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Some practical points to consider with respect to thermal conductivity and electrical resistivity of ceramic substrates for high-temperature gas sensors☆

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ABSTRACT

In the field of gas sensors and high temperature flow sensors, ceramic thick-film-based structures play a key role, particularly in harsh environments. Their substrates have to be electrically insulating and chemically inert. Ceramic substrates, especially alumina ones, are often considered as ideal sensor substrates. However, neither their electrical resistivity nor their chemical inertness is ideal. Even the thermal conductivity is that temperature dependent that one has to consider it when modeling temperature profiles. In this contribution, measurements on the resistivity and the thermal conductivity between room temperature and 800 °C of two related materials used for gas sensors substrates – alumina and LTCC ceramics – are presented. Additionally, resistance data of uncoated interdigital structures when exposed to NO_2 at around 300 °C indicate that reactions between substrate and NO_2 may occur and have to be kept in mind.

1. Introduction

Metal oxide gas sensors as well as air flow sensors are often designed for operating temperatures above 300 °C. Therefore, the number of suitable substrate materials is limited, particularly, if the sensors are applied in harsh environments [1–4]. Here, ceramic substrates are the materials of choice. Besides the chemical and mechanical stability, electrical insulation and thermal conduction properties of the applied substrates dominate the material selection. The substrates have to be highly electrically insulating and their resistivity, ρ, should not depend on the chemical species in the ambience. Also their thermal conductivity, λ, should be taken into account. To design gas sensors with a uniform temperature distribution in the area of the functional film (active area), a high thermal conductivity of the substrates is preferred.

For instance, if interdigital electrodes are applied on top of a substrate and the substrate is heated by a reverse-side heater as depicted in Fig. 1, the substrate has to homogenize the temperature distribution in the active area, on which the gas sensitive functional film is applied. However, to decouple two different heat sources, as it is the case for sensors measuring heat differences (calorimeter, flow sensors [5–7]), a low λ is preferred. In this case, the substrates manufactured in LTCC technology seem to be more suitable due to their lower thermal conductivity [8–10].

Whereas alumina is the most-used material in thick-film technology, increasingly often LTCC ceramics are used to build gas sensors. Therefore, this article, which discusses some practical aspects that should be considered when dealing with conductometric gas sensors, focuses on both materials.

2. Temperature dependency of thermal conductivity

A design process of a gas sensor begins with thermal calculations, very often supported by Finite Elements Analysis (FEA). Therefore, for proper calculations of thermal effects, knowledge of the temperature dependent thermal conductivity of the substrates, $\lambda(T)$, is mandatory [5]. In this study, the thermal conductivity was determined with a laser flash device (LFA1000 Laser Flash, Linseis, Selb, Germany). We measured the thermal conductivity of pellets with a diameter of 10 mm and thicknesses up to 2 mm between room temperature and 800 °C. The measurements were conducted for two alumina samples (96% and 99.99%) as well as

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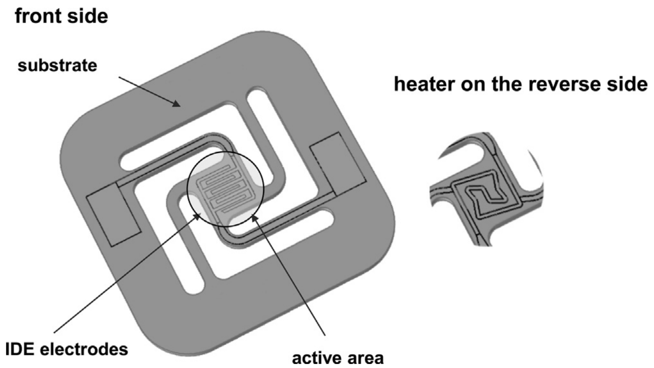

Fig. 1. Example of a ceramic gas sensor substrate in form of a hot-plate. Interdigital electrodes may be covered by a functional, gas sensitive film.

for two commercially available LTCC tapes (DP951, DuPont and CT800, Heraeus), respectively. As shown in Fig. 2, the thermal conductivity depends strongly on temperature. Therefore, the λ(*T*)-behavior needs to be considered when calculating temperature profiles and/or the required heater power to achieve a distinct operating temperature for alumina meso hot-plates [11,12]. Since the thermal conductivity of 96% alumina decreases by a factor of 3 from 21.6 W/(m K) at room temperature down to 7.6 W/(m K) at 800 °C and in the case of 99.99% alumina by a factor of 3 from 29.2 W/(m K) to 9.6 W/(m K) at 500 °C, neglecting the temperature dependence may yield strong errors.

