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Operation limits of langasite high temperature nanobalances

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Abstract

The high temperature properties of langasite ($La_3Ga_5SiO_{14}$) are presented in order to evaluate its ability to serve as a high temperature nanobalance. Langasite resonators exhibit bulk oscillations at temperatures of up to 900°C. At 800°C, the mass load response for 780 μm thick resonators is approximately -6.5 cm^2 Hz μg^{-1}. The temperature dependent frequency shift, about -100 Hz K^{-1} at 600°C, may be effectively compensated by monitoring the difference frequency of closely mounted resonators. As an example, the response of a TiO_{2-x} coated langasite nanobalance to different oxygen partial pressures at elevated temperatures is presented. The strong frequency shift due to switching from oxidizing to reducing conditions cannot be attributed to mass changes of the sensor film. Mechanical stress caused by changes in the oxygen stoichiometry is the most likely explanation for the frequency changes.

Keywords: Electrical conductivity; Langasite; Piezoelectric properties; Sensors

1. Introduction

Current acoustic wave devices with specific surface affinity layers are highly attractive for gas phase chemical sensing. Piezoelectric resonators coated with sensor films are used as nanobalances to monitor gas composition. The resonance frequency shift of the transducer is correlated with very small mass changes due to gas composition dependent adsorption.

While gas sensors based on stoichiometry changes of thin films by thermogravimetry are, in principle, feasible, the application temperature of current piezoelectric devices is, however, limited by the intrinsic properties of the piezoelectric materials. Materials which exhibit attractive room temperature piezoelectric properties either decompose (e.g. $LiNbO_3$ at 300°C) or exhibit phase transformations (e.g. $Li_2B_4O_7$ at approx. 500°C) at elevated temperatures. The highest current application temperature of about 450°C is reached by quartz resonators above which high losses and phase transformations prevent its use.[1,2]

A promising candidate material for piezoelectric applications at high temperatures is langasite (LGS or $La_3Ga_5SiO_{14}$).[3] Since langasite does not undergo phase transformations up to the melting temperature of 1470°C and due to the availability of high quality crystals,[4,5] this material is of particular interest.

Previous investigations by the authors confirmed that langasite exhibits low oxygen diffusion coefficients relative to the gas sensitive materials which might be utilized within a langasite nanobalance.[6]

In this study, we investigate the operation of langasite as a high temperature bulk acoustic wave (BAW) resonator in different atmospheres and the ability of a langasite nanobalance with integrated TiO_{2-x} film to serve as oxygen partial pressure sensor at elevated temperatures.

2. Sample preparation and experimental

Resonator devices were prepared from polished langasite plates cut from Czochralski-grown single crystals.[4] The diameter of the Y-cut resonators was 19 mm with the plate thickness varying from 632 to 780 μm. The resonators were contacted on both sides with 200 nm thick key hole shaped platinum electrodes (contact 1 and 2 in Fig. 1).

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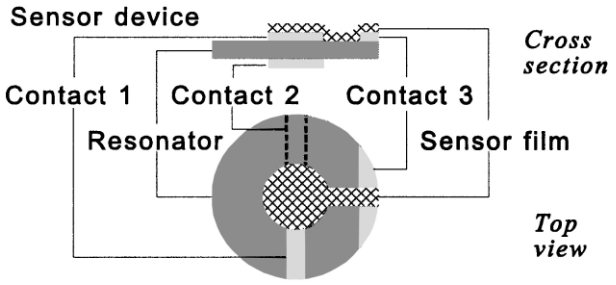

Fig. 1. TiO_{2-x} coated langasite resonator device with associated contacts.

All resonators were cut from the same crystal boule and contacted in the same manner. The first resonator (M) was loaded with different *masses* by controlled deposition of Pt. Identical *reference* (R) and a *blank* (B) resonators were also prepared without additional deposited films. Since the application of langasite resonators as high temperature nanobalance is the aim of the work a TiO_{2-x} film on resonator (T) serves as oxygen partial pressure dependent mass load.

The 120 nm thick TiO_{2-x} film was deposited onto one side of the resonator by laser ablation using a 193 nm excimer laser (LPX 325i, Lambda Physik, 20 ns pulse length). The langasite substrate was unheated.

The resonance behavior of the langasite plates was investigated using a high speed network analyzer (HP E5100A, 10 kHz–180 MHz) by monitoring the real and imaginary parts of the impedance spectra. The peak frequency f_P of the real part of the impedance curve was chosen as the characteristic resonator frequency and determined by fitting the center frequency of a Gaussian function to the experimental data. The resonance frequency is not suited for mass determinations. It is strongly influenced by damping above 500°C and represents, in part, the change of the intrinsic properties of the resonator material.

