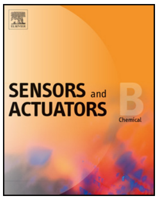
Sensors and Actuators B 187 (2013) 247–253

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



Variation of the vibration profile of piezoelectric resonant sensors with different electrode conductivity at high temperatures

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ARTICLE INFO

Article history:
Available online 19 November 2012

Keywords:
Laser Doppler interferometer
Langasite
High-temperature
Piezoelectricity

ABSTRACT

Gas sensors for applications at elevated temperatures provide improved gas selectivity if fabricated using high-temperature stable piezoelectric resonators. The high-temperature and chemical stability of devices based on langasite coated with metal oxide films supports their application at extreme environments. The vibrational behavior of these resonators is influenced by changes in the electrical and mechanical properties of the metal oxide film.

Measurements of the spatial distribution of the displacement characteristics of thickness shear mode resonators are realized using a laser Doppler interferometer at high temperatures and oxygen partial pressures (p_{O_2}) down to 10^{-27} bar. The p_{O_2} dependent changes of the properties of a CeO_{2-x} sensor film and the influence on the vibration profile of the resonator are determined. At low p_{O_2} the conductivity of the film increases. Due to the design of the device, the increase of the conductivity results in an enlargement of the effective electrode area of up to 18%. This is reflected in a broadening of the vibration profile of the resonator. Impedance spectroscopy provides comparable results for a p_{O_2} dependent increase of the effective electrode area. The influence of the electrode thickness on the vibration profile is investigated and a decrease of the profile width of up to 11% with increasing thickness is demonstrated. The latter is attributed to an increased energy trapping.

1. Introduction

To cover the future needs of sensors for many energy conversion processes the research in this field has to adapt to new requirements. When focusing on fuel cells or decentralized power plants new sensors have to provide high sensitivity and selectivity in gas detection up to temperatures of about 900 and 1500 °C, respectively, leading to strong requirements for the materials stability. Furthermore, for a large-scale application, devices are needed that can be manufactured easily and cost-effectively. In this context, piezoelectric gas sensors show several advantages in comparison to optical or resistive sensor systems.

A suitable candidate for building sensors with such properties is the single crystalline piezoelectric material langasite ($La_3Ga_5SiO_{14}$) which exhibits a high thermal and chemical stability. It shows no phase transition up to its melting point at 1470 °C and low damping up to about 1000 °C [1–3]. In contrast to common quartz resonators which are limited to operation temperatures below 450 °C [4,5], langasite can be used as a piezoelectric transducer up to temperatures of at least 1000 °C. In a next step langasite based sensors could be miniaturized and used in sensor arrays.

In order to establish such sophisticated functionality a detailed knowledge of the physical properties of the devices is crucial. This includes investigation of the electrical and mechanical properties as well as the influence of the specific design of the device such as the geometries of an applied sensor film. To understand and optimize the dependencies on those design parameters, the correlation of the sensor film properties and the spatial distribution of the vibration amplitude of the resonator have to be determined. The latter is realized with a laser Doppler interferometer at temperatures up to at least 600 °C at ambient air and at reducing atmospheres.

2. Sensor principle and previous research

The gas sensor principle is based on langasite bulk acoustic wave (BAW) resonators, excited to thickness shear mode vibration. The resonators are coated with a gas sensitive metal oxide film. In order to obtain different sensor parameters, two different operation modes are used (see Fig. 1). In both modes keyhole shaped platinum electrodes of different diameter are applied on front and back side of the resonator. Operating the sensor in the commonly applied microbalance mode [6] with the sensor film on top of the larger electrode, atmosphere-induced changes of the film mass can

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http://dx.doi.org/10.1016/j.snb.2012.11.015

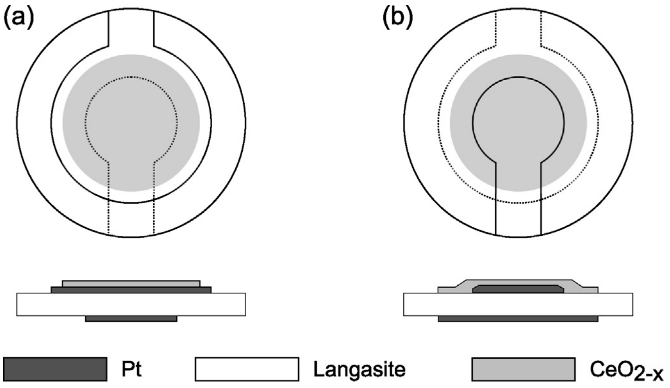

Fig. 1. Electrode layout for piezoelectric resonators operated in the microbalance mode (a) and the conductivity mode (b).

be detected as a frequency shift. For the conductivity mode, the sensor film is applied on top of the smaller electrode, thereby exceeding the electrodes boundaries. In this mode a change in the composition of the surrounding gas influences the conductivity of the film from insulating to conducting, resulting in an enlargement of the effective electrode diameter.

