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Resonant Sensor for Selective In-situ Gas Monitoring at High Temperatures

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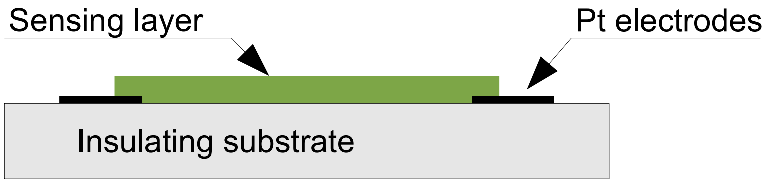
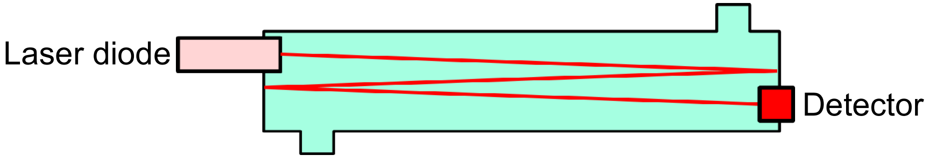
Motivation

- *In-situ* Gas monitoring at elevated temperatures (600–900 °C)
  - Gas reforming for fuel cells
  - Waste combustors
  - Requirement of distinction between CO and H_2

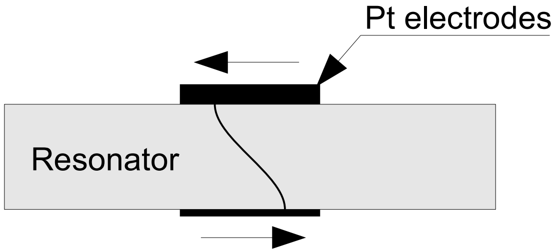
- Sensor principles
  - Resistive gas sensors



  - Optical gas sensors



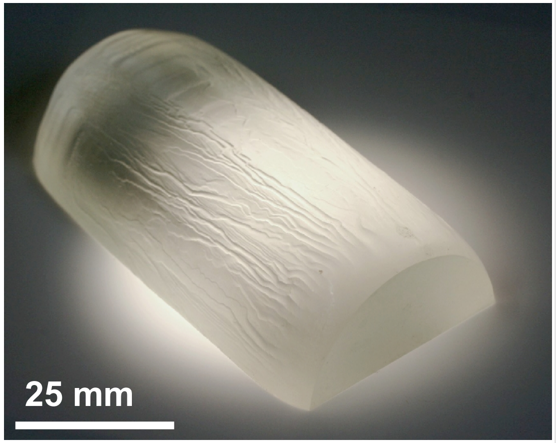
  - Resonant sensors



Langasite ($La_3Ga_5SiO_{14}$)

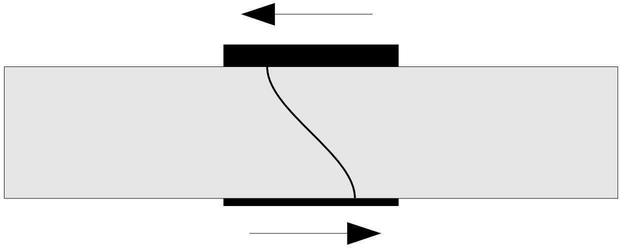
- Piezoelectric material
- Crystal structure like Quartz
- Operation up to the melting point at 1470 °C:
  - No phase transformation
  - Excitation of bulk acoustic waves
  - At 600 °C stable for $p_{O_2} > 10^{-20}$ bar
- 4” wafers commercialy available

- Suitable for high-temperature applications
  - Thickness shear mode of vibration
  - Y-cut
  - 5 MHz



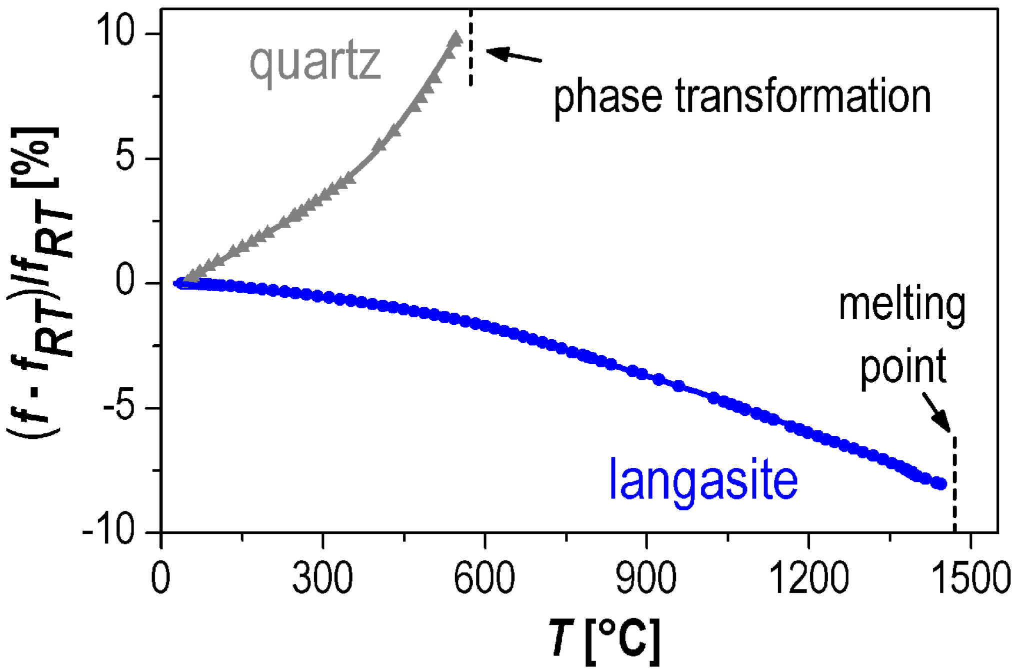
Single crystal of langasite grown using the Czochralski-technique