The network analyzer allows the simultaneous investigation of two resonators. Pairs of resonators were closely mounted (distance 5 mm) in an alumina support and inserted into a gas tight furnace (diameter 40 mm). Resistivity measurements of the TiO_{2-x} film were performed by measurement of the current flowing between contacts 1 and 3 upon application of 1 V (see Fig. 1).

During the high temperature experiments, different gases such as oxygen and 6% H_2/Ar, were provided with flow rates of about 1 $cm^3\ s^{-1}$. The atmosphere was switched by repeated pumping (rough vacuum) and subsequent backfilling with the new gas. This process temporarily causes undefined temperature and pressure fluctuations and thus less reliable frequency shifts.

3. High temperature mass sensitivity

The mass load response of langasite resonators at elevated temperatures was determined by examining the frequency shift induced by the deposition of platinum layers with well defined masses.

Fig. 2 shows the temperature dependent peak frequency f_P of resonator M for two different thicknesses of the platinum contacts. The corresponding mass loads m enable the calculation of the mass sensitivity S for a given area A defined by $S = A \times \Delta f_p/\Delta m$. Table 1 lists the resulting mass sensitivities at temperatures of up to 800°C.

The comparison of langasite and quartz resonators at the same resonance frequency results in a relative mass sensitivity $S_L/S_Q = 0.65$ (Y-cut, room temperature) taking the material data from Smythe et al.[7] Since the relative sensitivity is only slightly lower than unity, langasite resonators may yield the same mass sensitivity as quartz resonators by fabricating slightly thinner plates.

4. Temperature dependent frequency and temperature compensation

With increasing temperature, a significant broadening of the resonance curve is observed. Nevertheless, it remains possible to monitor the peak frequency at elevated temperatures as shown for resonator M in Fig. 2. In contrast to standard resonator materials, langasite devices exhibit bulk oscillations at temperatures of up to 900°C.

The parabolic temperature dependence of f_P (solid lines in Fig. 2) agrees with surface acoustic wave (SAW) measurements.[2] The upper part of Table 2 lists the absolute temperature dependence of the resonators B, R and T in the range from 400–600°C. The experiments were performed in oxygen, assuming that the TiO_{2-x} film does not measurably change its stoichiometry.

Taking values of mass and temperature sensitivity of frequency from Tables 1 and 2, one calculates that

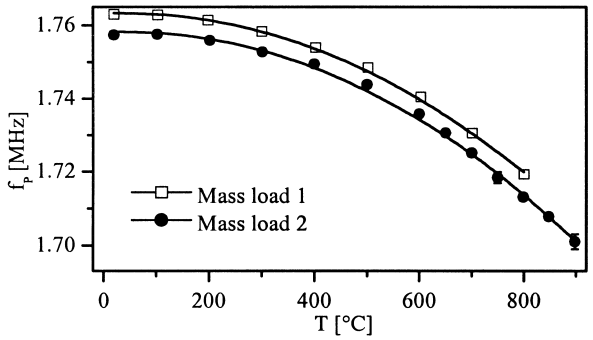

Fig. 2. Temperature dependence of the peak frequency for different mass loadings.

Table 1
Mass sensitivities of the 780 nm thick langasite resonator

T	(°C)	20	200	400	600	800
S_{M1}	(cm^2 Hz μg^{-1})	−5.26	−5.29	−5.52	−5.92	−6.49

Table 2
Temperature dependence of the absolute and the difference frequency

	Temperature range T_1–T_2	(°C)	400–500	500–600
Reference (R)			−81	−112
Blank (B)	Temperature dependence $f_P(T_2)-f_P(T_1)/T_2-T_1$	(Hz K^{-1})	−78	−107
TiO_2 coated (T)			−78	−106
Blank (b) and reference (R)			3	5
	Differential temperature dependence $f_D(T_2)-f_D(T_1)/T_2-T_1$	(Hz K^{-1})		
TiO_2 coated (T) and reference (R)			3	6

temperature changes of only 0.1 K around 600°C would correspond to a mass change of 620 ng. Consequently, for accurate mass measurements, the temperature induced frequency shift requires effective compensation. Simultaneous frequency measurements of closely mounted resonators and the evaluation of the difference frequency $f_D = f_{PX} - f_{PR}$ (X = device under test, R = reference) decrease the temperature sensitivity significantly. Values obtained for f_D for the temperature ranges 400–500 and 500–600°C are listed in the lower part of Table 2. Taking the example mentioned above, a temperature change of 0.1 K would result in an apparent mass change of about 30 ng. Further improvements should be possible by insuring that test and reference resonators experience the same temperature changes.