The shift of the resonance frequency Δf of BAW resonators induced by an additional mass load Δm can be described using the Sauerbrey equation [6]

$$\Delta f = -S \cdot \Delta m. \tag{1}$$

The factor S is the average mass sensitivity of a resonator and can be used to calculate the frequency shift for a homogeneous mass load. In order to determine the frequency shift of a resonator with an inhomogeneous mass load, the spatial distribution of the local mass sensitivity s has to be considered. With integration of s over the electrode area A_E one gets the average mass sensitivity S for a homogeneous mass distribution.

$$S = \frac{1}{A_E} \int_{A_E} s \cdot dA \tag{2}$$

Assuming a radial symmetry for circular resonators and electrodes, the mass sensitivity is dependent on the position on the sample [7]

$$S = \frac{1}{\pi \cdot r_e^2} \int_0^{r_e} s(r) \cdot 2\pi r \, dr, \tag{3}$$

with r_e as electrode radius.

In case of an inhomogeneous mass distribution, which is given with applied electrodes or sensor films, the resonance frequency shift is then

$$\Delta f = \frac{1}{\pi \cdot r_e^2} \int_0^{r_e} s(r) \cdot m(r) \cdot 2\pi r \, dr. \tag{4}$$

Accordingly, the resonance frequency is influenced by the mass distribution of electrodes and film. The mass sensitivity, which is proportional to the vibration amplitude, strongly depends on the geometries of electrodes and sensor film.

A partially covered resonator is excited by the electric field which is mainly located between the electrodes leading to a Gaussian-like distribution of the amplitude even for (hypothetical) massless electrodes [8]. The coupling between the excited and the outer part is disturbed even more for mass-loads, e.g. real electrodes, and the vibration cannot propagate far beyond the electrode boundaries [9]. Therefore, the vibration energy is strongly localized in the electrode area (energy trapping).

The displacement distribution of resonators with different electrode diameters is shown schematically in Fig. 2. The Gaussian-like distribution shows a maximum in the center of the electrodes [10]. Its spatial distribution and, thereby, the mass sensitivity depend on the size of the excited area of the resonator. Hence, the extent of the vibration profile is determined by the diameter of the conductive electrodes.

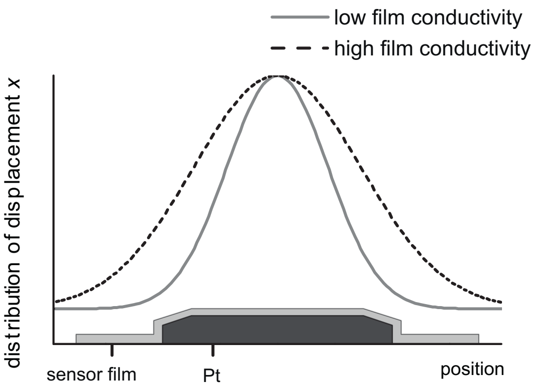

Fig. 2. Model of the change of the effective electrode area depending on the conductivity of the CeO_{2-x} sensor film.

To investigate the influence of the effective electrode diameter on the vibration profile, resonators operated in the conductivity mode are used. A metal oxide film is deposited on top of the smaller platinum electrode. Under reducing atmospheres the conductivity of the film increases which results in an enlargement of the effective electrode area, as shown schematically in Fig. 3.

The effect of the localization of the vibration amplitude to the center of the electrode can be enforced with increasing thickness of the electrode. The difference between the resonance frequencies of the part with and without electrodes increases, resulting in an even narrower vibration profile as shown in [11] for comparable resonator configuration.

2.1. Electrical properties of CeO_{2-x} and TiO_2 sensor films

The p_{O_2} dependent conductivity of thin CeO_{2-x} films at 600 °C is published in [15]. In the following the results are discussed briefly since similar films (preparation method, thickness) are used later in this study. As shown in Fig. 4a, the conductivity depends on the p_{O_2} according to $\sigma \sim p_{O_2}^m$ with $m = -1/10$ for p_{O_2} below 10^{-12} bar and $m = -1/6$ for higher p_{O_2}'s. Related results for thin TiO_2 films are published in [15,19]. Here, the slopes of the conductivities are $m = -1/6$ for p_{O_2} below 10^{-12} bar and $m = -1/4$ for higher p_{O_2}'s (Fig. 4b). Similar results are found by other groups as presented in [12–14].

2.2. Effective electrode size

A common approach for the description of BAW resonators excited in thickness shear mode is the approximation using the Butterworth–van Dyke (BvD) equivalent circuit (EC) [2,16–18]. Here, the material properties of the resonator are expressed by electrical parameters, which are often easier to determine. The BvD EC consists of a static arm with the parallel capacitance C_b. In the

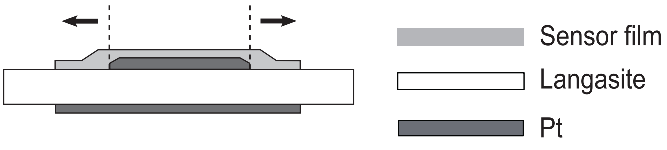

Fig. 3. Schematic drawing of a resonator with platinum electrodes and sensor film. Area between dotted lines indicate the excited area, arrows the increase of the area in reducing atmospheres.