$$\Delta f \sim \Delta m$$


Schematical representation of thickness shear mode of vibration

Stability of Langasite

- Mixed ionic and electric conductivity
- Slow self diffusion of oxygen
- Negligible gallium loss at elevated temperatures

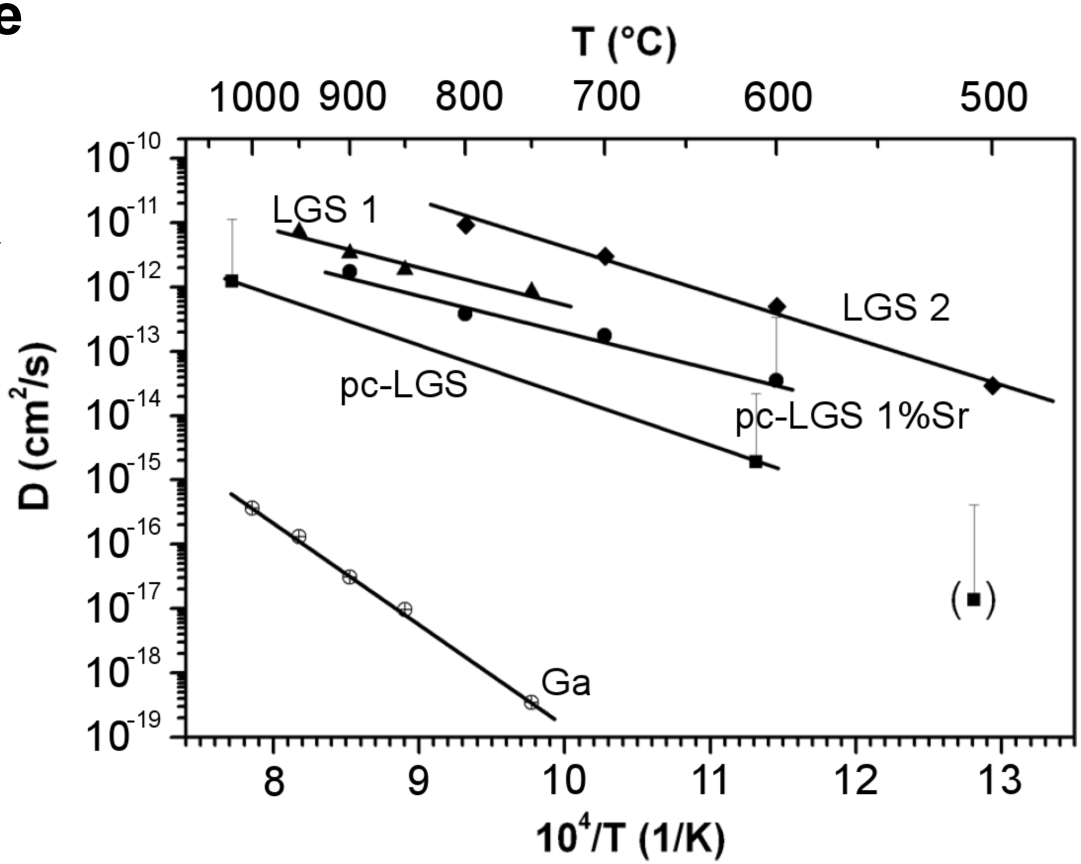


Relative resonance frequency change of langasite and quartz and their operation limits

M. Schulz, J. Sauerwald, D. Richter, H. Fritze, *Electromechanical properties and defect chemistry of high-temperature piezoelectric materials*, Ionics, 15 (2009) 157–161
H. Fritze, M. Schulz, H. Seh, H.L. Tuller, S. Ganschow, K. Jacobs, *High-temperature electromechanical properties of strontium-doped langasite*, Solid State Ionics, 177 (2006) 3171–3174

Stability of Langasite

- Mixed ionic and electric conductivity
- Defect chemistry already known
- Atomic transport investigated



