High Temperature LGS SAW devices with Pt/WO_3 and Pd Sensing Films

J. A. Thiele and M. Pereira da Cunha

Dept. of Electrical and Computer Engineering, University of Maine, Orono, ME, USA

ABSTRACT -- This paper reports on the fabrication of high temperature LGS SAW devices to be used as gas sensors. SAW resonators and delay lines have been designed, fabricated, and tested up to 750°C. An additional 7dB loss in the transmission coefficient, $|S_{21}|$, of the two port 167 MHz SAW resonators tested has been observed for operation at 750°C with respect to room temperature. Original films have been fabricated for the two port SAW gas sensor resonators tested from 250°C to 550°C. A combination of platinum/tungsten trioxide (Pt/WO_3) films has been used in the detection of C_2H_4 in N_2. In the detection of H_2 in N_2 an all palladium (Pd) metallic structure has been employed. Frequency variations up to 10 KHz for the 167 MHz high temperature SAW sensors were measured. The devices have been continuously cycled from 250°C to 750°C for periods up to six weeks, with degradations in the $|S_{21}|$ response ranging from 2 to 7 dB. The high temperature LGS SAW devices and experiments reported in this work show the capability of these crystals to withstand prolonged exposure to temperatures ranging from 250°C to 750°C and to perform as high temperature gas sensors.

I. INTRODUCTION

In the past few years there has been an increasing interest in the langasite family of crystals (LGX) for surface acoustic wave (SAW) applications in communications, frequency control, and sensors. Several interesting properties of this material include: up to about six times higher electromechanical coupling than quartz ST-X; existence of temperature compensated cuts with zero power flow angle and minimal diffraction; and up to 26% reduction in phase velocities with respect to quartz ST-X, which allows the fabrication of smaller devices. In addition, crystal phase transitions, such as the quartz $\alpha\beta$ transition at 573°C, are not observed up to the crystal melting point (around 1470°C) [1]. As a result of this last property, bulk acoustic wave (BAW) and SAW langasite (LGS) devices have been recently considered for high temperature SAW temperature sensor [2], SAW gas sensor [3], and BAW sensor [4, 5] applications. SAW devices are appropriate for sensitive gas and liquid sensors applications due to attractive characteristics such as small size, reduced cost when produced in large quantities, and wide dynamic range [6].

There is the need to design and fabricate gas sensors to operate in hostile environments for the aerospace, space exploration, and safety industries [7]. High temperature sensors are a necessity in the detection of fuel leaks in jet engines, fire in its initial stages, and other combustion gases. The development of high temperature gas sensors for the aerospace industry, in particular, will help increase fuel efficiency in the combustion cycle, decrease travel costs and reduce environmental pollution. Typical gases that one is interested in quantifying for the high temperature applications mentioned above are hydrocarbons, oxygen, hydrogen, carbon dioxide, carbon monoxide, and nitric oxide [7].

In a previously reported work [3] the authors verified the capability of LGS crystals to operate up to 750°C for periods of at least 3 weeks. A modest seven dB increase in the magnitude of the transmission coefficient, |S21|, 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). In the same work, the loss of piezoelectric activity for quartz was verified around 570-580°C, as expected. 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°C to 750°C are reported. Original films for two port SAW resonators

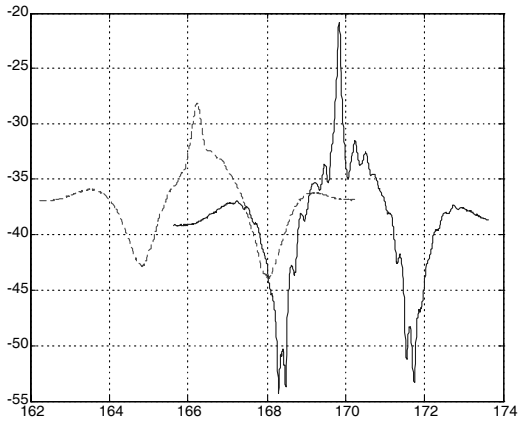

Fig.1 Measured |S21| for the LGS two port SAW resonator. Solid: 25°C Dashed: 750°C [3].

