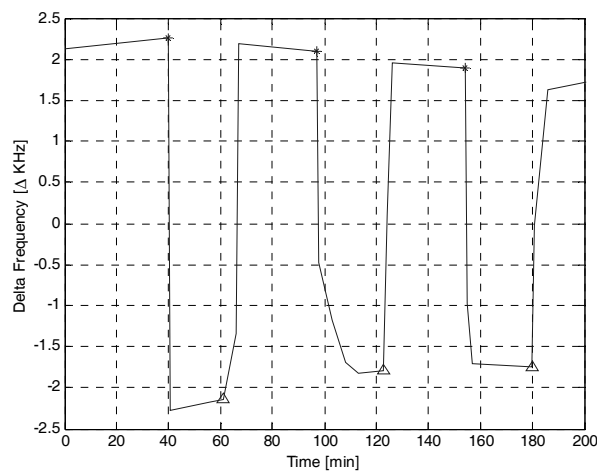
High temperature sensors must remain operable under conditions of extended exposure to elevated temperatures. The LGS devices tested and reported in this paper were tested at temperatures of at least 250°C to up to 750°C for a period of no less than two weeks and up to six weeks, with 2-7 dB degradation in |S<sub>21</sub>|.

## 5. CONCLUSIONS

Multiple device structures were fabricated and tested on LGS substrates for the application of a high temperature gas sensor. The selection of electrode metal and substrate was proven to allow for high temperature sensing. Platinum, palladium, and tungsten trioxide



**Figure 5: Cycling exposure to hydrogen with an oxygen baseline. ‘\*’ H<sub>2</sub> on, ‘Δ’ H<sub>2</sub> off (f<sub>0</sub> 84.999 MHz)**



**Figure 6: Cycling exposure to hydrogen with a nitrogen baseline. ‘\*’ H<sub>2</sub> on, ‘Δ’ H<sub>2</sub> off (f<sub>0</sub> 167.1455 MHz)**

sensing films were investigated and tested with gas exposure to either hydrogen or ethylene gas. The results presented in this paper verify that LGS is an applicable substrate to be used as a high temperature gas sensor over an extended time period, with minimal degradation in response. Of the films reported, palladium produces the most sensitive results [11].

## 6. ACKNOWLEDGEMENTS

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