Diffusion coefficient of oxygen and gallium in langasite

M. Schulz, J. Sauerwald, D. Richter, H. Fritze, *Electromechanical properties and defect chemistry of high-temperature piezoelectric materials,* Ionics, 15 (2009) 157–161
H. Fritze, M. Schulz, H. Seh, H.L. Tuller, S. Ganschow, K. Jacobs, *High-temperature electromechanical properties of strontium-doped langasite*, Solid State Ionics, 177 (2006) 3171–3174

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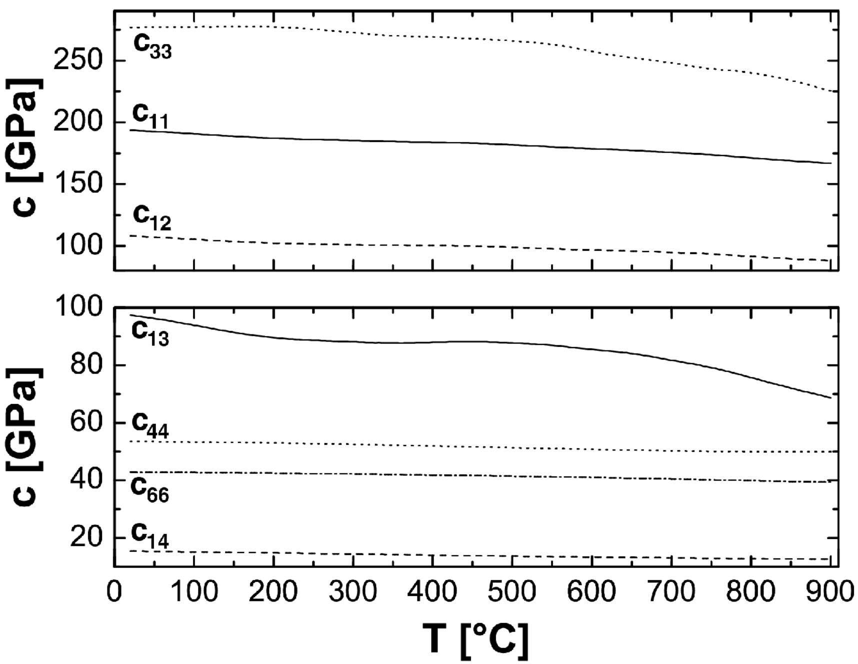
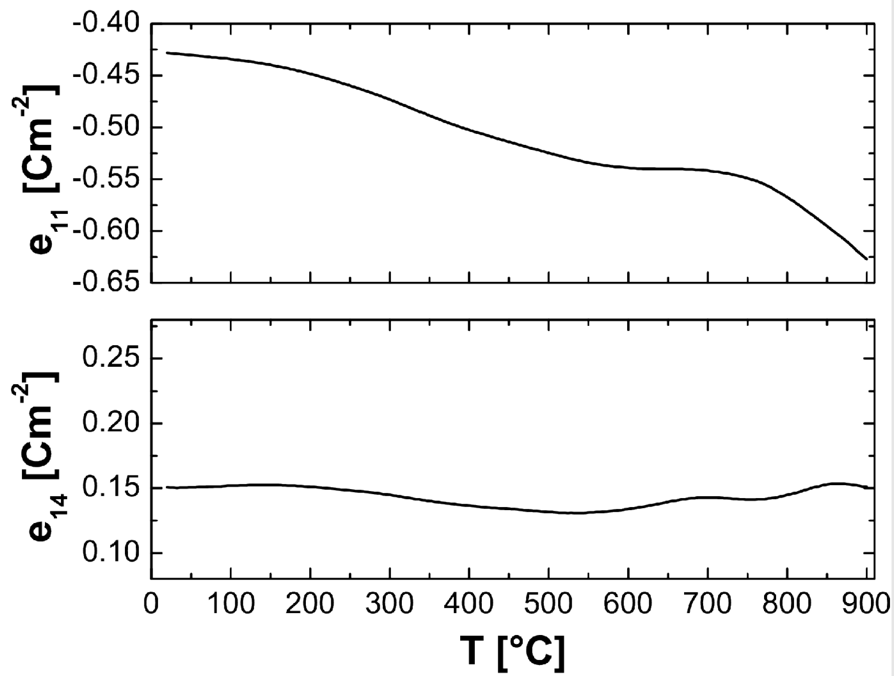
Stability of Langasite

- Electromechanical parameters
  - Full set known up to 900 °C

$$\left[\begin{array}{cccccc|ccc}
c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 & e_{11} & 0 & 0 \\
c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 & -e_{11} & 0 & 0 \\
c_{13} & c_{13} & c_{33} & 0 & 0 & 0 & 0 & 0 & 0 \\
c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 & e_{14} & 0 & 0 \\
0 & 0 & 0 & 0 & c_{44} & c_{14} & 0 & -e_{14} & 0 \\
0 & 0 & 0 & 0 & c_{14} & c_{66} & 0 & -e_{11} & 0 \\
\hline
e_{11} & -e_{11} & 0 & e_{14} & 0 & 0 & \varepsilon_{11} & 0 & 0 \\
0 & 0 & 0 & 0 & -e_{14} & -e_{11} & 0 & \varepsilon_{11} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \varepsilon_{33}
\end{array}\right]$$



