Langasite SAW temperature and oxygen multi-sensor

P. Zheng,[1,2] D.W. Greve,[1,3] I.J. Oppenheim,[1,4] and V. Malone[4]
[1]National Energy Technology Laboratory, Pittsburgh, PA, USA
[2]Department of Physics, Carnegie Mellon University, Pittsburgh, PA, USA
[3]Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA, USA
[4]Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA, USA
Email: pengzhen@andrew.cmu.edu

***Abstract*—We report here a langasite SAW device suitable for sensing temperature and oxygen concentration, with applications such as monitoring the exhaust of oxy-fuel combustion systems. In this paper we report on the observed temperature dependence of oxygen sensitivity, explain the mechanism for this behavior, and present a scheme for temperature compensation.**

I. INTRODUCTION

Langasite ($La_3Ga_5SiO_{14}$) surface acoustic wave (SAW) devices have potential applications in harsh-environment sensing. Important applications include exhaust gas oxygen sensors for the control of oxy-fuel combustion systems. In such combustors it is possible to achieve a nearly pure carbon dioxide exhaust suitable for geologic sequestration. In this application oxygen sensing in the temperature range from 500 to 1000 ºC is needed. Langasite SAW devices have been operated as resonators up to 1000 ºC [1]; langasite SAW sensors for H_2 and C_2H_2 gas have been operated up to 550 °C [2]; and wireless temperature sensing has been demonstrated up to 850 °C [3,4]. Here we report recent results obtained for langasite SAW oxygen sensors. We particularly focus on the temperature dependence of these sensors, and a method for reducing the impact of temperature flucuations on gas sensing.

II. TEMPERATURE AND GAS SENSING

The SAW sensors considered here utilitze the electroacoustic effect, where a conducting layer near the piezoelectric surface influences the surface wave velocity. Gas sensing is achieved by using a layer with a conductivity that depends on the gas concentration. The most suitable conducting layers for this high-temperature application are metal oxides, which exhibit a semi-conducting behavior with conductivity dependent on the oxygen defect concentration. In metal oxides with predominant electron conduction, a reversible reaction occurs with gas-phase oxygen of the form

$$O_o^x \leftrightarrow V_{\ddot{o}} + 2e' + \tfrac{1}{2}O_2^{(g)} \tag{1}$$

where O_o^x is the concentration of oxygen atoms on an oxygen site, $V_{\ddot{o}}$ is the concentration of doubly-negative oxygen vacancies, e' is an electron, and $O_2^{(g)}$ is an oxygen molecule in the gas phase. Higher oxygen partial pressure in the gas phase drives the reaction to the right, decreasing electron concentration and increasing the electrical conductivity. It can be shown that the conductivity is given by

$$\sigma = Ae^{-E_A/kT}P_{o_2}^{1/m} \tag{2}$$

where E_A is the activation energy for conduction, kT is the thermal energy, and P_{O_2} is the oxygen partial pressure. Increasing conductivity of the sensing layer decreases the surface wave velocity, as the redistribution of charge in the sensing layer reduces the stored energy in the electic field above the surface, reducing the piezoelectric stiffening. The change in velocity can be predicted analytically; Figure 1 shows the calculated change of surface velocity for a (0, 138.5, 26.6) langasite SAW device.

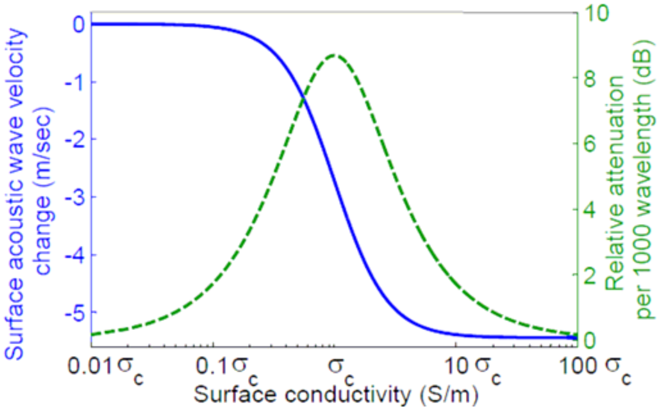

Figure 1. Calculated surface acoustic wave velocity changes (solid blue line) and relative attenuation (green dashed line) of langasite substrate with Euler angle (0, 138.5, 26.6) as a function of surface sensing film conductivity.