have been employed in the detection of C_2H_4 in N_2 and H_2 in N_2. A combination of platinum/tungsten trioxide (Pt/WO_3) films has been used in the detection of ethylene (C_2H_4) in N_2, and all palladium (Pd) two-port SAW resonators have been fabricated and tested for the detection of H_2 in N_2. A high temperature gas chamber has been designed and fabricated, along with a high temperature gas delivery system to introduce ethylene, hydrogen, oxygen, and nitrogen gases into the gas chamber.

Section II discusses the fabricated devices, including the metal selection for the interdigital transducers (IDTs). The selection of gases to be tested is also discussed in Section II. **Section III** discusses the gas delivery system and the gas test system implemented. In **Section IV** the experimental results are given and discussed. **Section V** is dedicated to the conclusions.

II. Device Fabrication

Fabrication of SAW devices to operate at high temperatures requires metal films that can withstand those temperatures. Aluminum (Al), the most used metal for the fabrication of the IDTs, is not capable of withstanding high temperatures since it has a melting point of 660°C and leads to quick device degradation due to the electromigration phenomenon well known in the semiconductor and SAW industry [8].

Sandwich films, which incorporate two or more layers of different metallic films, are used in high power, and thus high temperature applications. However the maximum target temperatures in these applications is around 200°C [8], which is below the range aimed at with this work.

For the reasons discussed above, other solutions had to be sought for the high temperature gas sensor in this work. Two alternatives have been implemented. The first uses platinum (Pt) electrodes overlaid with WO_3 for the detection of C_2H_4 in N_2. Pt has a melting point of 1769°C and has also been adopted in [2] for high temperature SAW temperature sensors. Titanium (Ti) is used in [2] as adhesion layer. In this work, Zirconium (Zr) was used as the adhesion layer, due to the fact that the Zr does not migrate into the Pt layer at elevated temperatures [9]. Since Pt has a higher density than Al, a thinner layer of Pt was used to reduce mass loading effects in the devices performance. WO_3 is known to detect C_2H_4 in semi conducting metal oxide sensors [10]. The WO_3/Pt resonator was fabricated with a 40 Å Zr and 500 Å Pt film electron-beam evaporated on the surface using a lift-off photolithographic process. A 200 Å layer of tungsten trioxide (WO_3) was RF sputtered across the entire Pt two-port resonator, including the non-metal surface.

The second high temperature film alternative implemented in this work is an original all palladium (Pd) two port SAW resonator for the detection of H_2 in N_2. In this device Pd, which has a melting point of 1554.9 °C, is used as the metal electrode and the sensing film. Pd acts as a sponge, absorbing up to 900 times its own volume of H_2 [11-12]. The Pd resonator was fabricated with a 200 Å Zr layer and 3000 Å Pd film, electron-beam evaporated.

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

III. Test Setup

The implemented high temperature test set-up required metals or ceramics capable of withstanding elevated temperatures for prolong periods of time. A high temperature stainless steel (SS, melting point 1440°C) dual-chamber was designed and fabricated for that purpose at the University of Maine. The two chambers in this fixture can house two SAW resonator devices, which are air tightly sealed and isolated from each other. The SAW resonators were mounted on 50-ohm coplanar waveguides fabricated with Pt films on sapphire substrates. The fixture allows for easy replacement of SAW devices with minimal disturbance to the system setup. The chamber is equipped with entrance and exit gas connectors made out of 316 SS and capable of withstanding up to 1000°C.

Two high temperature 50-ohm transmission lines, from Meggitt Safety Systems, capable of withstanding temperatures up to 1000°C, were used to extract the RF signal. In order to heat the devices and the device chamber up to the desired temperature a Thermolyne 6000 furnace (0-1200°C) was employed.

