Selectivity Improvement of High-Temperature Resonant Gas Sensors Using Micro Machined Membrane Arrays

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Different types of piezoelectric langasite ($La_3Ga_5SiO_{14}$) membranes are manufactured using wet chemical etching. The membranes show thicknesses as low as 25 µm, leading to a resonance frequency of 60 MHz. Arrays of membranes are coated with platinum electrodes and different metal oxide sensor films such as CeO_2 and SnO_2 using pulsed laser deposition.
The sensor arrays are tested at 600 °C at different oxygen partial pressures in hydrogen and carbon monoxide containing gas mixtures. In comparison to conventional bulk acoustic wave resonators with larger thickness, i.e. lower fundamental frequency, the frequency shift caused by stoichiometry changes of the sensor films is increased by one order of magnitude, thereby enabling improved distinction between the above mentioned gases. CeO_2 coated resonators show large changes of its resonance frequency at oxygen partial pressures below about 10^{-15} bar, while SnO_2 can be used to monitor gas mixtures at oxygen partial pressures above about 10^{-12} bar.

Introduction

Due to economical and ecological reasons there is an increasing interest in gas sensors for high temperature applications (T ≥ 600 °C) like gas reformers for fuel cells or combustion systems. Common metal oxide conductivity based gas sensors show a good sensitivity to different gases, but their gas selectivity is, in general, poor. New concepts to increase the selectivity of metal oxide based sensor systems are required. Piezoelectric materials like langasite ($La_3Ga_5SiO_{14}$) enable the realization of resonant sensors for high temperature application. Unlike quartz, which can only be used up about 450 °C, langasite shows resonances up to its melting point at 1470 °C.

Conventional langasite bulk acoustic wave resonators show resonance frequencies of about 5 MHz. Using different sensor film materials and different electrode layouts, they are able to distinct between hydrogen and carbon monoxide at high temperatures [1]. Thereby, different sensor modes, reflecting variations in mechanical and electrical properties of the sensor films are used. TiO_2 and CeO_2 coated resonators enable the detection of about 2 % of CO in H_2 [2].

Miniaturization is a consequent step to increase the sensitivity of resonant bulk acoustic wave sensors since the mass sensitivity ($\sim\Delta f/\Delta m$) of such devices increases quadratically with increasing fundamental frequency f. For small changes $\Delta m/m < 2$ %, the frequency shift Δf can be calculated according to Eq. 1 (Sauerbrey equation [3]):

$$\Delta f = -\frac{f\Delta m}{m} = -\frac{f\Delta m}{\rho_r d A} = -\frac{2f^2}{\sqrt{\mu_r \rho_r}}\frac{\Delta m}{A} \qquad (1)$$

Thereby, m is the mass of the active, i.e. the piezoelectrically excited, resonator volume. The thickness d, the active area A, the shear modulus μ_r and the density ρ_r are constant for a given resonator.

Another advantage of the miniaturization is the option to create arrays of differently coated resonators, which improves the gas selectivity. Arrays can be realized on a single substrate and decrease, thereby, the costs of the sensor device.

This work focuses on the preparation of langasite membranes using wet chemical etching and their resonance behaviour at high temperatures. Further, the characteristic of sensor film coated membranes in reducing atmospheres at elevated temperatures is presented to demonstrate the potential of micro machined langasite resonators.

Sample preparation

Etching of langasite

Mechanical thinning of langasite resonators is not feasible due to mechanical instabilities of thin membranes. Therefore, a suitable wet etching process is developed. Phosphoric acid is tested at different temperatures. Fig. 1 shows the obtained etch rates in langasite as function of temperature and crystal orientation. Exponential temperature dependence is observed.