It is apparent from Figure 1 that significant velocity changes are only obtained for a limited range of sensing layer conductivity. As the conductivity is thermally activated according to (1), a particular sensing layer will have a limited temperature range where it exhibits useful response. Further, changes in temperature will also cause a change in surface wave velocity. We focus here are removing the impact of small temperature changes on the surface wave velocity. We will also determine the temperature range over which on particular sensing layer is useful. In a practical sensor, the temperature and oxygen concentration need to be measured independently; this will be addressed in future work.

III. EXPERIMENTAL

SAW devices used in this work were fabricated on 76 mm diameter, 0.5 mm thick langasite wafers (Roditi International, UK) with Euler angles (0, 138.5, 27) using a lift-off technique. The metallization was e-beam deposited and consisted of 100 nm platinum with 10 nm titanium as an adhesion layer.

The SAW devices used in this work have the transmitter located in the center with open reflectors were located on two sides. The IDTs had 2 µm finger widths and gaps, yielding an 8 µm surface acoustic wavelength and a center frequency of 334 MHz at room temperature. For gas sensing, A 200 nm ZnO sensing film was deposited by reactive RF sputtering from a Zn target at a pressure of 4 mT and RF power 50 W, in 25% O_2/ 75% Ar. ZnO was masked from the IDT terminals using Mylar tape. The SAW device was then spin coated with polysiloxanes (IC1-200 and DC4-500 from Futurrex, Inc.). The polysiloxanes film was partially removed using a cotton tip with acetone and then annealed in air at 400 °C for 30 min to form a 100 nm SiO_2 insulating film on the IDT transmitter and terminals region.

XRD characterization of the sputtered ZnO film showed a wurtzite structure with a 30 nm grain size. In some experiments temperature sensing was performed at the same time using a second SAW device with longer path lengths, so that its reflections were not coincident with the first reflections of the gas-sensing device.

The SAW device(s) were placed in a furnace (Lindberg STF55433C) with computer-controlled gas flows. Connection to the measuring electronics was made using shielded thermocouple wire as a transmission line, connected to the SAW device using fine thermocouple wire and conductive ceramic paste. Measuring electronics consisting of a National Instruments (NI PXI-5670) and a vector signal analyzer (NI PXI 5661) [5] was used to measure the phase changes resulting from temperature and/ or gas concentration changes. Measurement of the phase changes requires a reference pulse; this reference pulse consisted of either another SAW reflection or the attenuated exciting pulse.

We first discuss separate measurements of temperature and gas concentration. Figure 2 shows the extracted effective velocity change as a function of temperature. The velocity decreases monotonically with temperature, consistent with previous reports [4,6,7].

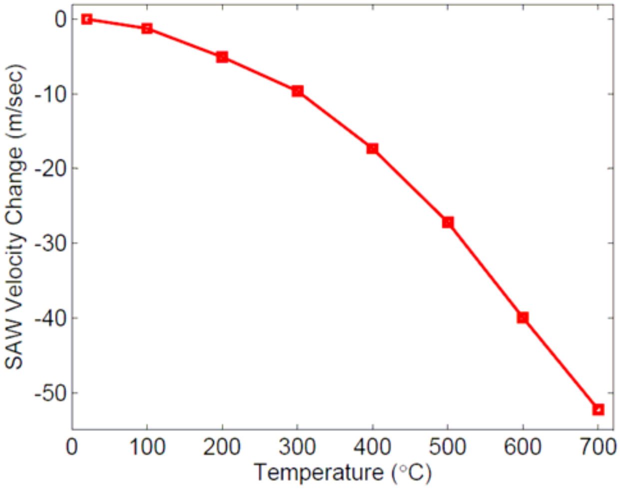

Figure 2. Extracted effective SAW velosity change as a function of temperature.