For the gas delivery system Tylan mass flow controllers and appropriate electronics were used to control the oxygen (O_2), nitrogen (N_2), 1000-ppm hydrogen in nitrogen (H_2), and 10-ppm ethylene in nitrogen (C_2H_4) gases used in the experimental tests.

A HP 8753ES network analyzer and a PC were utilized to save the measurement data. Fig. 2 is a block diagram of the system setup.

IV. Experimental Results

For the detection of C_2H_4 the previously discussed WO_3/Pt resonator was exposed to 10 ppm C_2H_4 for a period of 20 minutes followed by the same flow rate of pure oxygen for 40 minutes. The greatest sensitivity for this WO_3 film was observed at 350°C, with a 1.5 KHz frequency shift [13]. In this single device test, the temperature was carefully monitored, and kept within ± 0.2°C with ample time for temperature stabilization in the Thermolyne 6000 furnace.

Fig. 3 plots the results of H_2 exposure to the Pd resonator with an O_2 baseline at 250°C. The '*' indicate the turning off of O_2 gas and the introduction of H_2 gas, where the 'Δ' represents the turning off of H_2 and the reintroduction to O_2 gas. A constant drift in the center

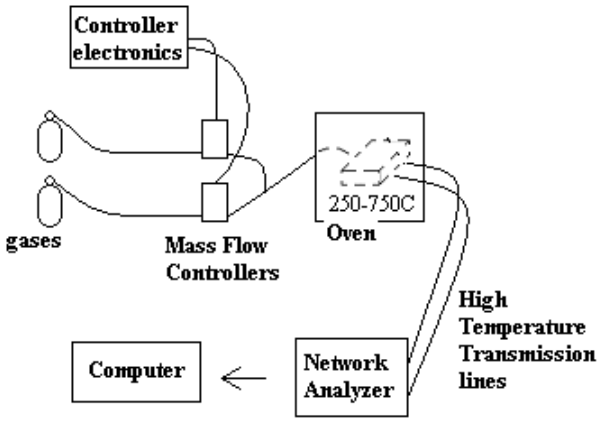

Fig. 2 Block Diagram of measurement setup.

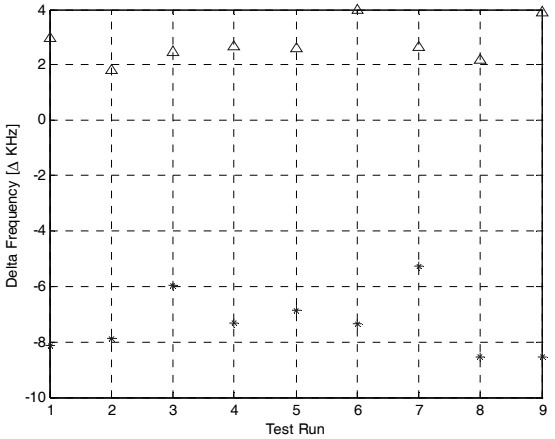

Fig. 4 Delta f [KHz] of multiple exposures and recoveries of Hydrogen/Oxygen cycling, '*' H_2 on, 'Δ' H_2 off.

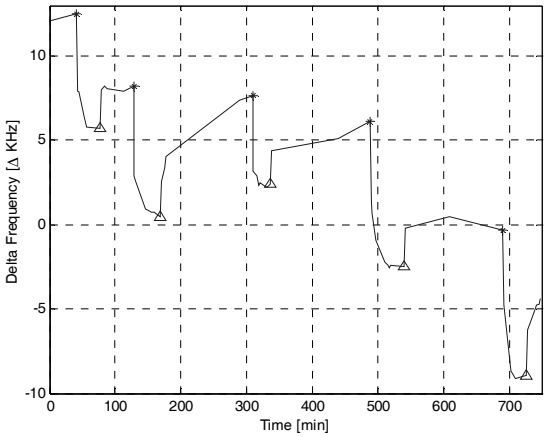

Fig. 3 Cycling exposure to hydrogen with an oxygen baseline. '*' H_2 on, 'Δ' H_2 off (f_O 167.205 MHz).