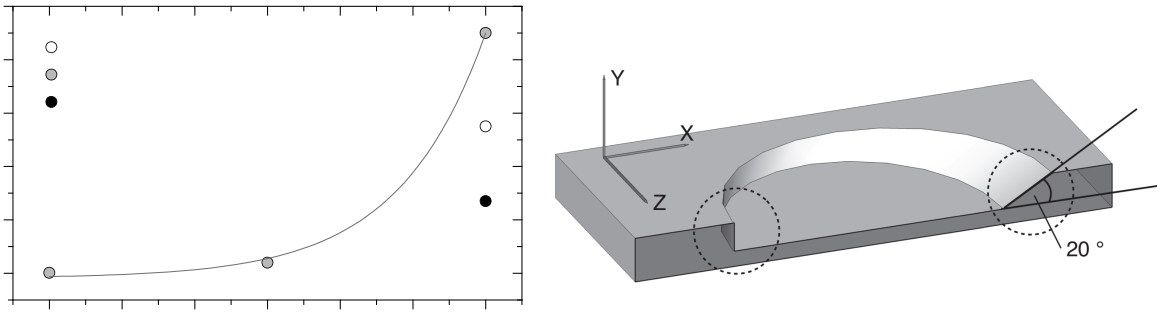

Fig. 1: *Etch rates in langasite at langasite using phosphoric acid at different temperatures (left). The etching process exhibits a strong asymmetry in +X and –X direction as described in the text (right).*

The etching process shows a strong anisotropy with its maximum etching rate in *Y* (90 μm/h at 90 °C) and lower etching rates in *X* (55 *μ*m/h) and *Z* direction (27 *μ*m/h). The etch profiles obtained using circular masks on *Y* cut samples exhibit strong asymmetry in *+X* and *–X* direction as visualized in the right part of Fig. 1. The circles in the scheme mark walls of different slope. The unequal etch rates are related to the three fold symmetry axis parallel to the *Z* direction of the langasite crystal. A similar etching behaviour is observed in quartz crystals [4] having the same crystal symmetry. Steep side walls are the result of a large anisotropy in etching rates between the axis perpendicular to the surface and to the wall, respectively [5]. The angle of the less steep side wall is measured using a surface profiler. The value is about 20° as indicated in the scheme. This is in rough accordance to the slope of about 30°, which follows from the ratio of the measured etch rates in *X* and *Y* direction.

Since *Y* cut resonators are mostly used for langasite bulk acoustic wave resonators, phosphoric acid is suitable for fast processing of langasite membranes. During the etching process a white precipitation is observed, which is identified to be SiO_2 using EDX-analysis. A constant flow of the etch medium along the sample surface is required to prevent the formation of a thin SiO_2 film, which could cause an inhomogeneous etching of smaller structures.

Due to the anisotropic etching rates, small scratches and the surface roughness are enlarged during the etching process. Therefore, the substrate has to be polished very smooth. Further, the etching rate is very

sensitive to small inhomogeneities, which can cause etch channels on the material surface [6]. This effect may depend on the manufacturer of the actual langasite crystal.

Langasite membranes

Different langasite membrane arrays are prepared using Y cut plates (thickness 270 μm, diameter 10 mm, manufacturer: Fomos Materials, Moscow, and Institute for Crystal Growth, Berlin) using the previously described etching process. Two or three membranes with a diameter of about 3 mm could be realized on one substrate. Different membranes with thicknesses between 60 and 23 μm are etched.

The steps of the manufacturing process are shown in Fig. 2. The relatively small slope of the side wall (marked in Fig 2.3 by the circle), can be used to apply electrodes without the risk of interruption, which can occur at very steep walls. For deposition of the high temperature stable platinum electrodes and the sensor films pulsed laser deposition (KrF excimer laser, 248 nm) is used.