The effect of oxygen concentration was examined by measuring the phase change between \the exciting pulse and a reflection normalized for a 1 µs propagation time. The oxygen concentration was changed in a stepwise fashion with the balance of the gas being nitrogen. The oxygen concentration was varied by changing the mass flow controller setpoints while keeping the total mass flow constant. Figure 3 shows the results for three temperatures, where the phase changes consistent with *n* type conduction in the ZnO. While the phase changes are consistent with velocity changes due to the electroacoustic effect, they could also be caused by temperature variations in the furnace due to imbalanced gas flow. This is a particular concern at lower temperatures where the observed phase changes are small.

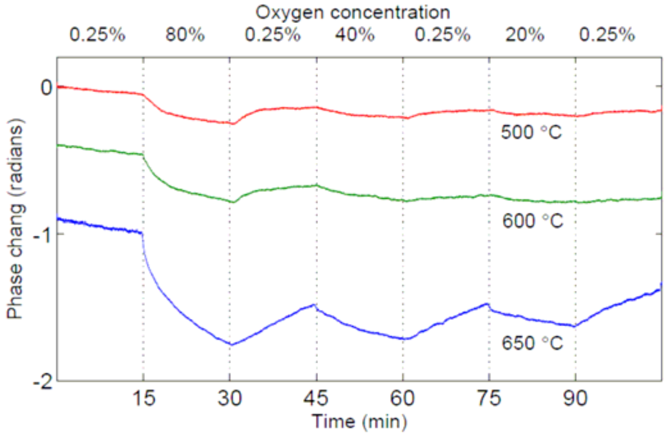

Figure 3. Phase change resulting from changes in the oxygen concentration.

The influence of small temperature variations can be removed by simultaneously measuring SAW reflections on two propagation paths, one with and one without without a ZnO sensing layer. This can be achieved by patterning the sensing layer so that some reflections are not influenced by the change in sensing layer resistivity. Alternatively, two separate SAW devices can be connected in parallel, one with and one without a ZnO sensing layer (Figure 4). In this case the SAW devices must be different so that the reflections are distinguishable.

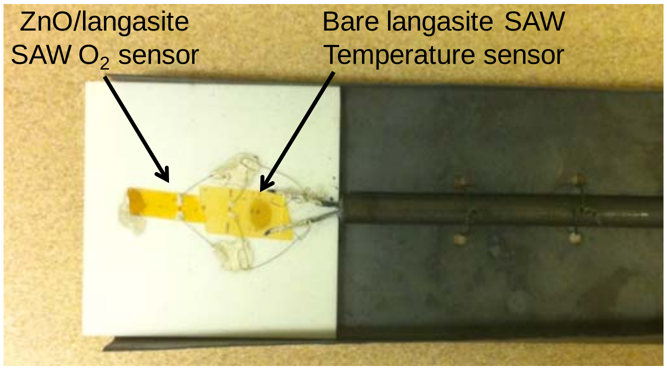

Figure 4. Two langasite SAW devices connected in parallel, one with and one without a ZnO sensing layer.

Figure 5 shows the observed reflections for two SAW devices connected in parallel at room temperature. Here the second series of reflections are from the temperature-sensing SAW device without a ZnO sensing layer. These reflections are strongest despite the longer path length; this is because the ZnO sensing layer causes additional attenuation [5].

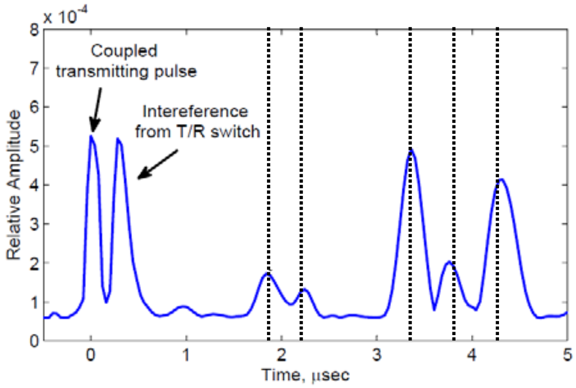

Figure 5. Reflections for two SAW devices wired in parallel at room temperature.