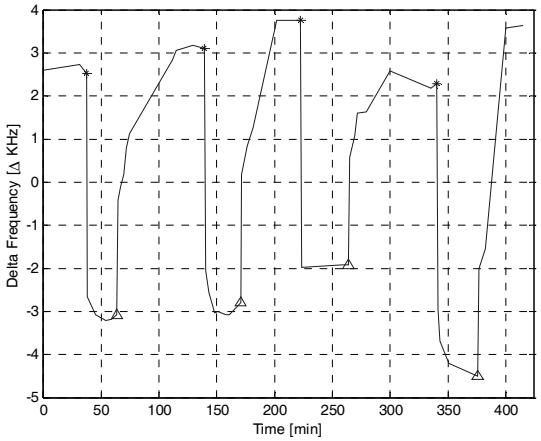

Fig. 5 Cycling exposure to hydrogen with a nitrogen baseline, '*' H_2 on, 'Δ' H_2 off (f_O = 167.1475 MHz).

frequency response of the devices was observed. One possible explanation for this constant frequency decrease is that the surface is being cleaned of carbon atoms, by a reduction-oxidation cycle.

In terms of the sensing mechanism, however, the constant cycling of H_2 and O_2 gas produced an average change in frequency that is approximately constant. Fig. 4 plots the change in frequency from subsequent H_2 exposure cycling at 250°C. There is a consistent decrease in frequency with exposure to H_2 in the range of 5 – 8 KHz. The recovery with the removal of H_2 and reintroduction of O_2 is approximately half of the previous level, or 3 KHz.

Fig. 5 plots the results of H_2 exposure to the Pd resonator with a N_2 baseline at 250°C. As can be seen the exposure and recovery are consistent and repeatable, with the same order of magnitude of change, 6 KHz. As is also seen the constant drift over time is no longer observed when using N_2 as a baseline as opposed to O_2 as the baseline gas.

Fig. 6 plots the change in frequency from subsequent H_2 exposure cycles at 250°C for the N_2 baseline case. The constant decrease in frequency with exposure to H_2 is in the range of 2 - 3 KHz. After H_2 gas is turned off, and the N_2 baseline is turned back on, the increase in frequency is around 3 KHz. This sensor is recoverable after H_2 exposure. The '*' in Fig. 5 and Fig. 6 indicates the turning off of N_2 gas and the introduction of H_2 gas, where the 'Δ' represents the turning off of H_2 and the reintroduction to N_2 gas.

In comparing Fig. 6 (N_2 baseline) and Fig. 4 (O_2 baseline), a more stable baseline with more consistent frequency variations for the decrease and recovery of the measurand gas is observed for the N_2 baseline case.

Long-term exposure to high temperatures is a necessity for high temperature sensors. The Pd LGS two port resonators tested and reported in this paper were continuously operated at 250°C for six weeks with a 2 dB degradation in $|S_{21}|$ over time.

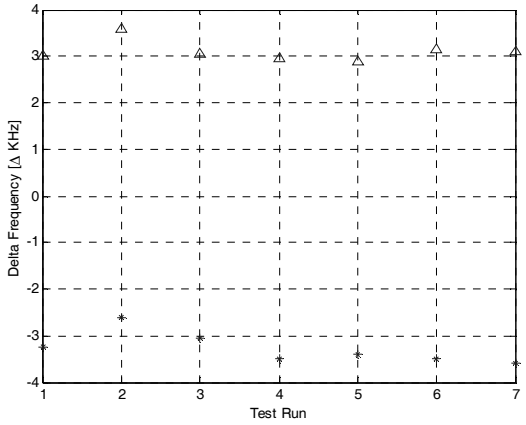

Fig. 6 Delta f [KHz] of multiple exposures and recoveries of Hydrogen/Nitrogen cycling, '*' H2 on, 'Δ' H2 off.