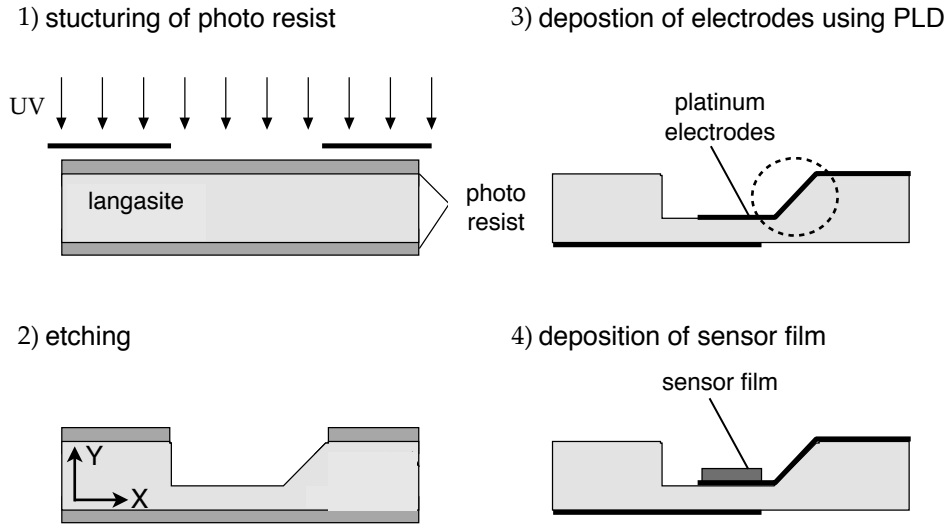

Fig. 2: *Processing steps for manufacturing langasite membranes.*

Measurements and discussion

Operation of langasite membranes at high temperature

Langasite membranes are characterized at temperatures of up to 900 °C. For data acquisition, a network analyzer (HP5100A) is used. In order to obtain the resonance frequency of the resonators, a lorentzian function is fitted to the real part of the admittance. The parameters of the lorentzian function also permit a simple estimation of the *Q*-factor, which follows from the resonance frequency *f* and the bandwidth Δf according to $Q \sim f/\Delta f$.

The membranes could be operated up to 900 °C. Thereby, planar membranes with a thickness of 23 μm (60 MHz) exhibit a *Q*-factor of 100 at the maximum temperature. Higher *Q*-factors can be obtained by shaping biconvex membranes due to an improved energy trapping compared to planar resonators. The convex surfaces are realized using a multi-step etching with different masks. Fig. 3 shows the resonance frequency and the *Q*-factor of a biconvex 16 MHz membrane as a function of temperature. At 700 °C, the *Q*-factor is still 500. Nevertheless, the measurement of such highly damped spectra is hardly feasible by simple oscillator circuits. In contrast, the usage of a network analyzer permits an accurate determination of the resonance frequency at high temperatures. In addition, this technique allows the determination of

additional parameters like damping and may, therefore, improve the application potential of such a sensor devices.

It has to be noted, that the operation temperature limit is not determined by the resonator material itself. The failure of the device is caused by the degradation of the platinum electrodes. A further development of suitable electrode materials is expected to broaden the temperature range.