All components of stiffness tensor as function of temperature



All components of piezoelectric tensor as function of temperature

M. Schulz, H. Fritze, *Electromechanical properties of langasite resonators at elevated temperatures*, Renewable Energy, 33 (2008) 336–341

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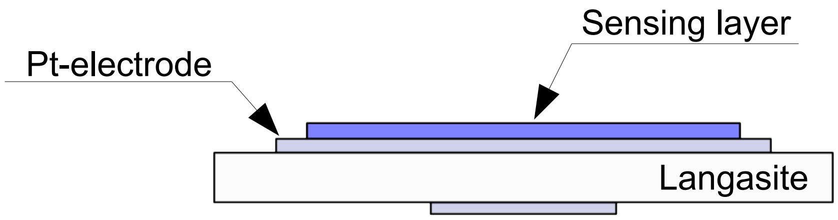
Selective High-Temperature Gas Sensor

- Microbalance mode
- Large underlying platinum electrode
  - Shift of resonance frequency due to mass change

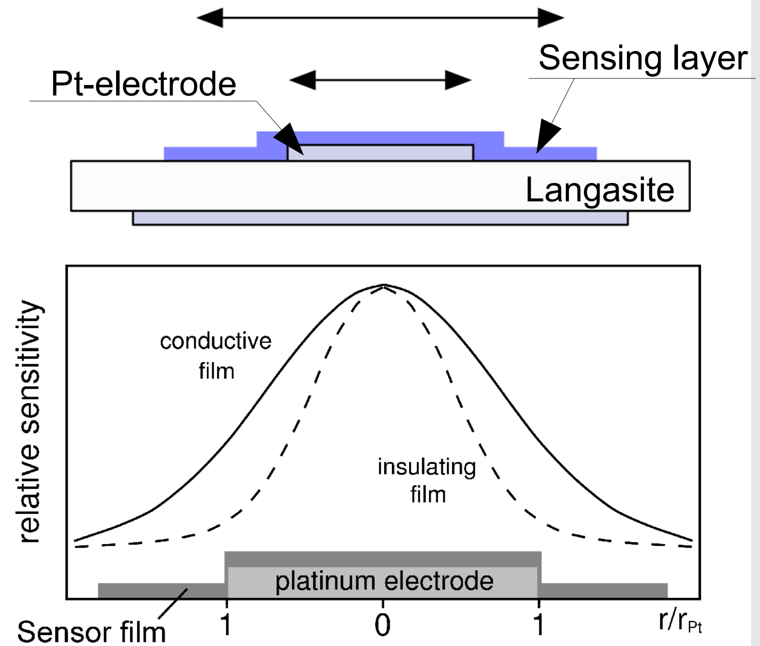
$$\Delta f_r = \frac{2 f_r^2}{A\sqrt{\rho c_{66}}} \Delta m$$

- Sensor film
  - Thin oxide layer with affinity to specific gas
  - Redox reaction and adsorption → mass change
  - Conductivity change



Selective High-Temperature Gas Sensor

- Conductivity mode
  - Modification of microbalance principle
- Small underlying platinum electrode
  - Effective area of electrode affected by conductivity changes
  - Increase of area → increase of sensitivity
- Electrical properties dominate the frequency shift



Relative sensitivity of thickness shear mode resonator as function of sensing layer's conductivity

D. Richter, H. Fritze, T. Schneider, P. Hauptmann, N. Bauersfeld, K.-D. Kramer, K. Wiesner, M. Fleischer, G. Karle, A. Schubert, *Integrated high temperature gas sensor system based on bulk acoustic wave resonators,* Sensors & Actuators B, 118 (2006) 466-471