5. Oxygen partial pressure dependent frequency and TiO_{2-x} based oxygen partial pressure sensor

Gas sensors based on the stoichiometry change of films deposited onto resonators require gas composition independent operation of the resonator platform. Therefore, the frequency stability of langasite resonators was investigated under both oxidizing (O_2) and reducing conditions (6% H_2/Ar).

Fig. 3 shows the absolute frequency changes of the blank (B) and the reference (R) resonators following a switch of the atmosphere from oxygen to 6% H_2/Ar and back to oxygen at 600°C. The sharp shifts in frequency accompanying the atmosphere exchanges are attributed to turbulence effects. Apart from these temporary disturbances, the curves show no significant frequency changes. Long-term treatments performed under reducing conditions at 600°C, for up to 3 days, confirm stable resonator operation. Moreover, for nominally identical resonators the difference frequency f_D is independent of atmosphere as shown in Fig. 3.

High temperature gas sensors most commonly rely on gas induced changes in the electrical conductivity of oxide semiconductors. High temperature resonators coated with sensor films provide means for acquiring additional information including mass changes induced by changes in stoichiometry of the film.

Fig. 4 shows both the time dependence of the difference frequency f_D of the TiO_{2-x} coated resonator vs. reference resonator and the current flowing through the TiO_{2-x} film at 600°C. A significant frequency drop and current increase result upon the change from oxygen to 6% H_2/Ar. Initially, the difference frequency and current change relatively quickly but then tend to saturate with f_D approaching a maximum value f_{D0}. This frequency drop f_{D0} corresponds to an apparent mass gain of 26 μg taking the mass sensitivity from Table 1 corrected for resonator thickness. The current, however, drifts slightly at elevated temperatures as illustrated in Fig. 4. This behavior may be attributed either to polarization effects or to changes in the langasite conductivity. To minimize these effects, the current I_0 is taken at the atmosphere switching time t_0 by extrapolation of the

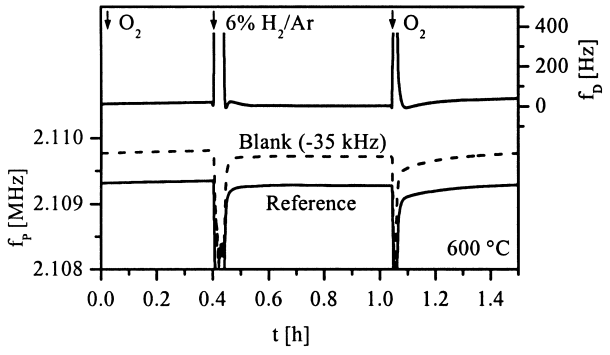

Fig. 3. Peak frequency and difference frequency for the blank and the reference resonator exposed to oxygen and 6% H_2/Ar.

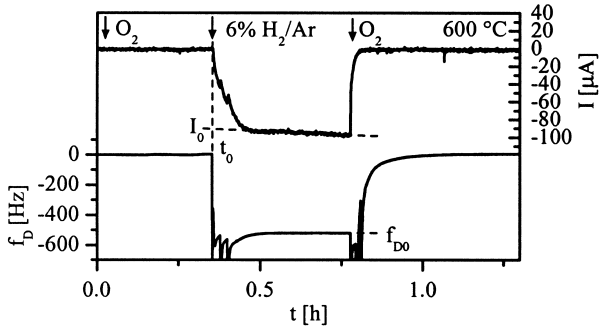

Fig. 4. Difference frequency, f_D, for the TiO_{2-x} coated and the reference resonators (lower curve) and current transients in the TiO_{2-x} film measured at 600°C under changes in atmosphere.

current curve as indicated in Fig. 4. Under reducing conditions, the measured resistivity using contact 1 and 3 (see Fig. 1) is more than two orders of magnitude lower than the resistivity of the langasite substrate taking into account the geometry. Therefore, the langasite resistivity may be neglected.