V. CONCLUSIONS

The results are novel in the area of high temperature gas detection. The devices are confirmed to operate at elevated temperatures for periods longer than one month, with only a slight degradation in insertion loss [2-7dB]. The fabrication procedure has been developed and produces consistent results. Results from ethylene and hydrogen gas detection have been presented. The detection of hydrogen using the LGS devices is repeatable and consistent. The potential of LGS as a high temperature gas sensor has been proven. The devices fabricated on the LGS substrate achieve the desired objectives of a high temperature operable gas sensor.

VI. ACKNOWLEDGEMENTS

Funding for this project was provided by the Maine Space Grant Consortium under projects MSGC EP-02-08 and MSGC SG-03-15, with partial assistance from the National Science Foundation projects NSF ECS-0134335 and NSF EEC-9820332. The authors would also like to thank Farzad Kialashaki from Meggitt Safety Systems for his assistance with the High Temperature 50-ohm transmission lines.

VII. REFERENCES

[1] M. Pereira da Cunha, S.A. Fagundes, "Investigation on Recent Quartz-Like Materials for SAW Applications," *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, v. 46 no. 6, pp 1583-1590, Nov. 1999.

[2] J. Hornsteiner, E. Born, G. Fischerauer, E. Riha, "Surface Acoustic Wave Sensors for High Temperature Applications," *Proceedings of the Annual IEEE International Frequency Control Symposium*, p615-620, 1998.

[3] M. Pereira da Cunha, J.A. Thiele, "High temperature surface acoustic wave devices: Fabrication and characterization," *Electronics Letters*, v 39, n 10, pp 818-819, May 15, 2003.

[4] H. She, H. L. Tuller, H. Fritze, "Langasite for high-temperature acoustic wave gas sensors," *Sensors and Actuators B 93*, pp 169-174, 2003.

[5] M. Pereira da Cunha, E. L. Alder, D. C. Malocha, "BAW Temperature Sensitivity and Coupling in Langanite," *Proceedings of the Annual IEEE Ultrasonics Symposium*, pp 883-886, 1999.

[6] G. Fischerauer, A. Mauder, and R. Muller, "Acoustic Wave Devices," Sensors A Comprehensive Survey Micro- and Nano- sensor Technology/Trends in Sensor Markets, ed. W. Gopel, J. Hesse, J.N. Zemel, vol. 8, pp 136-175, 1995.

[7] G.W. Hunter, P.G. Neudeck, C.C. Liu, B. Ward, Q.H. Wu, P. Dutta, M. Frank, J. Trimbol, M. Fulkerson, and B. Patton, "Development of chemical sensor arrays for harsh environments and aerospace applications," *in Proc. of the IEEE Sensors 2002*, pp. 1126-1133, June 2002.

[8] Y. Satoh, T. Nishihara, O. Ikata, " SAW Duplexer Metallizations for High Power Durability," *Proceedings of the Annual IEEE Ultrasonics Symposium*, pp 17-26, 1998.

[9] G. Bernhardt, C. Silvestre, N. LeCursi, S.C. Moulzolf, D.J. Frankel, and R.J. Lad, "Performance of Zr and Ti adhesion layers for bonding of platinum metallization to sapphire substrates," *Sensors and Actuators B 77*, pp 368-374, 2001.

[10] S. Pitcher, J.A. Thiele, H. Ren, and J.F. Vetelino, "Current/voltage characteristics of a semiconductor metal oxide gas sensor," *Sensors and Actuators, B: Chemical 93*, pp 454-462, 2003.

[11] D.R. Lide, H.P.R. Frederikse, CRC Handbook of Chemistry and Physics, 74th edition, CRC Press, p 4-21, 1993-94.

[12] A. D'Amico, A. Palma, and E. Verona, "Surface Acoustic Wave Hydrogen Sensor," *Sensors and Actuators 3*, pp 31-39, 1982/83.

[13] J. A. Thiele, M. Pereira da Cunha, "High Temperature SAW Gas Sensor on Langasite," *Proceedings of the Annual IEEE Sensors Conference*, October 2003 [in press].