The thermal conductivity of LTCC ceramics is much lower. This can be advantageous when designing flow sensors or calorimeters. Moreover, as shown in Fig. 3, its thermal conductivity is almost independent of temperature. In case of DP951, the changes are about 10% (from 2.75 to 2.49 W/(m K) at 500 °C). CT800 shows an even lower temperature dependency, from 1.80 to 1.71 W/(m K), respectively. One should notice that the measured values differ from the ones given in the manufacturer's datasheet. However, these values are comparable with those reported recently in [13] at room temperature. The reason of this low thermal conductivity is the composition of the LTCC ceramics. It is a mixture of alumina, glass, and other additives, but the glass fraction can vary between 10 and 50% [14]. This may also explain the different thermal conductivity values between both LTCC materials. Moreover, in many

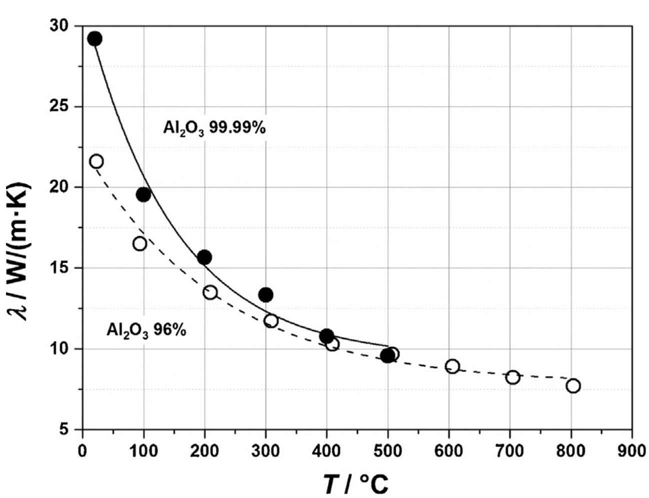

Fig. 2. Temperature dependency of the thermal conductivity, λ, of 96% and 99.99% alumina substrates. A good approximation for λ(*T*) for practical purposes is a fit function acc. to Eq. (1) with the following parameters: B = 141.43 W/(m K), T_d = 147.44 K, and B_0 = 9.43 W/(m K) for 99.99% Al_2O_3 and B = 50.97 W/(m K), T_d = 220.27 K, and B_0 = 7.79 W/(m K) for 96% Al_2O_3. These functions are plotted as lines.

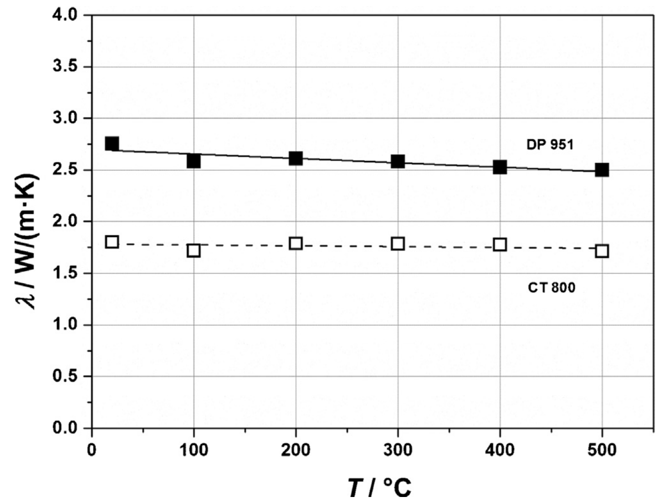

Fig. 3. Temperature dependency of the thermal conductivity, λ, of two commercially available LTCC materials, for details see text. Dots are measured. The drawn lines are fitted linearly.

LTCC materials, new phases that recrystallized from the glass phase are observed after firing [15]. This may affect the overall thermal conductivity of LTCC materials as well.

For the thermal simulation of temperature distributions in gas sensors, especially in ceramic hot-plates, the temperature dependence of the thermal conductivity of alumina is very often neglected. However, this may cause errors. A small simulation example shown below illustrates that.

With the FEM software COMSOL Multiphysics, we simulated a temperature distribution on a ceramic hot-plate gas sensor with dimensions of 11 mm × 11 mm × 0.5 mm ($W \times L \times H$, hot-plate size 2.1 mm × 2.1 mm, for further details see [11]). Two cases were considered: when the thermal conductivity is assumed to remain constant over the entire temperature range, i.e. λ = 29 W/(m K) and when λ is a function of temperature as shown in Fig. 2. For that, the measured thermal conductivity data were fitted by an exponential function.

$$\lambda(T) = B \cdot \exp\left(-\frac{T}{T_d}\right) + B_0 \qquad (1)$$

Herein, B is a factor, T the temperature in K, T_d a decay constant in K, and B_0 denotes an offset, respectively. As boundary conditions, convection and radiation were assumed. The heater current value was set as the same for both cases. In Fig. 4, temperature profiles across the hot-plate structure are evaluated to compare both cases.

When assuming a constant (higher) λ-value, the maximum temperature is about 25% lower since the higher thermal conductivity at low temperatures leads to higher heat diffusion in the beams of the hot-plate towards the frame. Therefore, the temperature in the frame is significantly higher. This is important, if one intends to solder wires on the frame. Whereas the temperature difference on the active area for a constant (high) thermal conductivity can be lower than 6 K at 879 K (606 °C), it increases up to about 15 K at 1061 K (788 °C) if the temperature dependency is taken into account. At first glance, these differences seem to be not very significant. However, they can become critical if the sensitivity and/or selectivity towards specific gases are strongly temperature dependent, as it is very often the case for conductometric gas sensors. The differences become more obvious if one has a look at the temperature gradient over the entire hot-plate. This is shown in Fig. 5a for λ = 29 W/(m K) and in Fig. 5b for the temperature dependent thermal conductivity.

The temperature gradient in the active area case is significantly lower if one calculates with constant high λ due to a better homogenization of the temperature field. However, if one simulates with