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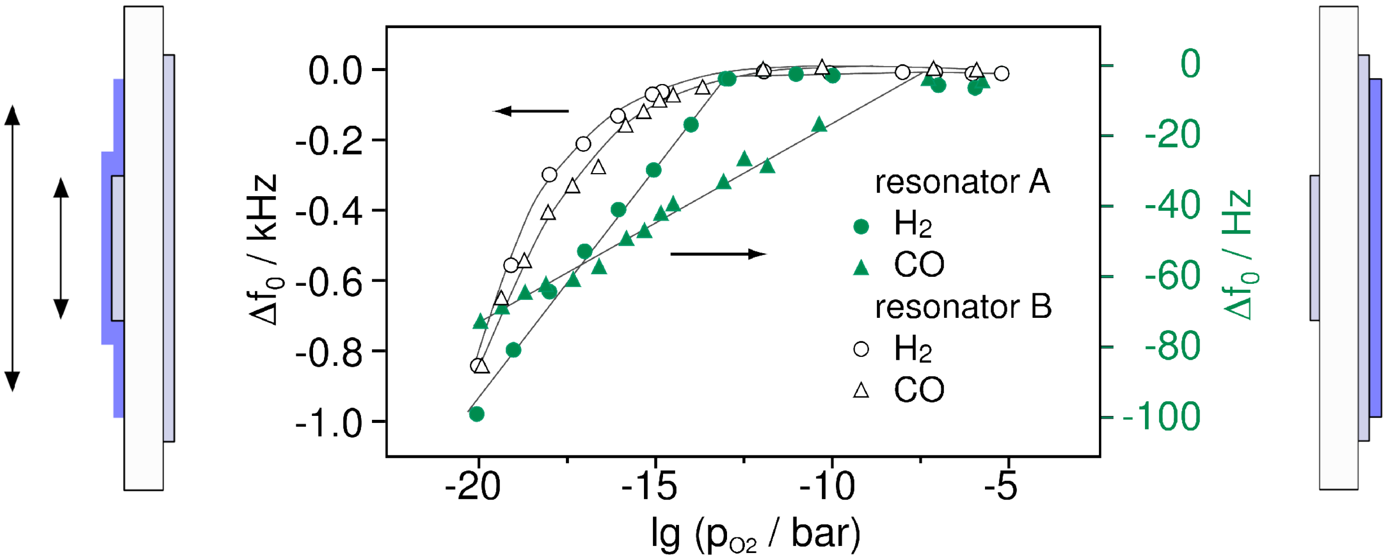
Selective High-Temperature Gas Sensor

- Resonators operated simultaneously in different modes
  - Operating temperature: 600 °C
  - Determination of gas concentrations
  - Measurement of p_{O_2}



Resonance frequency shift of TiO_2 coated langasite resonator operated at 600 °C in conductivity mode (black) and microbalance mode (green)

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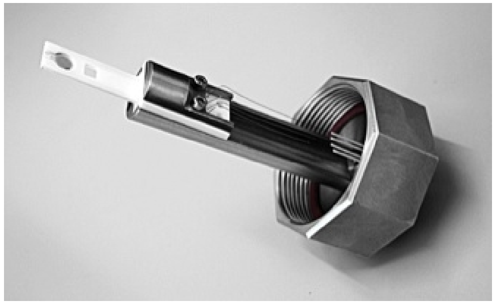
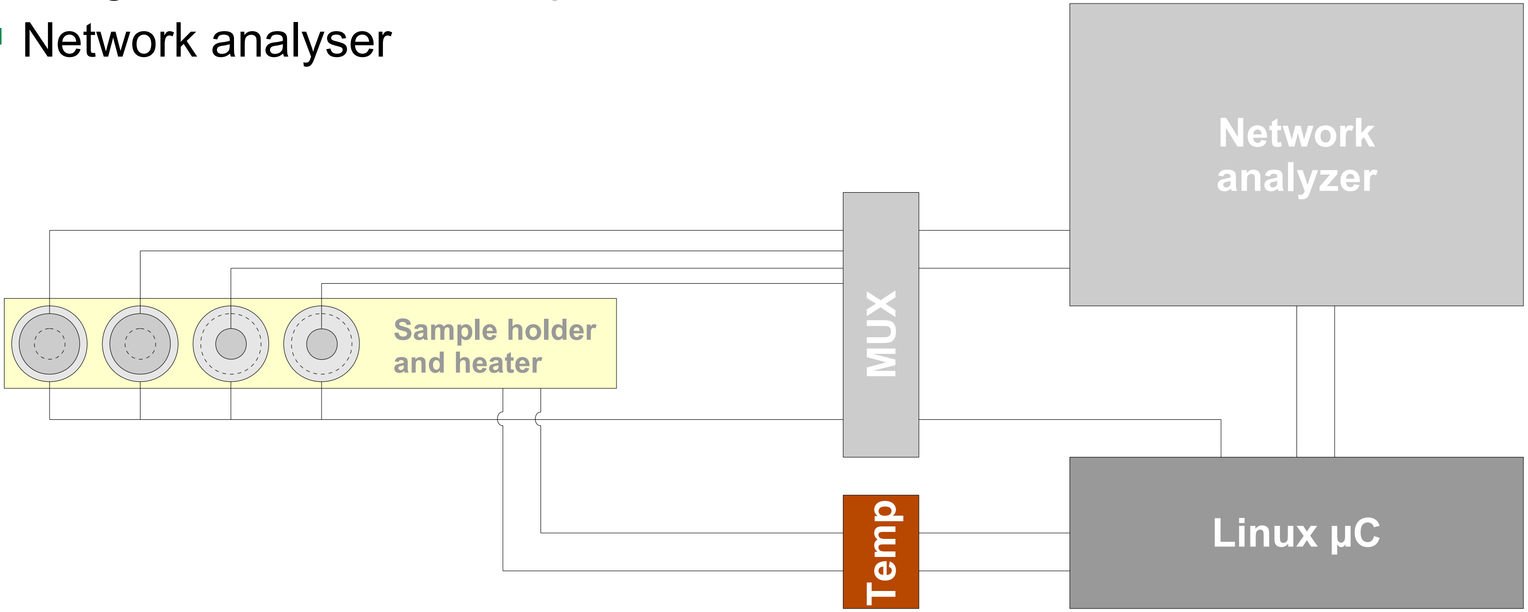
Sensor System

