



Thin Film Praseodymium-Cerium Oxide Languasite-Based Microbalance Gas Sensor

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Abstract. Languasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) has proven to be a viable piezoelectric material for use in high temperature bulk acoustic wave gas sensors. To detect changes in pO_2 under oxidizing conditions, we utilized a PLD deposited $\text{Pr}_{0.15}\text{Ce}_{0.85}\text{O}_{2-\delta}$ film as the gas sensitive layer given its ready reduction under these conditions. The sensor was operated at 600°C and showed strong sensitivity to changes in oxygen partial pressure, saturating at a frequency shift of -360 Hz below $1\%\text{O}_2/\text{Ar}$ ($\text{pO}_2 = 10^3$ Pa). The frequency shift was calculated to be too large to be solely accounted for by the corresponding change of mass in the PCO film. Stress induced by dilation of the PCO lattice upon reduction is viewed as being a likely source of sensor sensitivity.

Keywords: languasite, gas sensor, microbalance

Introduction

Bulk acoustic wave (BAW) devices, represented by the quartz crystal microbalance (QCM), characteristically provide exceptional mass sensitivity via measurable shifts in resonant frequency. Deposition of films with selectivity to specific molecules onto the device surface provides means for sensing gases with high sensitivity and selectivity (Fig. 1). As gas molecules adsorb on the film, they are detected with high resolution by monitoring the shift in resonant frequency. Because the QCM is relatively inexpensive and readily available, it is the system of choice for sensors that operate at or near ambient conditions. For many applications, however, higher temperature operation is required. The absolute maximum operating temperature of quartz-based devices, for example is limited by the destructive alpha-beta transition at 573°C . To overcome this limitation, a languasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) resonator, which exhibits no phase transitions up to its

melting point of 1470°C and for which high quality crystals are readily available, is utilized.

In initial investigations, a languasite bulk acoustic wave device was successfully operated as a microbalance to temperatures as high as 900°C [1]. By adding a TiO_2 film onto the languasite resonator, sensitivity to hydrogen gas was demonstrated at 600°C [2, 3].

In this study, we investigate the oxygen sensitivity of a languasite-based resonant gas sensor at high oxygen partial pressures. Praseodymium-cerium oxide (PCO) was chosen as the active film, given its highly non-stoichiometric nature at high oxygen partial pressures [4]. These conditions lie well within the chemical stability regime of languasite [5, 6].

Experimental Details

The solid solution $\text{Pr}_{0.15}\text{Ce}_{0.85}\text{O}_2$ (PCO) was deposited onto a single crystal Y-cut languasite resonator with Pt electrodes using pulsed laser deposition (PLD). The PCO film was 450 nm thick, measured using a

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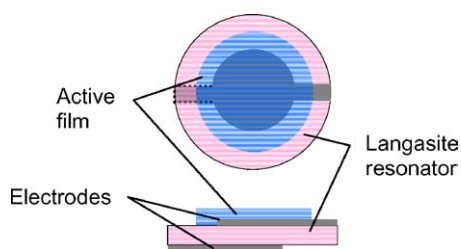


Fig. 1. Langasite resonant gas sensor.

profilometer. The single phase fluorite structure, characteristic of PCO, was confirmed using X-ray diffraction (XRD).

Shifts in resonant frequency of the gas sensor in response to changes in oxygen partial pressure at 600°C were monitored using a high-speed network analyzer. The temperature was monitored using a thermocouple, installed above the sensor. The oxygen partial pressure in the gas sensor chamber was varied by controlling the ratio of O₂/Ar in the gas mixtures. Before measurements, the PCO film was first annealed in 100% O₂ at 600°C for a day. The initial resonant frequency recorded was 4.08622 MHz. The sensor was calibrated at various temperatures and the calibration curve was used to compensate for temperature variations.

Results

Temperature Calibration

Figure 2 shows the temperature calibration curve obtained by monitoring the resonant frequency change

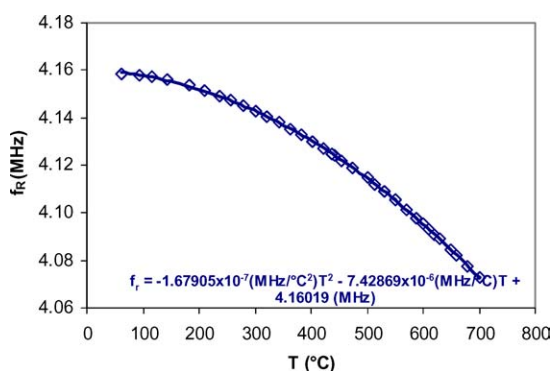


Fig. 2. Temperature calibration curve of langasite resonator at 100% oxygen atmosphere.

with variations in temperature in pure oxygen. The data points were fitted with a quadratic function, and the calibration equation was then used to compensate out the effect of temperature variations during gas sensor operation.

Monitoring Oxygen Partial Pressure Change

Figure 3 shows the frequency shift data, compensated for temperature fluctuations, obtained at different oxygen partial pressures at 600°C. The base line was re-zeroed for drift at 1 hour intervals each time pure oxygen was introduced. The resonant frequency was observed to decrease when the oxygen partial pressure decreased. The large fluctuations observed near the dotted vertical lines are ascribed to temperature fluctuations accompanying gas switching.