Figure 6 shows uncorrected phase measurements for the oxygen and temperature sensors (top two traces) and measurements compensated for temperature variations (bottom trace) at 650 ºC. Temperature compensation is achieved by subtracting the gas and temperature phase change measurements normalized for the propagation time. The data from the temperature sensor shows small perturbations (± 0.5 ºC) due to the gas flow switching. Removing these small perturbations shows that most of the phase change of the O_2 sensor was indeed resulting from the gas sensing layer.

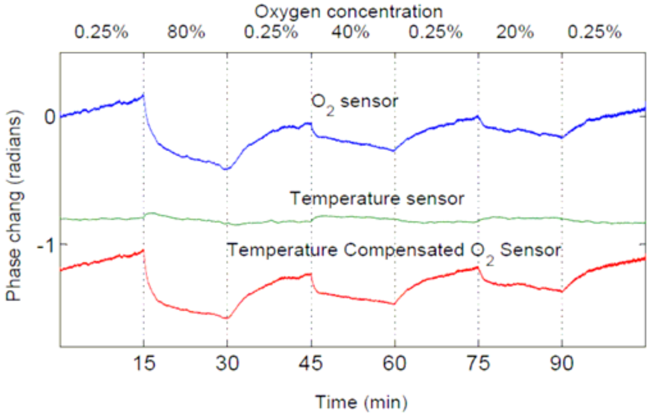

Figure 6. Compensation for temperature variations with a second SAW device.

Gas sensing performed over a wider range of temperature is presented in Figure 7. Data for 650 C and above has not been temperature-compensated due to failure of the temperature-sensing SAW device. Oxygen sensing however has been achieved up to 700 C.

This data shows clearly that sensing with a ZnO layer can only be performed over a limited temperature range. As shown in Figure 1, a significant change in propagation velocity is obtained only for a limited range of sensing layer conductivity. Due to the exponential dependence of conductivity on temperature, a peak in the sensitivity is expected at an intermediate temperature.

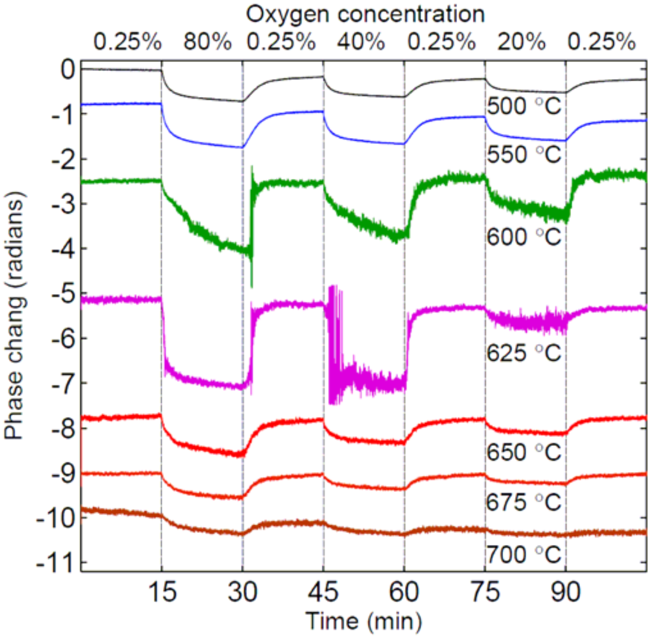

Figure 7. Oxygen sensing as a function of temperature.

The peaked behavior for the sensitivity as a function of temperature is an important issue in sensor design. In order to acheive accurate sensing over a range of temperature, sensing layers with little dependence on temperature are preferred. Recently some mixed-oxide sensing layers have been investigated that have reduced temperature sensitivity [8]. Even in this case, the activitation energy is not exactly zero so simultaneous temperature measurement will still be needed.