Fig. 5 shows the electrical conductivity of TiO_{2-x} plotted versus reciprocal temperature. Activation energies of 0.81 and 0.14 eV are observed in the high ($\geqslant 500°C$) and low ($\leqslant 450°C$) temperature range, respectively. The values correspond to the conductivity of hydrogen reduced TiO_{2-x} at an oxygen partial pressure of 0.2 Pa[8] (dashed lines in Fig. 6). Porous titanium dioxide[9] exhibits similar conductivities and activation energies (0.8–0.9 eV), which were used for further calculations.

The frequency drop as shown in Fig. 4 is in contradiction to the expected frequency increase in reducing atmospheres assuming a mass loss due to reduction of the TiO_{2-x} film. For clarification, the measured conductivity is used to estimate the oxygen nonstoichiometry x of the TiO_{2-x} film. Based on the assumption that TiO_{2-x} behaves as an *n*-type semiconductor due to oxygen vacancies $\left[V_o^{\bullet\bullet}\right]$ and taking the electron mobility mentioned above[9] ($\mu = 5 \times 10^{-4}$ cm^2 V^{-1} s^{-1}, extrapolation to 400°C), the oxygen vacancy concentration may be calculated according to $\left[V_o^{\bullet\bullet}\right] = 1/2\, n = 1/2\, \sigma/e\mu$ (n = electron density, σ = conductivity). The calculation results in $x \approx 0.1$ at 400°C. This corresponds to a mass loss of 435 ng (assuming $x = 0$ under oxidizing conditions) or a frequency increase of 7.8 Hz. Consequently, mass changes should contribute insignificantly to the observed frequency changes.

Fig. 6 shows the temperature dependent frequency drop induced by changes from O_2 to 6% H_2/Ar. Above 200°C, a linear behavior is observed. Mechanical stresses induced between the langasite resonator and the TiO_{2-x} film are tentatively held responsible for this behavior. Changes in stoichiometry of films are known to result in dimensional changes and thereby in mechanical stresses. For temperatures below ≅100°C, the frequency shift

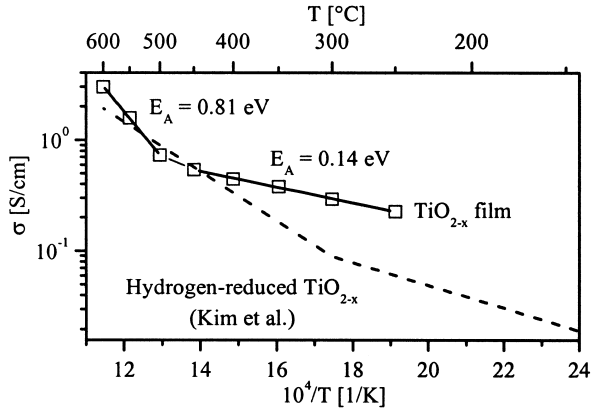

Fig. 5. Temperature dependence of the TiO_{2-x} conductivity annealed in 6% H_2/Ar and data from Kim et al.[8]

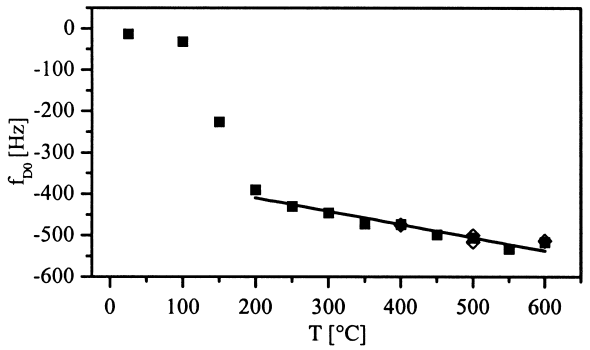

Fig. 6. Temperature dependent maximum difference frequency shift f_{D0} of the TiO_{2-x} coated and reference resonator due to switching the atmosphere from oxygen to 6% H_2/Ar.

becomes very small, which is likely due to kinetic limitations.

6. Conclusions

Langasite was successfully operated as a BAW resonator up to temperatures of 900°C. Measurement of the peak frequency of the real part of the impedance spectra is a feasible means for tracking the frequency shift. Bare langasite resonators are insensitive to oxygen partial pressure at temperatures of up to at least 600°C.

Due to their strong temperature sensitivity, reference resonators, operating under identical conditions, must be used. A langasite nanobalance coated with a p_{O_2}-sensitive TiO_{2-x} film exhibited atmosphere-induced frequency shifts larger in magnitude and in the direction opposite to that expected given corresponding changes in film resisitivity. These frequency shifts are tentatively ascribed to atmosphere-induced stresses produced in the TiO_{2-x} film.

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