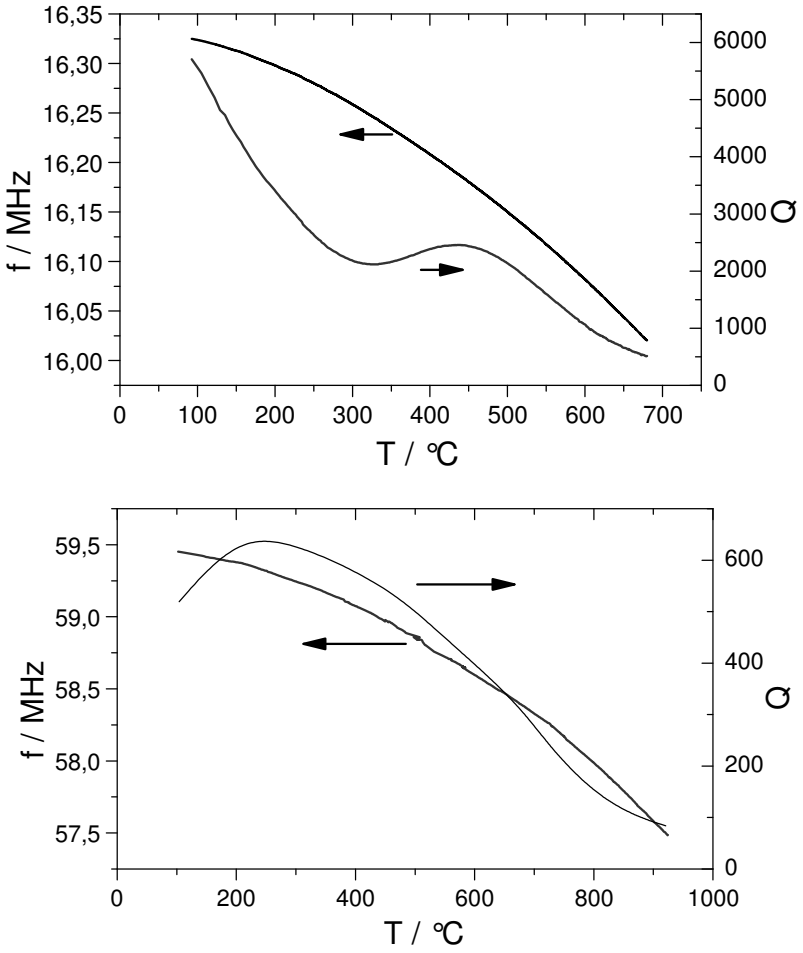

Fig. 3: *Resonance frequency and Q-factor of a biconvex 16 MHz membrane (top) and a planar 60 MHz membrane (bottom) as a function of temperature.*

Gas sensors

Arrays with differently coated membranes are prepared. Thereby, two different electrode layouts are applied to use different sensor effects. The sensor film is either deposited on the larger electrode (layout A, see Fig.4) or on the smaller electrode and exceeds its diameter (layout B). In the former case, the resonance behavior is predominantely determined by the mechanical properties of the sensor film such as mass and stiffness. The latter configuration leads to an effective electrode diameter, which depends on the conductivity of the sensor film. This change in the electrode diameter causes a strong frequency shift. A detailed description of the sensor effect can be found in [2].

Membranes, coated with 200 nm thick SnO_2 and CeO_2 sensor films, are operated in microbalance and conductivity mode, respectively. While SnO_2 should be operated at oxygen partial pressures above 10^{-12} bar due to thermodynamic instabilities, CeO_2 can be used at even lower oxygen partial pressures

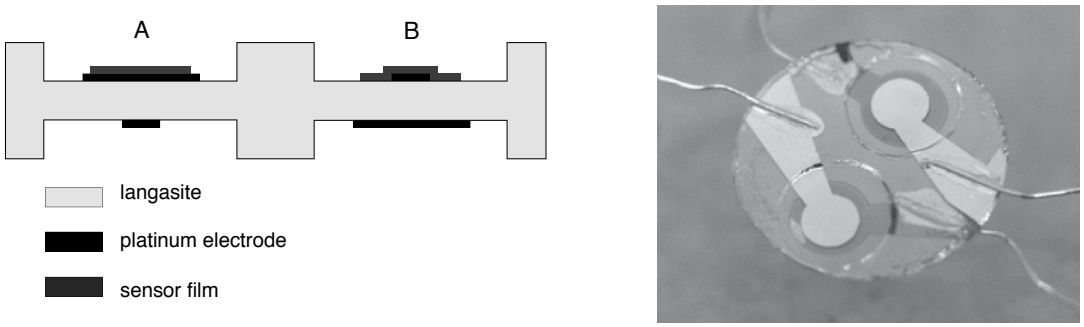

Fig. 4: *Schematic cross section (left) and photograph (right) of a langasite membrane array.*

The sensor arrays are tested in a high temperature furnace at 600 °C at different oxygen partial pressures in a hydrogen and carbon monoxide containing carrier gas (argon). The overall content of carbon monoxide and hydrogen was kept at 0.5 %, while the ratio of these two gases was changed. By adding small amounts of oxygen to the gas flow using a zirconia oxygen pump, the oxygen partial pressure is adjusted to the constant value.