Finally, we consider the issue of sensor stability. In early experiments, we evaluated the oxygen sensing as a function ot temperature at steadily increasing maximum temperatures of 630, 700, and 750 C. The total phase change resulting from an oxygen concentration change from 0.25% to 80% is plotted in Figure 8 for these three series of measurements. We see that the peak sensitivity shifts to lower temperatures with increasing temperature exposure. This change is consistent with increasing grain size in the ZnO layer, resulting in higher conductivity (increase in the factor *A* in equation (1)).

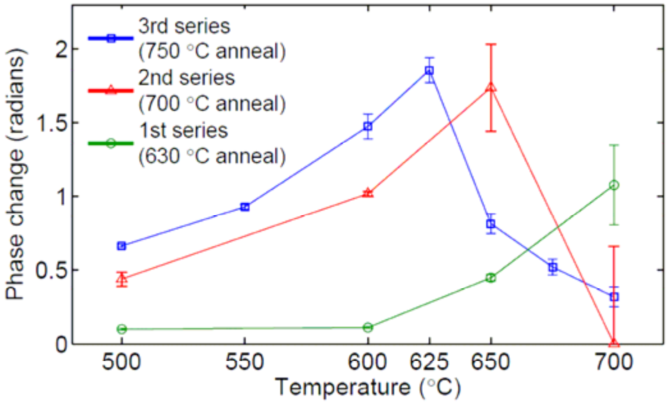

Figure 8. Measured phase change from 0.25% to 80% O_2 concentration at different temperature in three series of tests of the ZnO/langasite device.

In a subsequent series of experiments (not shown) closely similar results were obtained in three series of measurements. This suggests that the response of the sensing layer is stable when operated below the maximum anneal temperature.

IV. CONCLUSIONS

We have reported here on a langasite SAW sensor for simultaneous measurement of temperature and oxygen concentration. The sensitivity of the propagation velocity resulting to oxygen concentration depends on temperature because of the thermally activated conductivity of the sensing layer. As a result small perturbations in temperature will cause a change in the measured phase shift even if the oxygen concentration is constant. This effect can be minimized by using two SAW devices or two propagation paths, one with and one without a sensing layer.

We have also observed that the gas sensitivity can be influenced by aging of the sensing layer. This effect appears to be reduced when sensors are annealed at higher temperatures than used during operation.

ACKNOWLEDGEMENT

This work was performed in support of research on carbon storage at NETL under RES contract DE-FE0004000.

REFERENCES

[1] M. P. da Cunha, T. Moonlight, R. Lad, D. Frankel, and G. Bernhard, “High temperature sensing technology for applications up to 1000°C”, in 2008 Proc. IEEE Sensors Conference, pp. 752 – 755.

[2] J.A. Thiele, and M. P. da Cunha, “High temperature SAW gas sensor on langasite”, in 2003 Proc. IEEE Int. Conf. Sensors,Vol.2, pp. 769 – 772.

[3] A. Canabal, P.M. Davulis, G.M. Harris and M. P. da Cunha, “High-temperature battery-free wireless microwave acoustic resonator sensor system”, Electronics Letters, vol. 46, issue 7, pp 471 – 472, 2010.

[4] P. Zheng, et al., “Pulse-mode temperature sensing with langasite SAW devices,” in 2010 Proc. IEEE Int. Freq. Contr. Symp., pp. 297-300.

[5] P. Zheng, et al., “Langasite SAW Device with Gas-Sensitive Layer,” in 2010 Proc. IEEE Inter. Ultra. Symp. (in press).

[6] J. Bardong, et al., “Precise Measurements of BAW and SAW Properties of Langasite in the Temperature Range from 25 °C to 1000 °C,” IEEE International Frequency Control Symposium, 2008, pp. 326-301.

[7] S.Q. Wang, J. Harada and S. Uda, “A Wireless Surface Acoustic Wave Temperature Sensor Using Langasite as Substrate Material for High-Temperature Applications,” Jpn. J. Appl. Phys. 42, pp. 6124–612, 2003.

[8] F. Neri et al., “$FeSrTiO_3$- based resistive oxygen sensors for application in diesel engines,” Sensors and Actuators B: Chemical 134, pp. 647-653 (2008).