- Array of sensors
  - Several independent resonators
  - Alumina sample holder
  - Screen-printed platinum electrodes
- Integrated heater for temperature control
- Network analyser



Langasite resonators in alumina sample holder of gas reformer sensor



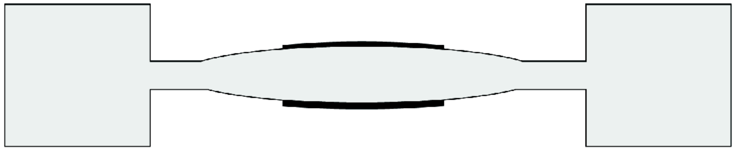
Scheme of the microcontroller-based standalone gas sensor

Sensor System

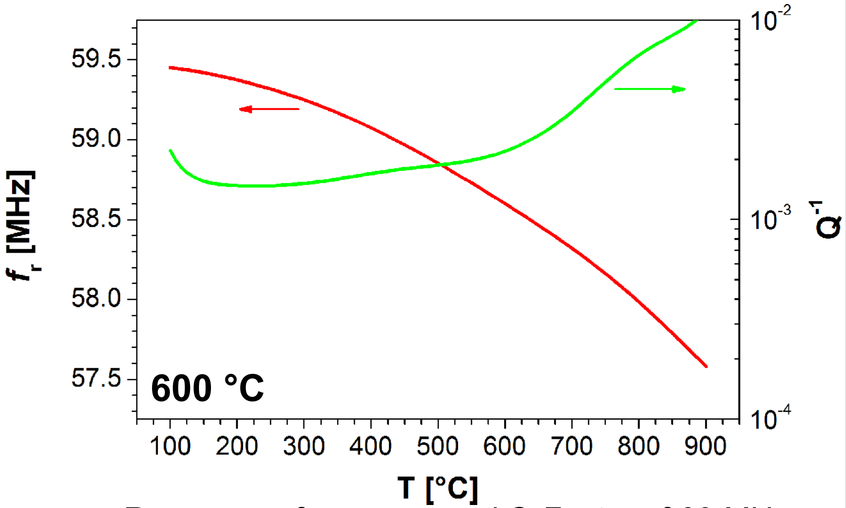
- Wet-chemical etched membranes
  - Resonance frequency: 60 MHz
  - Thickness: 23 µm
  - Diameter: 3 mm
  - Great mass sensitivity

    100 times higher than
    5 MHz resonator

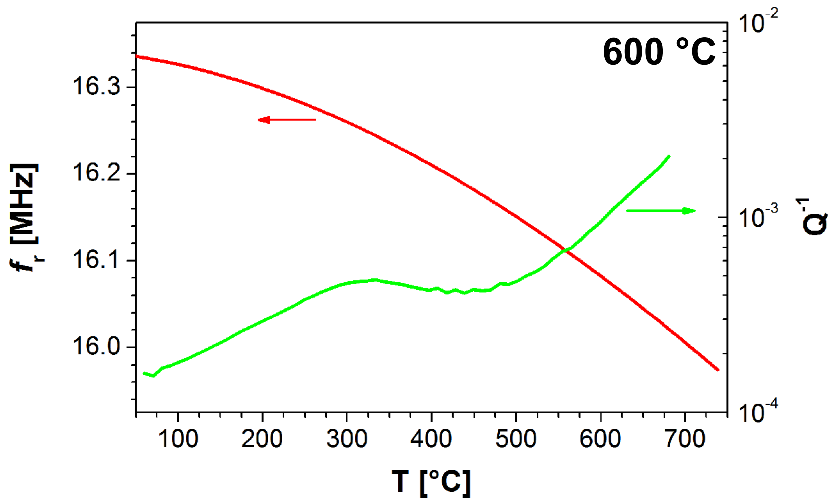
- Biconvex membranes
  - Improvement of Q-Factor
  - Energy trapping



Biconvex membrane



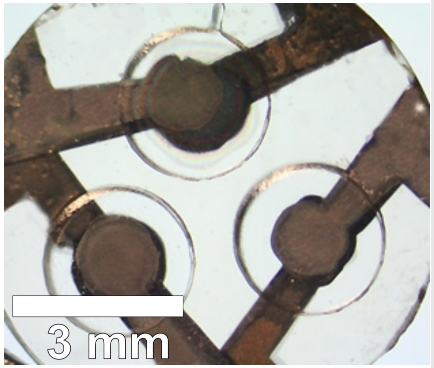
Resonance frequency and Q-Factor of 60 MHz micromachined langasite resonator as function of the temperature