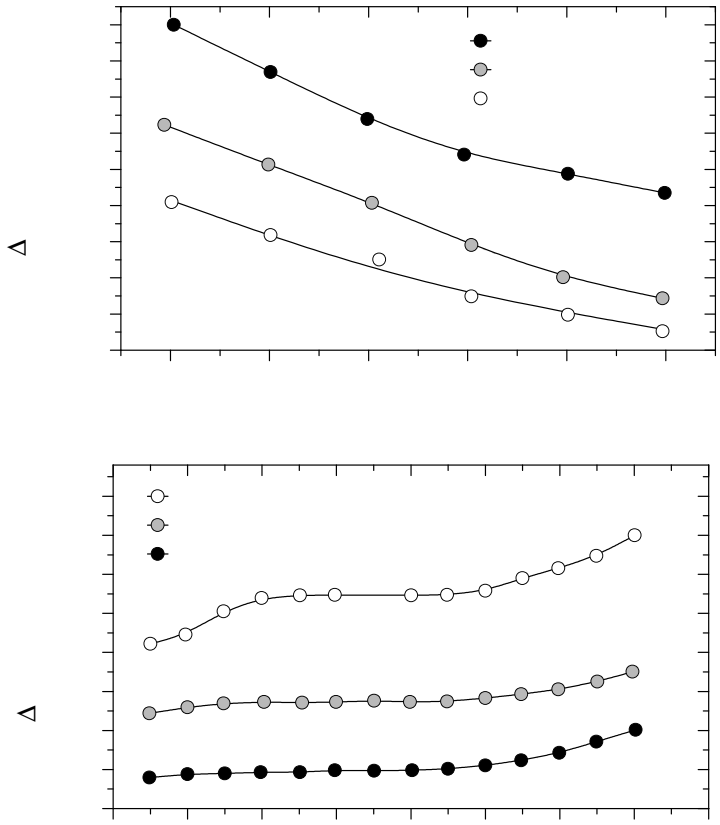

Fig. 5: *Temperature compensated resonance frequency shift Δf_{tc} of a langasite membrane as function of the oxygen partial pressure and the CO/H_2 ratio. The membranes are coated with a CeO_2 (top) and SnO_2 (bottom) sensor film and operated in microbalance mode (top) and conductivity mode (bottom).*

In order to reduce the influence of the temperature on the resonance frequency, a temperature compensation using the third overtone of the resonator is applied [7]. Fig. 5 shows the temperature compensated frequency shift Δf_{tc} of a CeO_2 and SnO_2 coated resonator operated in microbalance and conductivity mode in different gas atmospheres, respectively.

Compared to conventional bulk acoustic wave resonators with similar sensor film thickness, the frequency shift is increased by one order of magnitude, which also leads to an improved separation of the different gases for a given selectivity. Thereby, CeO_2 coated resonators show large changes of their resonance frequency at oxygen partial pressures below 10^{-15} bar. SnO_2 can be used to monitor gas mixtures at oxygen partial pressures above 10^{-12} bar. Both membranes show a different resonance behavior at different CO/H_2 ratios for a given oxygen partial pressure, which permits to distinct between hydrogen and carbon monoxide.

Conclusions

A wet chemical etching process based on phosphoric acid is developed to machine langasite structures. Thin langasite membranes with thicknesses as low as 23 µm could be operated at temperatures of up to 900 °C. Biconvex membranes exhibit significant higher *Q*-factors than planar membranes.

The use of thin membranes with gas sensitive layers results in an increased frequency shift due to a higher mass sensitivity compared to conventional bulk resonators. This effect leads to an improved detection limit for CO in H_2-containing gases.

References

[1] D. Richter, T. Schneider, S. Doerner, H. Fritze, and P. Hauptmann. Selective Gas Sensor System for CO and H_2 Distinction at High Temperatures Based on a Langasite Resonator Array. Solid-State Sensors, Actuators and Microsystems Conference TRANSDUCERS 2007 Lyon, 2007, pp. 991-994,

[2] H. Fritze, D. Richter, and H. Tuller. Simultaneous detection of atmosphere induced mass and conductivity variations using high temperature resonant sensors. Sens. Actuators B, 111-112, 2005, pp. 200-206.

[3] G. Sauerbrey, Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung, Zeitschrift für Physik A, 155 (2), 1959, pp. 206-222.

[4] T. Lebiois, C.R. Teilier, and T. Messaoudi. Chemical etching of Y-rotated quartz plates: experiments and theoretical approach. Sensors and Actuators A 61, 1997, pp. 405-414.

[5] J. S. Danel, F. Michel and G. Delapierre. Micromachining of Quartz and its Application to an Acceleration Sensor. Sensors and Actuators, A 21-23, 1990, pp. 971-977.

[6] I. Hyoung Jung, K. Bo Shim, K. Ho Auh, and T. Fukuda, The defect distribution and chemical etching of langasite crystals grown by the czochralski method, Materials Letters 46 (6), 2000, pp. 354-357.

[7] H. Fritze, H. Tuller. Langasite for high-temperature bulk acoustic wave applications. Applied Physics Letters, 78(7), 2001, pp. 976–977.