Frequency Change as a Function of Oxygen Partial Pressure

The average frequency change at each oxygen partial pressure was plotted against oxygen partial pressure in Fig. 4. The response is observed to saturate at 1%O₂/Ar, which corresponds to an oxygen partial pressure of 10⁻² atm.

Discussions

From Fig 4, we observe that the response saturates at ≤1%O₂/Ar, with a frequency change of about -360Hz. In comparison to TiO₂ [2, 3], the frequency shifts occur at much higher oxygen partial pressure, confirming that the film controls the response to changes in oxygen partial pressure under oxidizing conditions.

We found the sensor to possess an extremely high sensitivity to oxygen partial pressure variations at high pO₂. A similar resonator used in [6] had a mass sensitivity of approximately -21.9 cm² Hz μg⁻¹ at 600°C. Based on that mass sensitivity, the areal mass density change for the sensor used in this study would be 16.4 μg/cm² at 1%O₂/Ar and lower oxygen partial pressure. The areal mass density of the PCO

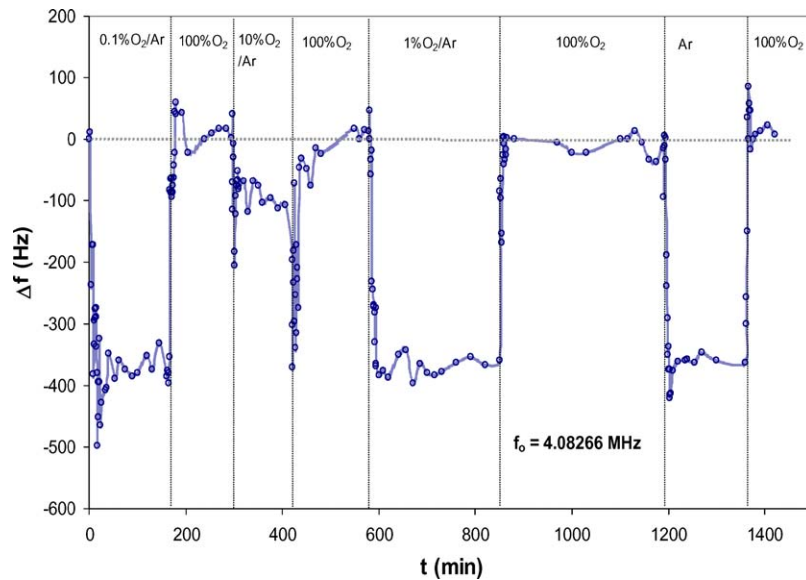


Fig. 3. Sensor response to different oxygen partial pressures.

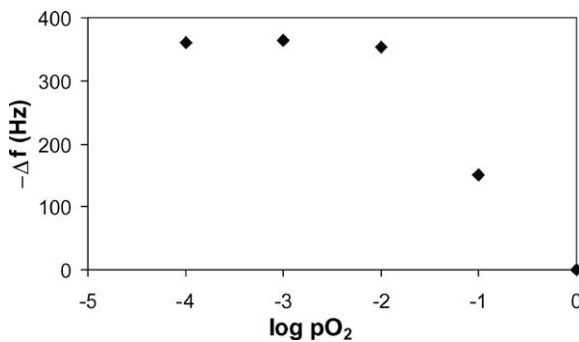


Fig. 4. Frequency change at various oxygen partial pressure—taking pure oxygen as baseline.

deposited, assuming a fully dense material (density at $\sim 7.1 \text{ g/cm}^3$), would be $\sim 320 \mu\text{g/cm}^2$. This represents a 5% increase in mass of the PCO film. This could not be explained on the basis of mass change alone, since the magnitude is too large for oxygen non-stoichiometry, and the direction of frequency change indicates a mass increase (instead of a mass decrease during reduction of the PCO film).

Both the anomalously high frequency change and the direction of the shift suggest a cross effect not directly related to the mass change. We suspect that stress induced by the dilation of the PCO lattice upon reduction of being a likely source of the sensor sensitivity.

We are presently in the process of investigating this hypothesis.

Conclusion

A thin film of $\text{Pr}_{0.15}\text{Ce}_{0.85}\text{O}_2$ was deposited onto a Y-cut single crystal langasite resonator using pulsed laser deposition (PLD). The resonator was successfully operated as an oxygen sensor at 600°C . The temperature dependence of the resonant frequency of the sensor was calibrated, and the result used to compensate for temperature fluctuations during operation. The sensor showed strong sensitivity to changes in oxygen partial pressure, saturating at a frequency shift of -360 Hz below $1\% \text{ O}_2/\text{Ar}$ mixtures ($p\text{O}_2 = 10^{-2} \text{ bar}$ or 10^3 Pa). The frequency change, however, was calculated to be too large to be accounted for by the corresponding change of mass in the PCO film. Stress induced by the dilation of the PCO lattice upon reduction is viewed as being a likely source of sensor sensitivity.

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