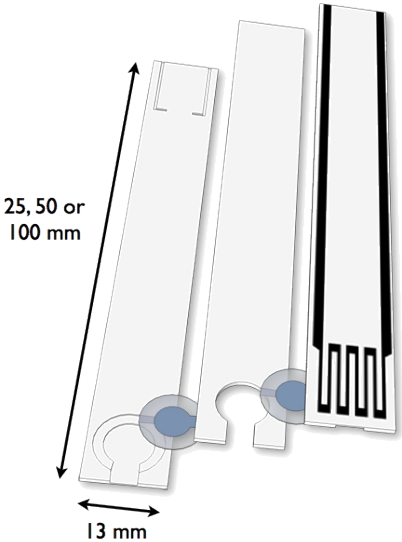
Resonance frequency and Q-Factor of 16 MHz biconvex membrane as function of temperature

Sensor System

- Micromachining of sensor arrays
  - Dimensions: 1.5 mm radius, 50 µm thickness
  - Higher frequency → higher mass-sensitivity
- Sample holder
  - Alumina
  - Screen-printed platinum contacts
  - Meander-platinum structure for temperature control
  - Simultaneous use of several arrays



Biconvex membranes wet-etched on langasite



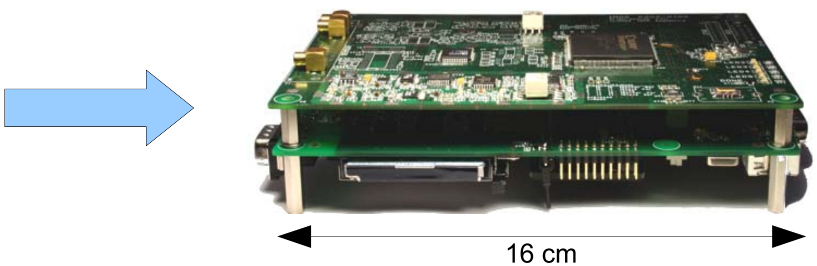
Sample holder for resonators

Sensor System

- Commercial systems:
  - Expensive laboratory equipment
  - Not suitable for industry application

- Development of the low-cost network analyser:
  - Designed with application in mind
  - Complete standalone system for gas monitoring

Typical network analyser used in laboratory conditions



Standalone miniaturized network analyser developed by our project partners

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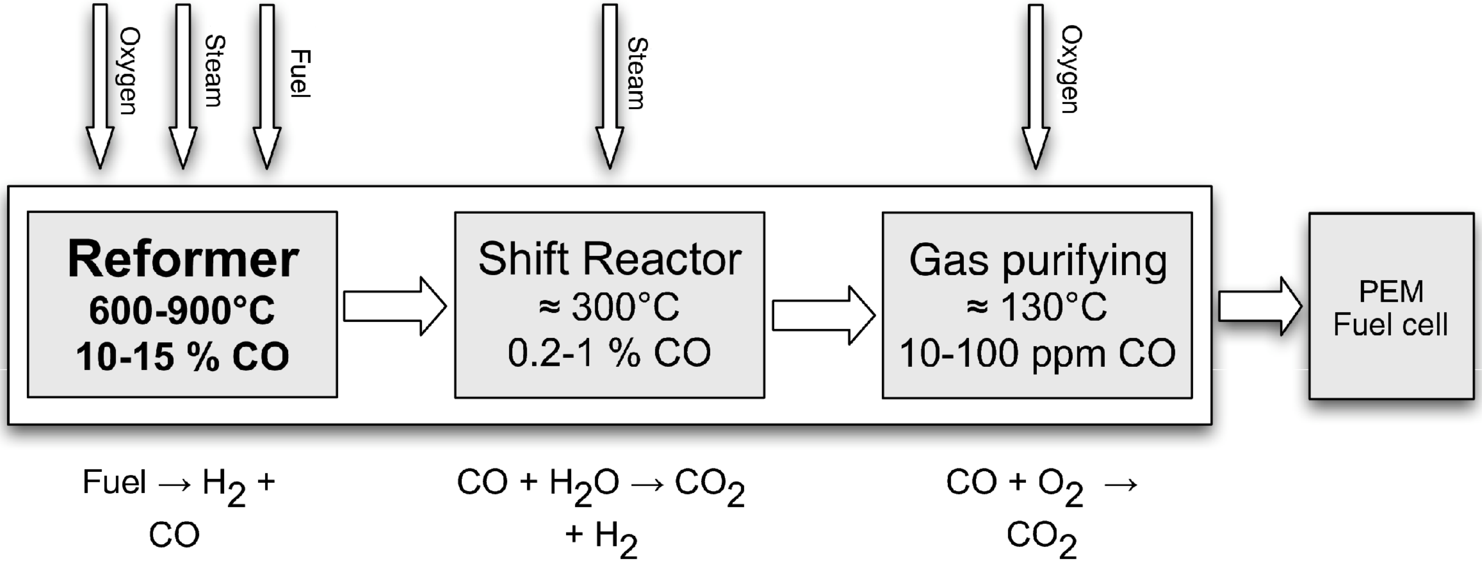
Application Example – Gas Reformer

- Gas control in reforming process
- Simultaneous measurement of H_2 and CO in the exhaust gas
- Low-cost solution

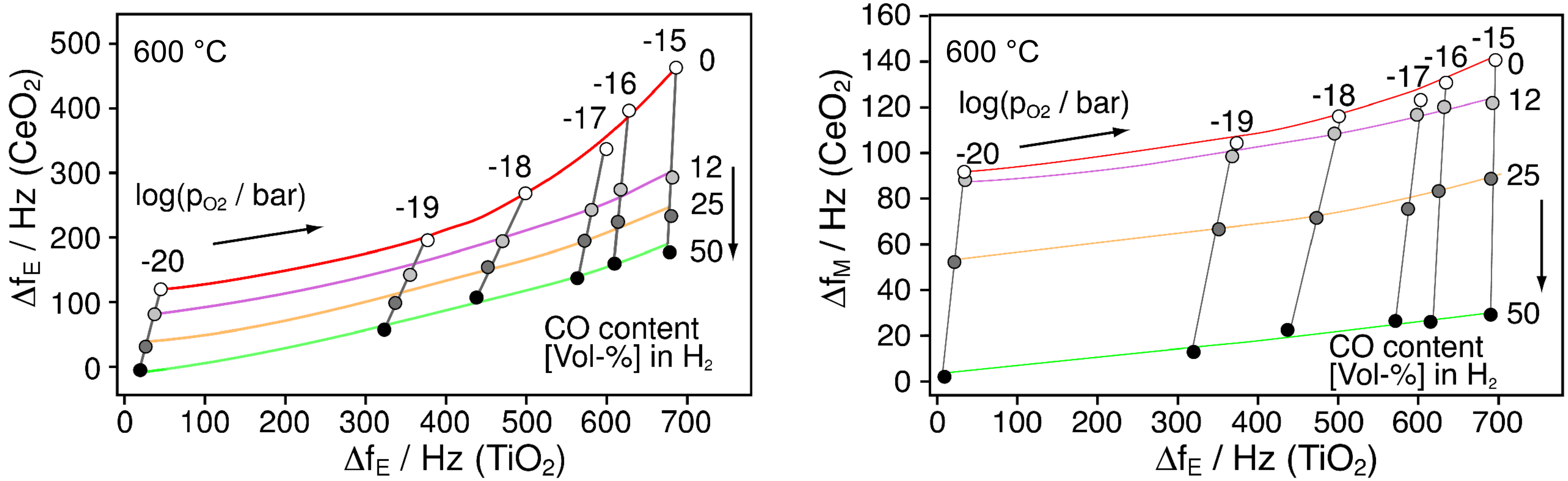


Schematic view of gas reformer for fuel cells

Application Example – Gas Reformer

- Two different oxide layers
  - TiO_2 – microbalance mode
  - CeO_2 – conductivity mode

- Successful simultaneous detection of H_2 and CO



Comparison between frequency shift of TiO_2 coated resonator (conductivity mode) and two CeO_2 coated resonators, operated in conductivity (left) and microbalance modes (right).

Conclusions

- Langasite based resonator operates up to the melting point at 1470 °C
- Increased frequency shift compared to regular resonators in case of conductivity operation mode
- Different materials for sensing layers reduce cross sensitivity
- Micromachining
  - Construction of several sensing membranes on one substrate
  - Improvement of Q-factor with biconvex membranes
- Standalone system for *in-situ* measurement of H_2 and CO content is developed

Other Gas-Sensing/Fuel Cell Related Projects

- ESA / EADS – Gas control and conditioning
  - *In-situ* measurement and control of oxygen partial pressure
  - Measurement of sensor cross sensitivity
  - Control of environment of levitation melts
  - Oxygen ion pump

- DFG research projects
  - Fundamental research on high temperature piezoelectric resonators and sensor materials
  - Micromachining of langasite
  - Array of resonators as temperature sensor for 200 – 900 °C range

Acknowledgement

- Financial support
  - German research foundation (DFG)
  - German Federation of Industrial Research Associations (AiF)
  - European Space Agency (ESA)

- Alumina machining
  - PSFU, Wernigerode

- Standalone network analyser
  - Institute of Micro and Sensor Systems, Otto-von-Guericke-University Magdeburg

- Langasite growth and sample preparation
  - Institute of crystal growth (IKZ), Berlin
  - Eberhard Ebeling (TU Clausthal)

Future Research Activities

- Improvements in mircomachining
  - Smaller arrays
  - Higher resonance frequencies
  - Better sensitivity
  -
- Investigation of sensing layers
  - More precise estimation of CO and H_2 concentrations
- Improvements of long-term stability
- Reduction of cost of the complete system
- Wireless temperature and gas sensors